

Fig. 2.—The effect of the binding of Ni^{II} on the electrophoretic mobility of bovine serum albumin (0° , acetate buffer, pH 6.5, ionic strength 0.20).

and Scoggan, offer advantages over the equilibrium dialysis method. In Fig. 2, the mobility of albumin is given as a function of $\bar{\nu}$. It is seen that the first few bound ions do not cause any measurable change in the mobility. However, there is a pronounced decrease in the (negative) mobility at $\bar{\nu} > 4$.

Discussion

From the plot of $\bar{\nu}/A$ vs. $\bar{\nu}$, the values of the first association constant, K_1 ($= kn$, where k is the intrinsic association constant) and n , the maximum number of binding sites are obtained. These are $K_1 = (7.5)10^3$ and $n \sim 16$. This value of n suggests that the binding sites are, perhaps, the imidazole groups of the albumin molecule. Based on concepts presented in an earlier paper,⁹ the intrinsic constant, corrected for the charge on the protein, has been calculated from the first association constant. The charge on the protein molecule is obtained from the electrophoretic mobility data and has a value of -16 (electron units). The intrinsic association constant thus obtained is $\log k^0 = 3.17$. This compares well with the first association constant for nickel-imidazole interaction, $\log k = 3.27$. The agreement between these values suggests that the imid-

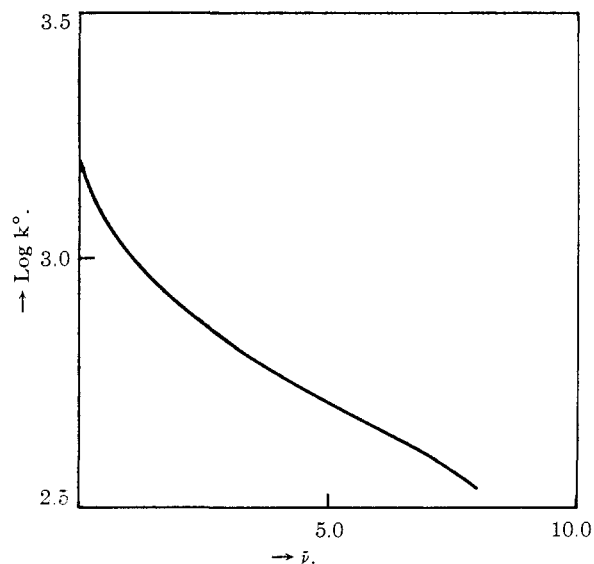


Fig. 3.—Intrinsic constants for 1:1 interaction with imidazole sites.

azole groups are the sites at which nickel ions are bound by the albumin molecule.

The binding data along with the mobility values can be utilized to calculate $\log k^0$ as a function of $\bar{\nu}$.^{1,9} If the binding sites are of the same class and are all equivalent, then $\log k^0$ should be independent of $\bar{\nu}$. However, from Fig. 3 it can be seen that there is a gradual decrease from the initial value of 3.17 and at $\bar{\nu} = 8.0$, $\log k^0 = 2.53$. This may be interpreted either as that all the sixteen imidazole groups are not equivalent or that there is an increasing participation of some group with a lower binding affinity than imidazole.

Binding measurements in the presence of 5 M urea, which is known to disrupt the helical structure of the protein, gave $\bar{\nu}$ values which fall on the same curve (Fig. 1). It is, therefore, likely that carboxyl groups which have a much lower affinity also compete with the imidazole groups for binding Ni^{II} .

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The Hydrolysis of Chloramine in Alkaline Solution

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RECEIVED SEPTEMBER 6, 1961

The hydrolysis of chloramine was investigated in alkaline solutions from $\text{pH} = 12$ to 12 molar NaOH . Hydroxylamine is produced in the primary step, nitrous oxide and nitrogen are the main final products of hydrolysis. Kinetic results show that the reaction is first order in chloramine with a linear dependence on the H_L acidity function. The kinetics of hydrolysis of dimethylchloramine have been investigated as well as the hydrogen exchange of this compound with water. These as well as other results suggest the nucleophilic substitution of chloride by a hydroxyl ion as the most probable mechanism of hydrolysis.

Introduction

Chloramine has been shown to be the first product of the hypochlorite-ammonia reaction which ultimately yields hydrazine.¹ This compound undergoes a decomposition in aqueous solutions,

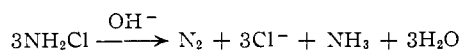
(1) F. Raschig, "Schwefel und Stickstoffstudien," Verlag Chemie G.m.b.H., Berlin, 1924, p. 50.

which was found both acid and base catalysed.^{2,3} Raschig examined the final products of decomposition of chloramine in alkaline solution (when $(\text{NH}_2\text{Cl}) = 0.1 M$) and found nitrogen, ammonia

(2) *Ibid.*, p. 60.

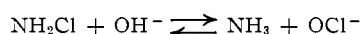
(3) J. Kleinberg, M. Tecotzky and L. F. Audrieth, *Anal. Chem.*, **26**, 1388 (1954).

and chloride ions in accord with the equation

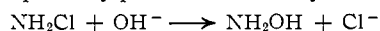


It is evident that these products are not formed in a single step and that certain compounds should be first formed which in subsequent interaction with chloramine yield the final products. The primary products of hydrolysis of chloramine suggested were either hypochlorite ions and ammonia or hydroxylamine and chloride ions.

The reversible hydrolysis of chloramine to hypochlorite and ammonia was suggested by Corbett, Metcalf and Soper⁴ who claim to have measured the equilibrium constant of this reaction.



McCoy,⁵ on the other hand, claims that hydroxylamine is the primary product. McCoy isolated cyclo-



hexanone-oxime from an alkaline reaction mixture containing chloramine and cyclohexanone. The formation of the oxime was interpreted as evidence for the formation of hydroxylamine as the primary product of hydrolysis.

The formation of hypochlorite would imply a positively polarized chlorine on chloramine, and the hydrolysis may be considered as a chlorination of water. Hydroxylamine as primary product indicates a negatively polarized chlorine which undergoes substitution by a hydroxide ion; the formation of hydroxylamine may alternatively be considered as an amination of water. Each of these different approaches implies a completely different mechanism of reaction.

It was the purpose of this study to determine the identity of the primary products in alkaline aqueous solutions and to elucidate the mechanism of their formation, as well as to obtain kinetic data on the rate of alkaline decomposition of chloramine.

Quantitative information about the alkaline hydrolysis reaction is a pre-requisite for any study of chloramine reactions in alkaline solution, in particular the formation of hydrazine from chloramine and ammonia.⁶

Experimental

Reagents. Water.—The purity of water was found to be essential for the reproducibility of kinetic results with chloramine. Doubly distilled water was deionized by passing through a column containing a layer of Dowex 1 cation exchange resin on top of a layer of Dowex 50 anion exchange resin.

Chlorine free hypochlorite solutions were prepared as described⁷ by dissolving *tert*-butyl hypochlorite in 10 molar NaOH. *tert*-Butanol was separated and the aqueous layer was diluted to the desired concentration. *tert*-Butyl hypochlorite was prepared from commercial hypochlorite solutions and *tert*-butanol.⁸

Ammonia solutions were prepared by distilling gaseous NH₃ into deionized water.

Chloramine.—Aqueous solutions of chloramine were prepared by the reaction of equivalent amounts of aqueous ammonia and hypochlorite (chloride free) solutions. The yield

of chloramine, when prepared in concentrations below 0.025 molar, was above 98%; the chloramine prepared by this procedure was not further purified. Stock solutions of chloramine were kept under refrigeration at pH 10; under these conditions the spontaneous decomposition was less than 10% in 30 days.

N¹⁵ labelled chloramine solution was prepared from N¹⁵-H₄Cl dissolved in water. Deuterium labelled chloramine was obtained from ammonia dissolved in 99.8% D₂O.

Solutions of dimethylchloramine were prepared by distilling dimethylamine (Matheson Ltd.) into deionized water.

All other materials used were commercial reagents of analytical grade. Storage and reaction vessels were treated with concentrated nitric and rinsed with deionized doubly distilled water.

Analytical Methods.—Hypochlorite was determined by iodometric titration with a standard sodium thiosulfate solution.

Ammonia was determined by the Nessler colorimetric method.⁹ Hydrazine was determined by the colorimetric *p*-dimethylaminobenzaldehyde method.¹⁰ Nitrite was colorimetrically determined by the sulfanilic acid- α -naphthylamine method.¹¹ Hyponitrite was determined in absence of chloramine by its absorption at 248 m μ .¹² Peroxynitrite, was determined by its absorption at 302 m μ .¹³ Hydroxylamine was precipitated by adding diacetylmonoxime-nickel reagent, and the dimethylglyoxime formed was determined gravimetrically. Formaldehyde was determined by the colorimetric chromotropic acid method.¹⁴

Chloramine concentration was determined either by iodometric titration with thiosulfate or by measuring its absorption at 243 m μ , as recommended by Kleinberg, Tecotzky and Audrieth.³ Their value for the molar extinction coefficient, $\epsilon = 458$, was confirmed. The main difficulty with both methods, in concentrated alkaline solution, is the formation of peroxynitrite in the presence of oxygen. This compound has an $\epsilon = 600$ at 243 m μ , and it is an oxidative reagent.¹³ Oxygen was not expelled from chloramine solutions since oxygen-free chloramine solutions were found to be unstable and the kinetic results were not reproducible. The contribution of pernitrite was corrected for by taking a reading at 302 m μ , ($\epsilon = 1200$) and subtracting half of this value from readings at 243 m μ (or 0.33 of this value from readings at 250 m μ).

Dimethylchloramine was determined by the same methods. The absorption spectra of these compounds were measured by Metcalf,¹⁵ but slightly different values were found by us: $\lambda_{\text{max}} = 263.5$ m μ instead of 263 m μ , and $\epsilon = 330$ instead of 300. No peroxy compounds were formed under these conditions.

Colorimetric and spectrophotometric measurements were carried out on a Beckman Model DU instrument.

Determination of the Products of Decomposition.—The decomposition was carried out in a two limbed reaction vessel attached to a vacuum line. This enabled outgassing of solutions before mixing. A predetermined amount of hypochlorite was introduced in one limb of the reaction vessel and was frozen after degassing. An equivalent amount of concentrated ammonia was then frozen on top of the frozen hypochlorite. The appropriate amount of potassium hydroxide solution was introduced into the other limb and outgassed. After attaining room temperature the solutions were mixed and were allowed to stand until decomposition was known to be complete. The gases formed were then transferred by a Toepler pump to a calibrated volume; the pressure was measured and the amount of gas produced was calculated. A sample of the gases was analysed by a CEC Model 20-401 Mass spectrometer in the mass range 2-52. The only masses present in

(9) We might remark that chloramine was found to be quantitatively determined by Nessler reagent, a fact which may be of interest in connection with industrial water analysis.

(10) (a) G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

(b) R. Freier and G. Resch, *ibid.*, **149**, 177 (1956).

(11) D. F. Boltz, Editor, "Colorimetric Determination of Non-metals," Interscience Publishers, Inc., New York, N. Y., 1958, p. 124.

(12) C. C. Addison, G. A. Gamlen and R. Thomson, *J. Chem. Soc.*, 338 (1953).

(13) G. Yagil and M. Anbar, to be published.

(14) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

(15) W. S. Metcalf, *J. Chem. Soc.*, 148 (1942).

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

(5) R. E. McCoy, *J. Am. Chem. Soc.*, **76**, 2829 (1954).

(6) G. Yagil and M. Anbar, *ibid.*, **84**, 1797 (1962).

(7) M. Anbar, S. Guttmann and R. Rein, *ibid.*, **81**, 1816 (1959).

(8) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1094 (1959).

TABLE I
THE RATE OF ALKALINE HYDROLYSIS OF CHLORAMINE, INFLUENCE OF VARIOUS FACTORS
 $T = 27.3^\circ$

No.	Date	Condition	Chloramine, 10 ² mole/l.	NaOH, mole/l.	10 ³ k _{obsd} sec. ⁻¹
1-1	16/9/59	O ₂ passed before reaction	2.0	0.9	68.7 ^a
1-2	30/9/59	C ₂ passed during reaction	2.0	1.0	64.0
1-3	2/4/60	N ₂ passed during reaction	2.0	1.0	63.0
1-4	5/4/60	No gas passed	2.0	1.0	62.5
1-5	28/9/59	No gas, vessels kept in the dark	2.0	1.0	64.0
1-6	23/9/60	No gas, 0.05% gelatine	2.0	1.0	62.0

^a Corrected to NaOH 1 molar.

significant amounts were 28, 30 and 44, indicating the presence of N₂ and N₂O. The relative peak heights of masses 28 and 30 were corrected for the contribution of N₂O which was determined from the spectrum of pure N₂O.

Kinetic Experiments.—Kinetic measurements were carried out at $27.3 \pm 0.05^\circ$. Measurements at 0.3 ± 0.1 and at $58.3 \pm 0.05^\circ$ were performed for determination of the energy of activation.

Reaction solutions were prepared by mixing appropriate volumes of chloramine solution at pH 10 with alkali hydroxide solutions. The solution was placed in a thermostat. Samples were drawn at intervals and their optical densities (o.d.) at 250 and 300 m μ were measured. In some of the experiments the change in absorption was automatically recorded. All the readings at 250 and 243 m μ were corrected for peroxyxynitrite as explained above. ($\log \text{o.d.} - \text{o.d.}_{\text{corr}}$) was plotted against time. Straight lines were obtained up to 3 half lives and over, $t_{1/2}$ was graphically determined and $k_{\text{obs}} = 0.693/t_{1/2}$ was calculated.

The effects of degassing by nitrogen or saturation of reaction mixture with oxygen of scattered light as well as changes in reagents quality or in water purity were examined. The results, summarized in Table I, show that these factors have little effect on the measured rate.

The hydrolysis of dimethylchloramine was followed by the same method

Tritium Exchange Between Chloramine and Dimethylchloramine and Water.—A solution of 0.1 molar chloramine in HTO was prepared by mixing 5 ml. of 0.2 M hypochlorite solution, 2 ml. of KOH 16.0 M and 2.5 ml. of HTO (38 $\mu\text{c./ml.}$ determined as hydrogen by internal counting in a Geiger counter), next 0.1 ml. of NH₃ 10.0 M or 0.42 ml. of (CH₃)₂NH 2.4 M were added, followed by water up to 10 ml. of volume. 1 minute after the addition of ammonia the solution was shaken with 25 ml. of scintillation solution (3 g. terphenyl and 100 mg. POPOP in 1 liter of toluene): 20 ml. of these were shaken repeatedly with CaCl₂, until a constant number of counts was obtained.

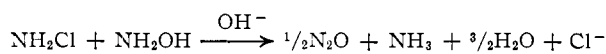
0.5 ml. of a standard solution of toluene H³ was then added to the same solution (standard solution No. NES-4 10.1.60 of New England Corporation Ltd., 2.44×10^6 dpm. $\pm 1\%$, diluted in toluene 1:50) and the number of counts in the final mixture was recorded. The additional number of counts related to the decompositions per minute of tritium in the standard solution added, gave the counting efficiency of the particular scintillation solution, from which the activity (in microcuries) of the dissolved chloramine was calculated.

The scintillation solution then was titrated iodometrically with 0.1 M sodium thiosulfate and the concentration of the chloramine was calculated. From these determinations the specific activity of the chloramine and consequently the per cent. of hydrogen exchange were calculated.

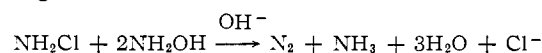
A separate experiment showed that the extraction of NH₃ (the major hydrogen containing product of hydrolysis) into the scintillation solution was negligible.

Results and Discussion

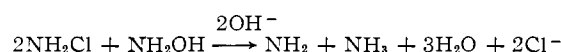
1. **The Products of the Hydrolysis. A. The Final Products.**—As stated above, there is evidence for the formation of hydroxylamine in the first step of the hydrolysis. A reaction between one molecule of hydroxylamine and one molecule of chloramine is likely to yield N₂O and NH₃ as final products



Whereas the stoichiometrical formulas leading to nitrogen would be either



or



A product analysis in dilute solution, where less interference of secondary reactions is expected, was carried out to determine the contributions of the alternative reaction paths. The results are presented in Table II. The two experiments shown are with initial concentrations 2×10^{-3} and 1×10^{-2} molar.

TABLE II
THE PRODUCTS OF HYDROLYSIS OF CHLORAMINE IN 3 M KOH, $T = 22^\circ$

Exp. No.	NH ₂ Cl, mole/l.	N ₂ , %	N ₂ O, %	N ₂ H ₄ , %	N ₂ O ₃ ⁻ , %	NO ₂ ⁻ , %	NH ₂ OH, %
2-1	2×10^{-3}	10.8	50	1.5	4	<1	2
2-2	10×10^{-3}	25.3	24.5	7	1	<1	<1

It can be seen that N₂O is a major product of the reaction as long as the chloramine concentration is low. On increasing the concentration of chloramine, more nitrogen is produced by the 2NH₂Cl + NH₂OH reaction. A scan of the mass spectra of the gaseous products shows that neither NO nor H₂ are formed. Quantitative tests showed that no chlorate or azide is formed. (Azide, hydrogen and chlorate were claimed to be formed in rather concentrated solutions^{16,17}). It is suggested that in highly diluted chloramine solutions the stoichiometry of hydrolysis is 4NH₂Cl + 4OH⁻ → N₂O + 2NH₃ + 4Cl⁻ + 3H₂O.

In the presence of oxygen another major product is formed, namely, peroxyxynitrite ion, ONOO⁻. The formation of this ion was detected when the behavior of an alkaline solution of 2×10^{-3} M chloramine saturated with oxygen was followed spectrophotometrically.¹³ Parallel to the decrease in absorption of chloramine an increase in absorption at higher wave lengths was observed. This absorption has a maximum at 302 m μ and is identical in shape with the absorption spectrum of peroxyxynitrite, as reported by Kortum and Finckh.¹⁸ No other compound possibly formed in the hydrolysed solution has a similar absorption spectrum

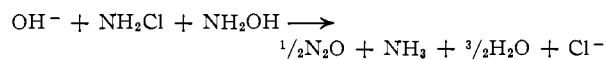
(16) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

(17) Ref. 1, p. 76-78.

(18) M. Kortum and B. Finckh, *Z. physik. Chem.*, **B48**, 42 (1941).

(except NO_3^- , which has $\epsilon = 9.6$ only). The yield of peroxyxynitrite formed was over 33% (based on $\epsilon = 1200$).¹³ Peroxyxynitrite containing solutions show an oxidative capacity on iodometry, thus will an alkaline solution of chloramine, in presence of oxygen, retain part of its oxidative capacity after all the chloramine has been decomposed. This effect may probably account for the hardly understandable results obtained by Audrieth and Rowe.¹⁹ More details about the formation of peroxyxynitrite by reaction of oxygen with chloramine (and hydroxylamine) and the mechanisms of these reactions will be discussed elsewhere.¹³

B. Hydroxylamine as Primary Product.—Hydroxylamine has been isolated in a small yield (<5%) from the completely hydrolyzed chloramine solution with diacetylmonoxime. The low yield of hydroxylamine is not surprising in view of the fast $\text{NH}_2\text{OH}-\text{NH}_2\text{Cl}$ reaction. It has been demonstrated that this reaction produces nitrous oxide: The interaction of 1.5×10^{-3} molar NH_2Cl with 2×10^{-3} molar NH_2OH in 3 M KOH yielded 48% N_2O . Although this result suggests the



formation of hydroxylamine as the main primary product, there may be alternative reactions by which N_2O might be formed, which would mean that the hydroxylamine isolated at the end of hydrolysis might be a product of a side reaction. Further evidence for the formation of hydroxylamine as the main primary product was therefore desirable.

An attempt was made to trap hydroxylamine while being formed by carrying out the hydrolysis in the presence of diacetylmonoxime: The dioxime was actually formed, but the rate of its formation was 20 times faster than the rate of chloramine hydrolysis under the same conditions. This result implies a direct interaction between chloramine and the carbonyl of the monoxime. Thus the formation of oximes from chloramine does not necessarily imply the presence of hydroxylamine as an intermediate.⁵

Riley, *et al.*,²⁰ examined the possibility of the formation of hydroxylamine as an intermediate in the decomposition processes of chloramine by an isotope dilution method. They interacted N^{15} labelled ammonia with hypochlorite in the presence of an excess of NH_2OH , containing nitrogen 15 at natural abundance. After 3–4 minutes hydroxylamine was isolated (as copper salicyldoxime) and the isotopic composition of the hydroxylamine was found unchanged, *i.e.* no hydroxylamine originating from their ammonia could be isolated. They inferred that hydroxylamine was not formed as an intermediate in the hydrolysis of chloramine.

Their procedure is open to certain objections: primarily OCl^- reacts faster with NH_2OH than with ammonia, so that little chloramine could ever be formed under their conditions. Secondly any chloramine formed would have reacted with NH_2OH preferentially to hydrolysis. Further-

(19) L. F. Audrieth and R. A. Rowe, *J. Am. Chem. Soc.*, **77**, 4726 (1955).

(20) R. F. Riley, *et al.*, *ibid.*, **76**, 3301 (1954).

more the decomposition of chloramine in 0.25 M KOH is much slower than a few minutes.

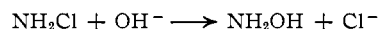
The first objection to Riley's procedure may be eliminated by following the interaction between chloramine and ammonia rather than hypochlorite and ammonia. Next the relative rate of hydrolysis of chloramine *versus* its rate of interaction with hydroxylamine should be taken into account. Further, the absolute rate of hydrolysis should determine the duration of the experiment.

1×10^{-3} molar $\text{N}^{15}\text{H}_2\text{Cl}$ (95.9 atom % N^{15}) plus 1×10^{-3} molar NH_2OH (0.04 atom % N^{15}) were introduced into 3 molar KOH. After 60 minutes hydroxylamine was separated and analysed by the procedure of Riley, *et al.* The N^{15} content of NH_2OH separated was 2.02 atom % N^{15} after one recrystallization, and 2.04 % N^{15} after two recrystallizations of copper salicyldoxime. A higher percentage of N^{15} can hardly be expected, in view of the fact that most of the chloramine will be consumed by the relatively faster reaction with hydroxylamine.

It may be concluded therefore, that the formation of hydroxylamine from chloramine can actually be demonstrated by an isotopic dilution method provided certain factors involved are taken into account.

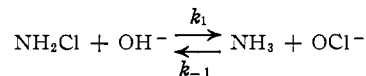
Two additional facts which support the formation of hydroxylamine as a primary product should be considered: first, it has been demonstrated by Theilhacker and Ebke²¹ that when chloramine is introduced into alcoholate solutions, alkylhydroxylamines are formed with high yields. Second, when oxygen reacts with hydroxylamine in alkaline solution pernitrite is formed, just as in the case of chloramine but the rate of formation is much higher. The rate of formation of pernitrite from hydroxylamine is dependent on oxygen concentration,¹³ whereas in the case of chloramine the rate of pernitrite formation is oxygen independent (see Table I). These results suggest that hydroxylamine is the precursor of pernitrite when formed from chloramine.

From all the experimental material presented, it may be concluded that hydroxylamine is the major primary product of chloramine hydrolysis, which proceeds according to



The mechanism of this step, whether it is a one step process or not, will be discussed after considering kinetic measurements of the hydrolysis. Before presenting these measurements, the possibility of chloramine hydrolysis to hypochlorite has to be considered.

C. Hypochlorite Ions as a Primary Product.—The equilibrium constant for the reaction



has been given by Corbett, Metcalf and Soper⁴ $K = 1.6 \times 10^{-3}$ at 15°. The rate constant k_{-1} at 15° can be calculated from the data of Weil and Morris²² for 1 M OH^- as $9.1 \times 10^1 \text{ mole}^{-1}$

(21) W. Theilhacker and K. Ebke, *Angew. Chem.*, **68**, 303 (1956).

(22) I. Weil and J. C. Morris, *J. Am. Chem. Soc.*, **71**, 1665 (1949).

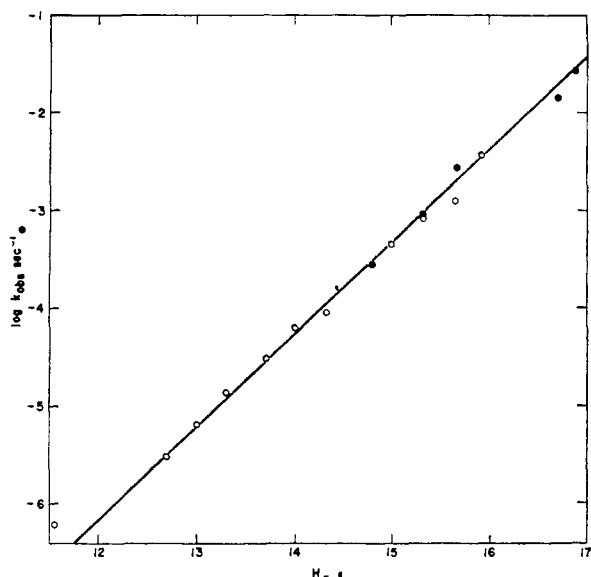


Fig. 1.—The hydrolysis of chloramine, $T = 27.3^\circ$: O, sodium hydroxide; ●, potassium hydroxide.

min.^{-1} . Consequently $k_1 = Kk_{-1}$ should be $1.46 \times 10^{-1} \text{ mole}^{-1} \text{ l. min.}^{-1}$, which implies that the half life of hydrolysis of chloramine at 15° is 4.7 min. It is expected that within 30 minutes complete equilibrium is attained consisting of 58% OCl^{-1} at 2×10^{-3} molar initial NH_2Cl concentration.

We attempted to verify these conclusions by following spectrophotometrically the hydrolysis of chloramine at 15° in absence of oxygen; observing both the absorption peaks of NH_2Cl ($243 \text{ m}\mu$) and of OCl^{-1} ($293 \text{ m}\mu$). Yet, after 60 minutes there was no indication for the formation of any OCl^{-1} while the concentration of NH_2Cl dropped by less than 10%.

The fact that no hypochlorite could be detected on hydrolysis of chloramine was confirmed in later kinetic experiments which were carried out at NH_2Cl concentrations down to 2×10^{-4} molar and KOH concentrations up to 10 molar. This result implied either that the rate constant of formation of chloramine as given by Weil and Morris is much too high or that there is a gross inaccuracy in the value given by Corbett, *et al.*, for the equilibrium constant. Consequently we have determined the rate constant for the formation of NH_2Cl at 1 molar NaOH at 0.3° from 7.5×10^{-4} molar NH_3 and OCl^{-1} ; a rate constant $k_{-1} = 8.10^1 \text{ mole}^{-1} \text{ l. min.}^{-1}$ was found as compared to $k_{-1} = 7.10^1 \text{ mole}^{-1} \text{ l. min.}^{-1}$ calculated from the data of Weil and Morris.

This last result leads to the conclusion that the value for K is much too high. From all our measurements an upper limit for K can be derived, $K < 10^{-8}$. The reevaluation of the equilibrium constant K should consequently require a revision of the values of the thermodynamic constants of chloramine.²³ The new value for ΔF of chloramine will necessarily change the value of its oxidation-reduction potential to a more positive value, *i.e.* chloramine is a mild oxidant and its chemistry should be comparable to that of hydroxylamine rather than that of hypochlorite.

(23) W. L. Jolly, *J. Phys. Chem.*, **60**, 507 (1956).

The Kinetics of Alkaline Hydrolysis of Chloramine.—The kinetics of hydrolysis of chloramine have been investigated in the alkaline region, from $\text{pH} = 11$ up to 12 molar hydroxide. The rate of hydrolysis was found to increase with alkalinity. The rate was found first order in chloramine concentration—this is demonstrated by the fact that a plot of $\log (\text{o.d.} - \text{o.d.}_\infty)$ vs. time gave straight lines up to 90% of the reaction and over (Fig. 1); further the rate constants were found independent of initial chloramine concentrations in the range 1×10^{-3} to 3×10^{-2} (Table III).

TABLE III
THE HYDROLYSIS OF CHLORAMINE AT VARIOUS CONCENTRATIONS OF CHLORAMINE
[NaOH] = 1 M, $T = 27, 3^\circ$

NH_2Cl , 10^3 mole/l.	$t_{1/2}$, min.	$10^6 k_{\text{obsd}}$, sec.^{-1}
30 ^a	220	52
30	225	51
10	205	56
2	170	68
1	170	68

^a Oxygen was passed.

A thirty fold change in concentration of chloramine results in a change of no more than 30% in the rate constant. It can be concluded that the reaction is first order in chloramine. The effect of hydroxide concentration on the rate of hydrolysis is presented in Table IV.

TABLE IV
HYDROLYSIS OF CHLORAMINE AT VARIOUS CONCENTRATIONS OF SODIUM AND POTASSIUM HYDROXIDE ($[\text{NH}_2\text{Cl}] = 2.0 \times 10^{-3} \text{ M}$; $T = 27.3^\circ$)

Exp. no.	NaOH, mole/l.	$\text{pH}(\text{H}_-)$	$t_{1/2}$, min.	$10^6 k_{\text{obsd}}$, sec.^{-1}
4-1	0.0035	11.55	18500	0.6
4-2	.05	12.70	2350	5.0
4-3	.1	13.00	1800	6.5
4-4	.2	13.30	790	14
4-5	.5	13.70	362	31
4-6	1	14.00	182	63.5
4-7	1.98	14.33	129	90
4-8	4.27	15.00	25.5	450
4-9	5.75	15.33	14	830
4-10	7.25	15.65	8	1250
4-11	8.70	15.93	3.1	3700
	(KOH), mole/l.			
4-12	3.00	14.80	43	270
4-13	4.70	15.32	12.5	920
4-14	5.70	15.67	4.1	2800
4-15	5.70 ^a	15.67	4.1	2800
4-16	8.50	16.70	1.01	11400
4-17	9.05	16.88	0.42	28000
4-18	12.0	18.00	<0.25	>50000

^a Gelatin added.

When the concentration of hydroxide is below 1 molar, k_{obsd} is proportional to base concentration (*cf.* 4.3–4.6). Above 1 molar, k_{obsd} rises much more rapidly than the concentration of hydroxide and the rate is different for equal concentrations of KOH and NaOH (*cf.* 4.9; 4–14). This unexpected effect can be correlated with the basicity of the solutions as expressed by the H_- function. Values of H_- in

alkaline aqueous solutions have been determined by Schwarzenbach and Sulzberger,²⁴ but to the best of our knowledge these have not been correlated with rate data in concentrated hydroxide solutions. Their values (for dissociation according to $\text{BH} + \text{OH}^- = \text{B}^- + \text{H}_2\text{O}$) are given in column III of Table IV. A plot of $\log k_{\text{obsd}}$ versus H_- is given in Fig. 1.

The experimental points, both for KOH and NaOH, fall on the same straight line which has a slope of 0.92. Such deviations from unity which may partially be accounted for by the temperature difference between our measurements and those of Schwarzenbach, are generally encountered with acid catalyzed reactions,²⁵ and it can be stated that there is a linear correlation between the rate of hydrolysis and the acidity function.

The effects of ammonia, chloride ions and of deuterated chloramine in deuterium oxide on the rate of hydrolysis are presented in Table V.

TABLE V
THE ALKALINE HYDROLYSIS OF CHLORAMINE. THE EFFECT OF NaCl, NH_3 AND D_2O
[NH_2Cl] = 2×10^{-3} M, $T = 27, 3^\circ$

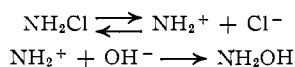
	Conc. mole/l.	KOH, mole/l.	H_- (pH)	$10^6 k_{\text{obsd}}$ sec. ⁻¹ corr. to $H_- = 14.80$
..	...	2.90	14.80	270
NH_3	2×10^{-2}	2.90	14.80	320
NaCl	1.0	2.90	14.80	265
D_2O	85%	2.75	14.75	340
D_2O	95%	2.70	14.72	380

Ammonia seems to accelerate the disappearance of chloramine. This effect may, however, be accounted for by considering the direct interaction between ammonia and chloramine which would contribute about 10% of the total decomposition.⁶ The fact that ammonia has no inhibitory effect on the rate of hydrolysis implies that a preequilibrium of the type



is not involved in the mechanism of hydrolysis.

Chloride ions were also shown to have no effect on the rate of hydrolysis which excludes the preequilibrium.

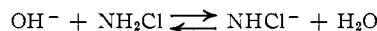


Moreover, it has been found that under our experimental conditions no isotopic exchange between NH_2Cl and chloride ions takes place.²⁶ The cataly-

(24) G. Schwarzenbach and R. Sulzberger, *Helv. Chem. Acta*, **27**, 348 (1944). One should be aware of the fact that these values were obtained in a two phase system and there is no way to derive values of activity coefficients of the indicator in the aqueous phase from measurements in the non aqueous phase. On the other hand, it should be remembered that the major factors determining the value of H_- are the activity coefficients of water and OH^- in the aqueous solution. The measurements of Schwarzenbach involve determinations of the changes in indicator absorption coefficients at different OH^- concentrations. Thus, if we assume no change in the ratio of the activity coefficients of the indicator in its acid and base forms with changing OH^- concentrations, we introduce only a minute error in the estimate of H_- . The good correspondence between our results and Schwarzenbach's values, which can hardly be believed to be accidental, justify this assumption.

(25) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1952).

tic effect of deuterium on the rate of hydrolysis $K_D/K_H = 1.3$ rules out the possibility of a proton abstraction in the rate determining step and suggests the existence of an acid base pre-equilibrium,²⁷ namely



The Effect of Temperature.—The rate of hydrolysis was determined at 0.3, 27.3 and 59.3°. From the result an energy of activation of 20.8 kcal./ml. and a frequency factor of $2.8 \cdot 10^{11}$ sec.⁻¹ were derived. This implies an entropy of activation of -6.4 e.u. at 25°.

Hydrogen Exchange Between Chloramine and Water.—The exchange of hydrogen between chloramine and water (tritium activity-0.171 $\mu\text{c./mmole}$) was examined under the following conditions: Initial chloramine 0.1 M, KOH 3.2 M $T = 22^\circ$. When the chloramine was allowed to hydrolyse for 1 minute before separation by extraction, an activity of 320 counts/min. was found after complete drying. The iodometric titration showed that 0.0365 millimols were extracted. The specific activity of the chloramine was therefore 0.163 $\mu\text{c./mmole}$, namely 96% of the specific activity of the water.

Exchange of hydrogen between water and chloramine is thus virtually complete under these conditions. This result corroborates the existence of the equilibrium $\text{NH}_2\text{Cl} + \text{OH}^- \rightleftharpoons \text{NHCl}^- + \text{H}_2\text{O}$, which was suggested above.

The hydrogen exchange of dimethylchloramine which was investigated under similar conditions ($(\text{CH}_3)_2\text{NCl} = 0.09$ M, KOH = 3.2 M, $T = 23^\circ$) gave after 25 minutes of hydrolysis a specific activity of 0.011 $\mu\text{c./mmole}$ of the extracted and dried compound. This specific activity corresponds to 2.2% of exchange, which indicated that the rate of hydrogen exchange is slower than the rate of hydrolysis under these conditions.

The Hydrolysis of Dimethyl Chloramine.—Dimethylchloramine was found to undergo hydrolysis in alkaline solutions at a comparable rate to that of chloramine. The reaction which was found first order in dimethylchloramine shows a dependence on alkalinity similar to that of chloramine (Table VI).

TABLE VI
THE RATE OF HYDROLYSIS OF DIMETHYLCHLORAMINE IN ALKALINE SOLUTIONS
[$(\text{CH}_3)_2\text{NCl}$] = 2×10^{-3} mole/l.; $T = 2, 3^\circ$

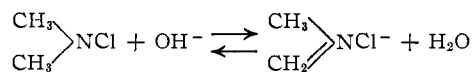
	Hydroxide, mole/l.	H_-	$t_{1/2}$, min.	$10^6 k_{\text{obsd}}$, sec. ⁻¹
KOH	3.01	14.85	36	320
KOH	3.01	14.85	34	340
NaOH	4.5	15.08	19	600
KOH	4.2	15.22	12.3	940
KOH	6.03	15.77	4.3	2700
KOH	9.05	16.70	0.6	20000

A plot of $\log k_{\text{ex}}$ vs. H_- gives a linear dependence with a slope of 0.94. The isotopic exchange of tritium between water and dimethylchloramine which has been followed in KOH 3.2 M as described

(26) M. Anbar and G. Yagil, *Bull. Res. Council. Israel*, **8A**, 139 (1958).

(27) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).

above, showed that the specific rate of this exchange is slower than $4 \times 10^{-6} \text{ mole}^{-1} \text{ l. sec.}^{-1}$ at this alkalinity. The rate of hydrogen exchange is thus slower than the rate of hydrolysis at the same alkalinity. This result excludes the reversible reaction



as a preequilibrium in the hydrolytic process of dimethylchloramine. The isotopic exchange of hydrogen between chloramine and water, which has been examined under similar conditions, was found to proceed over one hundred fold faster than the dimethylchloramine reaction.

The product of hydrolysis of dimethylchloramine reduced silver ions in ammoniacal solution and on hydrolysis in concentrated sulphuric acid it yielded formaldehyde with a yield of over 80%. These tests suggest that the primary product of alkaline hydrolysis of dimethylchloramine is N,N dimethylhydroxylamine. Formaldehyde may be formed from dimethylhydroxylamine in an analogous process to the dehydration of *tert*-butanol in acid solutions, which produces isobutylene. The analogous compound formed from $(\text{CH}_3)_2\text{NOH}$ will be $\text{CH}_2=\text{N}-\text{CH}_3$, which subsequently hydrolyses to $\text{CH}_2\text{O} + \text{H}_2\text{NCH}_3$.

The Mechanism of Alkaline Hydrolysis of Chloramine.—The hydrolysis of chloramine to form hydroxylamine proceeds according to the equation

$\text{NH}_2\text{Cl} + \text{OH}^- \longrightarrow \text{NH}_2\text{OH} + \text{Cl}^-$ as first suggested by McCoy.⁵ The catalytical effect of alkalinity may imply three alternative mechanisms of reaction:

1. A preequilibrium $\text{NH}_2\text{Cl} + \text{OH}^- \rightleftharpoons \text{NHCl}^- + \text{H}_2\text{O}$ followed by $\text{NHCl}^- + \text{H}_2\text{O} \xrightarrow{\text{slow}} \text{NH}_2\text{OH} + \text{Cl}^-$ (SN 2 CB) or by $\text{NHCl}^- \xrightarrow{\text{slow}} \text{NH} + \text{Cl}^-$; $\text{NH} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{NH}_2\text{OH}$ (EICB)

This mechanism has been suggested by Audrieth and Rowe¹⁹ for aqueous solutions and by Jander²⁸ for the behaviour of chloramine in liquid ammonia.

2. A proton abstraction $\text{NH}_2\text{Cl} + \text{OH}^- \xrightarrow{\text{slow}} \text{NHCl}^- + \text{H}_2\text{O}$; $\text{NHCl}^- + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{NH}_2\text{OH} + \text{Cl}^-$ or $\text{NHCl}^- \xrightarrow{\text{fast}} \text{NH} + \text{Cl}^-$ followed by $\text{NH} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{NH}_2\text{OH}$.
3. A nucleophilic substitution $\text{NH}_2\text{Cl} + \text{OH}^- \longrightarrow \text{NH}_2\text{OH} + \text{Cl}^-$.

The linear dependence on H_- function suggests in

(28) J. Jander *Z. anorg. allgem. Chem.* **280**, 264 (1955).

analogy to the Hammett-Zucker criteria²⁵ the formation of NHCl^- in a preequilibrium with a subsequent monomolecular decomposition to NH and Cl^- . The attack of water on NHCl^- (A-2 mechanism) is expected to show a linear dependence on OH^- concentrations. The applicability of the of the Hammett-Zucker criteria has been criticized,²⁵ and it has been experimentally demonstrated that a linear dependence on H_- is obtained in cases of nucleophilic substitution, *e.g.* the alkaline hydrolysis of ethyl iodide²⁹ as well as in cases of proton abstraction, *e.g.* the alkaline hydrolysis of serine phosphate.³⁰ It may be stated therefore that the linear dependence on H_- does not provide unambiguous corroboration for any of the three suggested mechanisms.

The fact that the hydrolysis of deuterated chloramine does not proceed at a slower rate than that of chloramine is a direct proof against the second mechanism (proton abstraction). The slight acceleration of hydrolysis in presence of deuterium might point to the first mechanism,²⁷ but it has been shown that a similar effect is observed in the hydrolysis of ethyl iodide²⁹ in D_2O , which is a typical nucleophilic substitution.

In order to decide between the first and the third mechanism, one may have to draw conclusions from the analogous hydrolysis of dimethylchloramine. This compound has no hydrogen attached to the nitrogen, thus only mechanism 3 may operate.

A preequilibrium with the formation of $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{NCl}^- \\ \diagup \\ \text{CH}_2 \end{array}$

has been excluded by comparison of the rate of hydrolysis with that of hydrogen exchange.

Furthermore the formation of $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{NCl}^- \\ \diagup \\ \text{CH}_2 \end{array}$ would be

$\text{CH}_3-\text{N}=\text{CH}_2 + \text{Cl}^-$ and no dimethylhydroxylamine would be formed. Thus it may be concluded that dimethylchloramine undergoes hydrolysis by a nucleophilic substitution. The comparable rates of hydrolysis of chloramine and dimethylchloramine strongly suggests a similar mechanism for both compounds. Another reaction in which a nucleophilic attack on chloramine is indicated is the reaction of hydrazine formation below $p\text{H} = 14$.⁶ Although the existence of NHCl^- has been demonstrated in the alkali catalyzed hydrazine formation,⁶ a nucleophilic substitution process by OH^- still seems the most plausible mechanism for the hydrolysis of chloramine.

(29) M. Anbar, M. Bobtelsky and G. Yagil, to be published.

(30) D. Samuel and B. Silver, unpublished results.