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The Kinetics of Hydrazine Formation from Chloramine and Ammonia

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The kinetics of hydrazine formation from chloramine and ammonia have been investigated in the alkalinity range $pH = 10.15$ to 9 molar hydroxide. The reaction which is first order in both reactants was found base independent up to about $pH = 14$. At higher alkalinities the base catalyzed reaction is proportional to the rise in the acidity function H_-. The rate of interaction of substituted amines and chloramines increased when hydrogens on ammonia were substituted by methyl groups, whereas it decreased with substituted chloramines. There was found no diminution in rate on substitution of hydrogen by deuterium, nor was there any appreciable change in rate in the presence of chloride or phosphate ions. These results imply a nucleophilic attack of ammonia and amines on chloramine or on the chloramide ion.

Introduction

The formation of hydrazine from chloramine and ammonia has been the subject of many investigations in recent years. There is, however, no agreement on the mechanism of this reaction.

One mechanism was suggested already by Raschig,[1] who discovered the formation of chloramine in the production of hydrazine from hypochlorite and ammonia. According to Raschig, a NH molecule is formed from chloramine and this species attacks ammonia to form N_2H_4.

Audrieth, *et al.*,[2,3] suggest that NH is formed by decomposition of the conjugate base of chloramine, $NHCl^-$

$$OH^- + NH_2Cl \longrightarrow NHCl^- + H_2O$$

chloramide either decomposes to form NH, which subsequently attacks ammonia to form hydrazine

$$NHCl^- \longrightarrow NH + Cl^-$$
$$NH + NH_3 \longrightarrow N_2H_4$$

or alternatively it attacks ammonia directly

$$NHCl^- + NH_3 \longrightarrow N_2H_4 + Cl^-$$

Their argument for this mechanism is the improvement of the yield of hydrazine with the increase of alkalinity, up to 0.25 molar hydroxide. This mechanism is supported by Jander[4] who claims that the addition of potassium amide improves hydrazine yield in liquid ammonia.

According to an alternative mechanism, there occurs a substitution of chloride in chloramine by ammonia in a single step.

$$NH_3 + NH_2Cl \xrightarrow{\text{slow}} N_2H_5^+ + Cl^- \xrightarrow{OH^-} N_2H_4 + Cl^- + H_2O$$

This mechanism was first suggested by Bodenstein[5] who found that the reaction (at $pH \sim 11$) is first order in either reagent. Cahn and Powell[6] showed that the yield of hydrazine found with different concentrations of reactant is in accord with this mechanism. In a recent kinetic investigation, Collier, Sisler, Calvert and Hurley[7] have shown that hydrazine formation from chloramine in liquid ammonia proceeds through the substitution mechanism.[8]

A kinetic investigation over an extensive range of alkalinity in aqueous solution would decide between the two suggested mechanisms. These and other experiments which helped to elucidate the mechanism have been carried out in the present study. In addition the kinetics of interaction of various methyl amines with chloramine and of methyl chloramine with ammonia have been measured, as this proved helpful in elucidating the mechanism of the ammonia–chloramine reaction.

It has been found that the rate of chloramine decomposition in aqueous alkaline solutions is rapid. In order to account for this reaction, which evidently affects the yield hydrazine formation, a separate kinetic investigation was undertaken.[9]

Experimental

Aqueous solutions of chloramine, methylchloramine and dimethylchloramine were prepared as described by the authors elsewhere.[9] Concentrated ammonia was prepared by distilling liquid ammonia into deionized water as described.[9] Methylamine, dimethylamine and trimethylamine solutions were prepared by dissolving the appropriate amount of reagent grade amine in water.

The concentration of ammonia and amine solution, as well as hydroxide concentrations over 0.1 *M*, were determined by acidimetric titration. Alkalinity up to $pH < 12$ was measured with a Beckman Model G *p*H Meter. The concentration of chloramine, methylchloramine and dimethylchloramine was determined either iodometrically or by measuring their absorption at 243, 253, 263 mμ, respectively.[9,10]

Hydrazine standardization was carried out by the direct iodate titration method.[11] In dilute solutions a colorimetric method was found to be more convenient. The method used was based on the formation of a yellow azine by reaction with *p*-dimethylamino benzaldehyde. A modification of the described method[12] was adopted: The reagent was an aqueous solution 0.1 *M* in *p*-dimethylamino benzaldehyde and 1 *M* in *p*-toluene sulfonic acid; this reagent was stable when kept in dark for a few weeks. 10 ml. of reagent was introduced into a 50 ml. volumetric flask with the appropriate amount of sample, water was then added to volume and the absorption at 454 mμ was determined. A calibration set of determinations in the range $10^{-6} - 2 \times 10^{-5} M$ showed that the Beer–Lambert law is obeyed and the molar extinction coefficient is $\epsilon = 59000 \pm 500$. This value was used to calculate hydrazine concentrations. 1,1-Dimethylhydrazine was determined by

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[1] F. Raschig in "Schwefel und Stickstoffstudien," Verlag Chemie G.m.b.H., Berlin, 1924, p. 68.

[2] L. F. Audrieth E. Colton and M. Jones *J. Am. Chem. Soc.* **76**, 1428 (1954).

[3] L. F. Audrieth, U. Scheibler and M. Zimmer, *ibid.*, **78**, 1852 (1956).

[4] J. Jander, *Z. anorg. u. allgem. Chem.*, **280**, 264 (1955).

[5] M. Bodenstein, *Z. physik. Chem.*, **139A**, 397 (1928).

[6] J. W. Cahn and R. E. Powell, *J. Am. Chem. Soc.*, **76**, 2565 (1954).

[7] F. N. Collier, Jr., H. H. Sisler, J. G. Calvert and F. R. Hurley, *ibid.*, **81**, 6177 (1959). Earlier discussion of this reaction mechanism are to be found in ref. 8.

[8] (a) H. H. Sisler, *et al.*, *ibid.*, **76**, 3912 (1954); (b) R. S. Drago and H. H. Sisler, *ibid.*, **77**, 3191 (1955); (c) G. M. Omietansky, A. D. Kelmers, R. W. Shellman and H. H. Sisler, *ibid.*, **78**, 3874 (1956).

[9] M. Anbar and G. Yagil, *ibid.*, **84**, 1790 (1962).

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

[11] L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1953.

[12] G. W. Watt and J. P. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

titration with a standard iodine solution as described by Rowe and Audrieth.[13]

All spectrophotometric and colorimetric measurements were made on a Beckman Model DU instrument. Cells with 1.000 cm. light path were used, except for very dilute solutions of chloramine.

Kinetic Measurements.—The kinetics of hydrazine formation were followed by observing the decrease of absorption of chloramine at 250 mμ (corrected for the absorption of pernitrite by measurements at 300 mμ, as previously described).[9] In most of the runs the formation of hydrazine was simultaneously followed. In these experiments samples were drawn at intervals and the hydrazine content was determined by the colorimetric method described above. It had to be verified that no hydrazine is consumed during acidification. To check this point, known amounts of hydrazine were added to the reaction mixture and the *increase* in the optical density was in accord with the hydrazine added. This proves that chloramine or other components of the reaction mixture do not interfere with the analytical determination, and it was unnecessary to add a quenching reagent prior to the determination of hydrazine.

Preparation of Reaction Mixtures.—Two different procedures were adopted: in the first procedure a separate reaction mixture was prepared for each measurement. The appropriate amounts of ammonia and chloramine stock solutions were introduced into a 10 ml. volumetric flask, filled to the mark and placed in a thermostat maintained at the required temperature (± 0.05°). At intervals two samples were drawn, one for measurements of optical density and the other for hydrazine determination. Another aliquot was taken from each vessel after the reaction was completed to determine $O.D._\infty$ and the final yield of hydrazine. This procedure gave a firm check on the reproducibility of the reaction kinetics. A fair reproducibility was established in spite of the reaction kinetics. A fair reproducibility was established in spite of the catalytic effects mentioned in the literature. This procedure also decreased losses of gaseous ammonia, a factor which was found less critical than anticipated, even in concentrated hydroxide solutions. In runs carried out by this procedure no gelatin was added, nevertheless high yields of hydrazine were obtained as long as the concentration of ammonia was higher than 1 molar. After reproducibility was demonstrated, a second procedure was occasionally followed in which a single reaction mixture was prepared. A sample of the reaction mixture was placed in a stoppered spectrophotometer cell, and the change of the absorption at 250 mμ was automatically recorded as function of time. Temperature in the cell compartment was maintained constant ± 0.1° by means of a double thermospacer set fed from a thermostat. At the end of each run the concentration of ammonia was redetermined by acidimetric titration or, at high concentrations of hydroxide, by the Nessler method.

In some of these experiments, in absence of gelatine, a sudden decrease in absorption occurred after over 70% of the chloramine was consumed. This indicates an induced reaction of chloramine with the hydrazine formed. The induction period for this reaction varied spuriously from run to run; a similar behaviour was found in liquid ammonia solutions.[7] Gelatine prevented this effect but had otherwise no effect on the rate of reaction. Wherever this induced reaction was encountered, hydrazine yields had to be obtained by extrapolation.

Evaluation of Results.—Log $(O.D. - O.D._\infty)$ (corrected for pernitrite wherever necessary) calculated from the experimental data was plotted against time. In general straight lines resulted up to at least one half life, (except a $pH < 11$ and at $[NH_2Cl] > > 4.10^{-3}M$). From these plots $t_{1/2}$ and $k_{obsd} = 0.693/t_{1/2}$ were calculated. The fact that straight lines have been obtained means that the rate of the reaction, which has always been carried out in presence of a large excess of ammonia, is first order in chloramine concentration. Deviations from a straight line were observed in cases when the chloramine–hydrazine reaction proceeded at a rate comparable to that of the chloramine–ammonia reaction. In such cases, exceptionally low yields of hydrazine were obtained and the k_{obsd} which was then derived by extrapolation was still higher than expected for the chloramine–ammonia reaction alone.

An attempt was made to get a quantitative estimate of the effect of the chloramine–hydrazine reaction on the measured rate of the chloramine–ammonia interaction. A series of exploratory rate measurements of the chloramine–hydrazine reaction in the absence of gelatine, yielded spurious results, with half lives ranging from seconds to hours under the same conditions. In presence of gelatine this reaction is a relatively slow process. At $pH = 13$ and $10^{-3}\ M\ N_2H_4$ the concentration of chloramine dropped to 50% after 220, 80 and 40.5 minutes, when the initial chloramine concentrations were 0.2, 1 and $5 \times 10^{-3}\ M$, respectively.

These results, compared with the half life of the chloramine–ammonia reaction (Table III), at the same pH in 1 M ammonia solutions ($t_{1/2} = 102$ min.), show that the reaction with hydrazine does contribute to the rate of chloramine consumption to a certain extent. The change in slope of the first order rate expression with time under the experimental concentrations should not exceed 30% at half life; the deviations observed were in fact smaller than this value. At higher ammonia concentrations and at higher alkalinities the contribution of the chloramine–hydrazine reaction was hardly detectable. Only in certain runs high in chloramine ($> 4 \times 10^{-3}\ M$), low in ammonia ($< 5 \times 10^{-1}\ M$) or at $pH < 11$, when the final yield of hydrazine was below 50%, considerable deviations from first order behavior were observed. In those cases the measured rate constants for chloramine consumption were higher than expected. When the over-all rate of the chloramine–hydrazine reaction is much faster than that of the reaction with ammonia, the hydrazine yield would be nil. Under these conditions one would find an apparent rate constant for the chloramine consumption three times that of the chloramine–ammonia reaction. In our study most of the runs yielded over 60% hydrazine, consequently the apparent rate constants may be off the "true" constant by a few per cent. only.

Rate constants derived from hydrazine determinations were occasionally up to 30% higher than those derived from following changes in chloramine concentration. This may be due to the uncertainty in determining the $O.D._\infty$.

At hydroxide concentrations above 0.5 M, k_{obsd} had to be corrected for the contribution of the hydrolysis reaction.[9] At lower alkalinities no such correction had to be applied as the rate of hydrolysis in this region is negligible. Since the reaction was found first order in ammonia (Table III), a bimolecular rate constant was calculated by dividing by the concentration of ammonia. $k_n = k_{obsd}/(NH_3)$. This constant is given in Table I, column 4.

The kinetics of the chloramine–ammonia reaction were found reproducible under our experimental conditions, as may be seen in Table I.

Values of $t_{1/2}$ (column 5) were calculated from hydrazine concentration measurements.

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(13) R. W. Rowe and L. F. Audrieth, *J. Am. Chem. Soc.*, **78**, 563 (1956).

TABLE I

THE REACTION BETWEEN CHLORAMINE AND AMMONIA AT $pH = 11.85$, $[NH_2Cl] = 2 \times 10^{-3}M$, $T = 27.3°$

	NH_3, mole^{-1} l.	$t_{1/2}$, min.	10^6k_n, mole^{-1} l. sec.$^{-1}$	$t_{1/2}$, min.	Yield hydrazine, %
Separate vessels O_2 passed	0.98	98	119	96	59
Separete vessels O_2 not expelled	.99	104	113	89	66
Separate vessels O_2 expelled by N_2	.955	109	111	92	59
One vessel O_2 not expelled	1.05	90	122	78	44
One vessel 0.05% gelatine present	1.05	97	113	95	56
	Average	115			

It is seen that the presence or absence of oxygen or of gelatine had no effect on the rate. The same rate constants were obtained using both kinetic techniques.

Results

The dependence of the rate of chloramine–ammonia reaction on base concentration was investigated in 1 M ammonia in the alkalinity range from $pH = 10.15$ up to 9 M hydroxide ion. Values of pH below 11.85 were obtained by adding ammonium perchlorate and above $pH = 11.85$ by adding sodium or potassium hydroxide. The results are presented in Table II.

TABLE II

THE REACTION OF AMMONIA WITH CHLORAMINE. DEPENDENCE OF THE RATE CONSTANT ON THE ALKALINITY OF THE SOLUTION. INITIAL [CHLORAMINE] 2×10^{-3} MOLE L.$^{-1}$, [AMMONIA] 1.0 MOLE l.$^{-1}$, $T = 27.3°$

Exp. no.		Conc., mole^{-1} l.	pH, H_-[a]	10^6k_{obsd}, sec.$^{-1}$	10^6k_{corr}, sec.$^{-1}$	$10^6k'b$, mole^{-1} l. sec.$^{-1}$	Yield hydrazine %
2-1	NH_4ClO_4	0.10	10.15	170	...	..	5
2-2	NH_4ClO_4	.05	10.35	155	...	..	10
2-3	NH_4ClO_4	.01	11.00	142	...	..	30
2-4	....	..	11.85	115	0	..	60
2-5	NaOH	.10	13.00	112	0	..	66
2-6	NaOH	.49	13.70	134	22	..	78
2-7	NaOH	.99	14.00	165	53	0	70
2-8	NaOH	1.97	14.40	380	270	140	50
2-9	NaOH	2.96	14.68	520	410	180	41
2-10	NaOH	4.55	15.08	920	810	280	40
2-11	NaOH	5.40	15.35	1850	1750	750	40
2-12	NaOH	6.75	15.58	2800	2700	1000	34
2-13	NaOH	7.95	15.80	3700	3600	1200	30
2-14	NaOH	8.20	15.85	5500	5400	2400	27
2-15	KOH	0.10	13.00	114	0	0	65
2-16	KOH	0.97	14.00	205	90	37	65
2-17	KOH	1.94	14.50	360	250	90	64
2-18	KOH	2.91	14.83	830	720	400	51.5
2-19	KOH	3.95	15.13	1550	1440	820	46
2-20	KOH	4.49	15.27	1990	1880	580	38
2-21	KOH	5.93	15.75	3250	3140	740	38
2-22	KOH	7.45	16.25	10300	10200	3000	32
2-23	KOH	7.95	16.45	14600	14500	3500	35.5
2-24	KOH	8.94	16.85	27500	27500	4500	30

[a] In this and following tables values below 13.00 are measured pH values; above 13.00 the given values were graphically interpolated from H_- data.[14]

It can be seen from Table II that up to 0.5 M OH^- ($pH = 13.7$) there is no significant change of the rate with rising alkalinity and the reaction can be said to be base independent. The bimolecular rate constant for this reaction is designated as k_n. The increase in k_{obsd} below $pH = 11$ may be accounted for by the secondary hydrazine–chloramine reaction, as it is indicated by the diminished yield of hydrazine at these alkalinities. At alkalinities above 0.5 M hydroxide there is a sharp increase in the rate. The observed rate constant increases by a factor of more than 30 when NaOH concentration is increased from 1 to 8 molar; the corresponding rise in KOH amounts to a factor of about 70. This increase is even more pronounced after the contribution of the base independent reaction is substracted; $k_{corr} = k_{obsd} - k_n$. This base catalysed behavior is best explained by applying the acidity function in NaOH and KOH as measured by Schwarzenbach and Sulzberger.[14] A linear correlation with this function has been demonstrated for the hydrolysis of chloramine and dimethylchloramine.[9] When the logarithms of the corrected rate constants, k_{corr}, was plotted against H_- a straight line with a slope of 0.90 was obtained (Fig. 1).

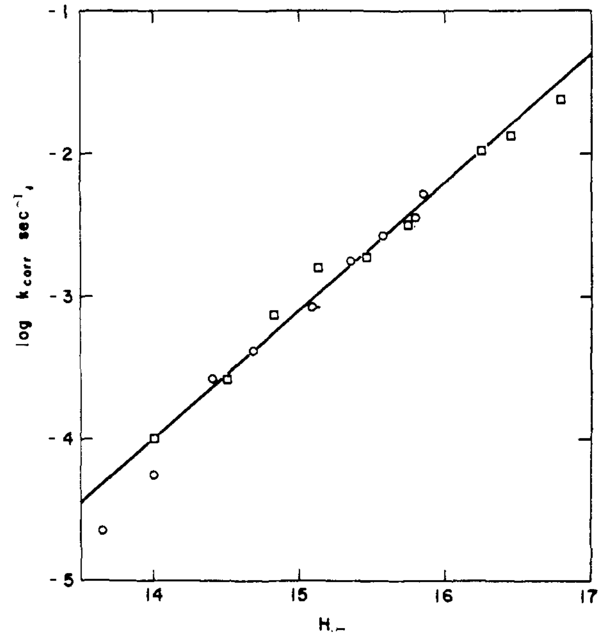

Fig. 1.—Base catalyzed chloramine ammonia reaction $[NH_2Cl] = 2 \times 10^{-3}$, $[NH_3] = 1.0$, $T = 27.3°$: ○, sodium hydroxide; □, potassium hydroxide.

In the highly alkaline range, competition of hydrolysis has also to be taken into account. Comparison of the rate constants in the presence of ammonia to the rate of alkaline hydrolysis shows that above $H_- = 15.00$ about 60% of the initial chloramine undergoes hydrolysis. Hydrazine yields drop gradually between $pH = 13.00$ and $H_- = 15.00$ from 70% to 30% (Table II). This explains the observation made by Audrieth, *et al.*,[15] that the

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(14) G. Schwarzenbach and R. Sulzberger, *Helv. Chem. Acta*, **27**, 348 (1948).

(15) M. Jones, L. F. Audrieth and E. Colton, *J. Am. Chem. Soc.*, **77** 2701 (1955).

TABLE III

THE REACTION OF AMMONIA WITH CHLORAMINE. THE RATE AT DIFFERENT INITIAL CONCENTRATIONS OF AMMONIA AND CHLORAMINE IN DILUTE AND IN CONCENTRATED ALKALINE SOLUTIONS, $T = 27.3°$

Exp. no.	(NH_2Cl), 10^3 mole^{-1} l.	(NH_3), mole^{-1} l.	(KOH), mole^{-1} l.	pH, H^-	10^6k_{obsd}, mole^{-1} l. sec.$^{-1}$	10^6k_n, mole^{-1} l. sec.$^{-1}$	$10^6k_b'$, mole^{-1} l. sec.$^{-1}$	Yield hydrazine, %
3-1	2.0	0.185	..	11.45	32	172	.....	5
3-2	2.0	0.98	..	11.85	120	118	.....	59
3-3	2.0	1.98	..	12.00	222	112	.....	75
3-4	2.0	4.42	..	12.25	500	114	.....	86
3-5	0.2	0.96	..	11.65	130	94	.....	66
3-6	1.0	.97	..	11.80	102	116	.....	59
3-7	2.0	.99	..	11.85	104	113	.....	60
3-8	4.0	.98	..	11.92	90	130	.....	25
3-9	2.0	..	4.00	15.13	750	..	750(k_s)	..
3-10	2.0	.55	4.00	15.13	1280	..	850	20
3-11	2.0	1.09	4.00	15.13	1480	..	690	33
3-12	2.0	1.63	4.00	15.13	2030	..	670	48
3-13	2.0	2.18	4.00	15.13	2300	..	570	54
3-14	2.0	4.36	4.00	15.13	3800	..	590	60
3-15	2.0	5.45	4.00	15.13	5300	..	730	65
3-16	2.0	6.54	4.00	15.13	6600	..	790	69
3-17	1.0	2.18	4.00	15.13	2800	..	830	78
3-18	2.0	2.18	4.00	15.13	2300	..	600	54
3-19	10.0	2.18	4.00	15.13	2700	..	780	18

highest yields of hydrazine are obtained when OH^- concentration is 0.25 molar. The observed rate constants in alkaline solution were therefore corrected for the base independent contribution ($k_n = 1.1 \times 10^{-4}$ sec.$^{-1}$) and the bimolecular rate constants for the hydrolysis reaction are given in Table III column 7.

The results demonstrate that the chloramine–ammonia reaction proceeds *via* two distinct paths, one base independent and the other base catalyzed; both reaction paths yield hydrazine. In the subsequent presentation the features of each path will have to be discussed separately.

The dependence of the rate on the concentrations of ammonia and of chloramine has been studied in both ranges of alkalinities. Chloramine and ammonia concentrations were independently changed by a factor 10 to 20. The results are presented in Table III.

The values k_n and k_b' in Table III were calculated from $k_n = k_{obsd}/[NH_3]$ and $k_b' = \frac{k_{obs} - k_h}{[NH_3]} - k_n$. k_b' is the bimolecular rate constant for the base catalysed chloramine–ammonia reaction at a specified alkalinity. The constancy of the values of k_n and k_b' show that both, the base independent and the base catalysed reactions, are first order both in ammonia and in chloramine. Exceptional higher values of k_n and k_b' were observed at the lowest ammonia and highest chloramine concentrations. These deviations which do not amount to more than 30% and which are accompanied by exceptionally low yields of hydrazine are accounted for by the secondary chloramine–hydrazine reaction. The results of Table III may be expressed by the equation

$$R = k_n(NH_2Cl)(NH_3) + k_b \xrightarrow[h_-]{K_w} (NH_2Cl)(NH_3)$$

The rate constants at 27.3° were $k_n = 1.1 \times 10^{-4}$ mole^{-1} sec.$^{-1}$ and $k_b' = 7.50\ 10^{-4}$ mole^{-1} l. sec.$^{-1}$ at $H_- = 15.13$.

As the slope of Fig. 1 deviates from unity by about 10% care should be taken when rates at different alkalinities are calculated.

Measurements of the reaction rate at temperatures between 0.3–58.5° are presented in Table IV. This table also shows the effects of sodium chloride and sodium phosphate on the rate, as well as the effect of deuterium substitution of the reactants and the solvent.

The energies of activation of the base independent and base catalysed reaction were calculated from the rate constants at different temperatures. The values obtained are

$$k_n = 1.05 \times 10^9\, e^{-17,700/RT} \text{ and } k_b' = 5.6 \times 10^7\, e^{-16,300/RT} \text{ at } H_-\ 15.13.$$

The rate of reaction between ND_2Cl and ND_3 in D_2O has been measured both in the base independent and in the base catalysed ranges (Expts. 4–4, 4–13). In both cases, given in Table IV, an acceleration of the rate is observed. These reactions show also a diminished yield of hydrazine (owing perhaps to a catalytic effect on the $NH_2Cl–N_2H_4$ reaction by some impurity in the D_2O), which generally causes an increase in the apparent rate constant. The observed acceleration in D_2O may thus be apparent only, anyway the effects observed exclude any appreciable retardation of the rate in deuteriated solutions. From the experiments given in Table IV, it can be seen that chloride (Expts. 4–5 and 4–14) and phosphate ions (Expt. 4–6) at relatively high concentrations have no effect on the rate of chloramine–ammonia reaction that cannot be accounted for by the secondary reaction or by a small salt effect on the value of H_- (secondary salt effect).

Substituted Amines.—The rates of reaction of primary, secondary and tertiary methyl amines with chloramine have been measured. The results are presented in Table V. It is known that the reactions between methyl amines and chloramine produce substituted hydrazines in high yields.[8c,18]

TABLE IV

THE REACTION BETWEEN AMMONIA AND CHLORAMINE IN DILUTE AND CONCENTRATED ALKALINE SOLUTION. THE DEPENDENCE OF RATE UPON TEMPERATURE, SUBSTITUTION OF DEUTERIUM AND ADDITION OF NaCl AND Na_3PO_4. INITIAL CONCENTRATION OF CHLORAMINE 2.0 × 10^{-3} MOLE/l.$^{-1}$

Exp. no.	Temp., °C.		Conc., mole l.$^{-1}$ or (%)	NH_3, mole l.$^{-1}$	KOH, mole l.$^{-1}$	pH, H$^-$	$10^6k_{obsd.}$, sec.$^{-1}$	$10^6k_n(k_h$*), l. mole^{-1} sec.$^{-1}$	$10^6k_b'$, l. mole^{-1} sec.$^{-1}$	Yield hydrazine, %
4-1	0.3	....	..	1.89	..	11.80	5.8	6.6	..	34
4-2	27.3	....	..	1.00	..	11.85	112	112	..	59
4-3	58.5	....	..	0.82	..	11.80	1650	1990	..	55
4-4	27.3	D_2O	(95)	0.94	..	11.90	220	235	..	20
4-5	27.3	NaCl	1.0	1.00	..	11.80	143	143	..	33
4-6	27.3	Na_3PO_4	0.25	1.00	..	12.48	140	140	..	58
4-7	27.3	....	..	2.18	4.00	15.13	2300	..	700	54
4-8	28.2	....	..	..	4.00	15.13	1900	1900[a]	..	..
4-9	38.2	....	..	2.18	4.00	15.13	6200	..	1800	57
4-10	48.5	....	..	..	4.00	15.13	5000	5000[a]	..	..
4-11	48.5	....	..	2.18	4.00	15.13	14800	..	4050	63
4-12	27.3	....	..	1.00	3.00	14.85	700	..	270	60
4-13	27.3	D_2O	(90)	..	2.95	14.83	450	450[a]	..	..
4-14	27.3	D_2O	(90)	0.94	2.95	14.83	1000	..	330	28
4-15	27.3	NaCl	1.0	..	3.00	14.85	285	285[a]	..	..
4-16	27.3	NaCl	1.0	1.00	3.00	14.85	890	..	460	48

* k_h.

[a] These k_h values are taken from ref. 9.

TABLE V

THE REACTION BETWEEN CHLORAMINE AND SUBSTITUTED AMMONIA IN DILUTE AND CONCENTRATED ALKALINE SOLUTION

T = 27.3°

Exp. no.	Amine	Conc., mole l.$^{-1}$	NH_2Cl, 10^3 moles l.$^{-1}$	KOH, mole l.$^{-1}$	pH, H$_-$	$10^3k_{obsd.}$ sec.$^{-1}$	$0^3k_n,k_b'$ mole$^-$ l. sec.^{1}.
5-1	NH_3	1.00	2.0	..	11.85	..	0.115
5-2	CH_3NH_2	0.098	2.0	..	11.70	1.3	13.3
5-3	CH_3NH_2	.250	1.7	..	11.70	8.35	14.0
5-4	CH_3NH_2	.098	2.0	1.0	14.0	1.4	14.2
5-5	$(CH_3)_2NH$	.053	1.55	..	11.70	4.3	81.0
5-6	$(CH_3)_3N$	.0156	1.55	..	10.95	2.7	184
5-7	$(CH_3)_3N$	.0315	2.0	..	11.20	5.1	163
5-8	$(CH_3)_3N$	.0510	2.0	..	11.60	9.2	182
5-9	$(CH_3)_3N$	.0315	0.4	..	11.20	6.0	193
5-10	$(CH_3)_3N$	.0156	2.0	0.1	13.00	3.2	190
5-11	....	....	2.0	4.5	15.30	0.83(k_h)	..
5-12	NH_3	1.00	2.0	4.5	15.30	1.60	0.67
5-13	CH_3NH_2	0.101	1.7	4.5	15.30	5.4	32
5-14	$(CH_3)_2NH$	.053	1.55	4.5	15.30	23	370
5-15	$(CH_3)_3N$	.0156	2.0	1.0	14.00	4.3	70
5-16	$(CH_3)_3N$	.0156	2.0	3.0	14.85	9.6	410
5-17	$(CH_3)_3N$	.0156	2.0	4.5	15.30	14.6	660
5-18	$(CH_3)_3N$	.0156	2.0	6.0	15.27	35	1980

In our experiments straight line plots were obtained in all cases, as the products did not consume chloramine by secondary reactions to any appreciable extent. The yield of 1,1-dimethylhydrazine from dimethylamine and chloramine was determined, and 98%, 91% were found at pH = 12.0 and at 3 M KOH, respectively. The results show that both the base independent and base catalysed paths do exist in the case of substituted amines. The reaction is again shown to proceed first order in chloramine and in the substituted amine concentrations. The H_- dependence of trimethylamine-chloramine reaction is demonstrated with a slope of 0.81. It was found that the rates of the various amines increase in the order $NH_3 < MeNH_2 < Me_2NH < Me_3N$ for both paths.

Substituted Chloramines.—The reactions of substituted chloramines with ammonia were investigated in parallel with those of substituted ammonia. An interaction was found and kinetics with a limited reproducibility could be followed. No 1,1-dimethylhydrazine could be detected in the products and there were appreciable deviations from first order kinetics. It seems probable that secondary reactions have a large effect on the rate of chloramine decomposition. The values of k_{obsd} presented in Table VI were graphically derived from initial slopes and a relatively large experimental error is expected in these runs. In the base independent region the relative rates of reaction decrease in the order $NH_2Cl > MeNHCl > Me_2NCl$. In the base catalyzed region the presence of ammonia hardly affects the rate of chloramine disappearance and the existence of a base catalyzed reaction between substituted chloramines and ammonia is rather doubtful.

Table V1

The Reaction between Ammonia and Substituted Chloramines in Dilute and Concentrated Alkaline Solutions

Exp. no.	Chloramine mole^{-1}	Conc., 10^3 mole^{-1} l.	NH_3, mole^{-1} l.	NOH, pH l.	pH, H_-	10^6k_{obsd}, sec.$^{-1}$
6-1	NH_2Cl	2.00	1.00	..	11.85	116
6-2	CH_3NHCl	2.00	1.00	..	11.60	17
6-3	$(CH_3)_2Cl$	2.00	0.93	..	11.50	9.7
6-4	$(CH_3)_2Cl$	2.00	..	..	11.50	0.8
6-5	NH_2Cl	2.00	1.00	4.5	15.30	1510
6-6	NH_2Cl	2.00	..	4.5	15.30	920
6-7	CH_3NHCl	2.00	1.00	4.5	15.30	317
6-8	CH_3NHCl	2.00	..	4.5	15.30	287
6-9	$(CH_3)_2NCl$	2.00	0.90	4.5	15.30	910
6-10	$(CH_3)_2NCl$	2.00	..	4.5	15.30	810

Discussion

Mechanism of the Base Independent Path.—It has been demonstrated in the results (Table II) that the chloramine–ammonia reaction proceeds by two independent paths, a base independent and a base catalyzed one. The base independent path will be discussed first.

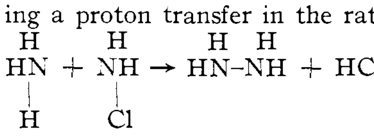
The prevailing species of ammonia and of chloramine in the pH range 10–14 are the neutral molecules NH_3 and NH_2Cl. A base independent rate law suggests a direct interaction between these species; alternative mechanisms which render an identical rate expression are the interaction of NH_2^- with NH_3Cl^+ or of NH_4^+ with $NHCl^-$. The interaction of NH_2^- with NH_3Cl^+ may be excluded by considering the concentrations of the species involved; the estimated pK of NH_3 is[16] at 35 and that of NH_3Cl^+ is 0,[17]; considering the experimental rate constant this would yield an unlikely bimolecular specific rate constant of over 10^{30} mole^{-1} l. sec.$^{-1}$. The participation of an amide ion seems improbable also in view of the existence of a reaction between trimethyl amine and chloroamine. Likewise the existence of the reaction between dimethylchloramine and ammonia makes the alternative mechanism rather improbable.

A preequilibrium in which NH_2^+ and Cl^- are formed from chloramine may be excluded in view of the fact that chloride ions do not retard the rate of reaction. Moreover, the nonexistence of an isotopic exchange between chloride ions and chloramine at a relatively fast rate[18] makes such a preequilibrium rather improbable. It may be concluded that the base independent path is an interaction between a molecule of NH_3 and a molecule of NH_2Cl.

A general base catalysed mechanism in which ammonia (or amine) acts as a general base can be envisaged. In this mechanism the amine would abstract a hydrogen ion from chloramine in a rate determining step, followed by a fast reaction between the chloramide ion formed and another molecule of ammonia

$$NH_3 + NH_2Cl \xrightarrow{slow} NH_4^+ + NHCl^-$$

$$NHCl^- + NH_3 \xrightarrow{fast} N_2H_4 + Cl^-$$

This mechanism is non-compatible with the hydroxide catalysed path which again is first order in ammonia concentration, *i.e.* ammonia is involved in the rate determining step not merely as a general base. Further, a proton transfer in the rate determining step is expected to be slowed down when deuterium substituted chloramine reacts with ammonia—no such effect could be demonstrated (Exp. 4–4); moreover, the absence of a catalytic effect in the presence of triphosphate ions exclude a general base catalysis of the chloramine–ammonia reaction. A four-center activated complex involving a proton transfer in the rate determining step  $\underset{H}{\overset{H}{HN}} + \underset{Cl}{\overset{H}{NH}} \rightarrow \overset{H\quad H}{HN\text{-}NH} + HCl$, seems rather improbable as no decrease in rate was observed when hydrogen in both reactants was replaced by deuterium (Expt. 4–4).

The most plausible mode of interaction is a nucleophilic attack by ammonia or amine on chloramine. This can be verified by a comparison of the relative rates of reaction of different amines with chloramine. A substitution of hydrogen on ammonia by methyl groups increases the electron density of the lone pair of electrons on the nitrogen, and consequently its nucleophilic reactivity. The relative rate constants of the reaction of ammonia, mono- di- and trimethylamine (ammonia = 1) is 1:120:700:1550. Comparable relative rates have been found for the substitution of chloride on dinitrochlorobenzene by ammonia and amines 1:80:850:?[19] and for the ammonolysis of methyl acetate 1:64: > 1000:?.[20] A nucleophilic attack by ammonia or amine on chloramine is thus indicated. The nucleophilic character of the reaction supports the conclusion that NH_4^+ ion or alkyl ammonium ions are not active species in the reaction.

The increase in rate on replacing hydrogen atoms on ammonia by alkyl groups has been pointed out. On the other hand the replacement of hydrogen on the substituted reagent by a methyl group is followed by a decrease in the rate of nucleophilic substitution. The carbon analogs of chloramine, methyl and dimethyl chloramine are methyl, ethyl and isopropyl halides; the relative rates of nucleophilic substitution are 1:0.14:0.08 for substituted chloramine (Table VI) as compared to an average of 1:0.03:0.009 for 20 substitution reactions of the three alkyl halides.[21]

It may be concluded that substitution of Cl^- on chloramine is analogous to the well known S_N2 substitution of alkyl halides by ammonia and amines; the electrophilic center in this case is a nitrogen instead of a carbon atom. The analogy between chloramine and methyl chloride is also demonstrated by the similar mechanism of their alkaline hydrolysis.[9]

The Mechanism of the Base Catalyzed Path.—The examination of the dependence of the rate of

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(20) E. M. Arnett, I. G. Miller and A. R. Day, *J. Am. Chem. Soc.*, **72**, 5635 (1950).

(21) A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).

the ammonia–chloramine reaction on alkali concentration (Table II) shows a rapid increase in rate above 1 molar hydroxide. The observed rate is higher than the rate of chloramine hydrolysis showing a similar dependence on alkalinity.[9] The rate of hydrazine formation which shows a linear H_- dependence in concentrated hydroxide solutions is first order in both reagents (Table III). This obviously implies the participation of ammonia and amines in the rate determining step.

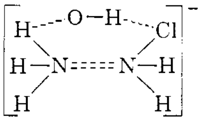
The fact that a base catalysed *bimolecular* reaction shows a linear dependence on H_- is surprising at first sight in view of the Hammett–Zucker criteria.[22] It might be explained if the ratio of activity coefficients fulfils the condition:

$$\frac{f_{NH_4} \cdot f_{NH_2Cl}}{f^*} = \frac{f_{BH}}{f_{B^-}}$$

This implies that ammonia is loosely bound in the activated complex and consequently f_{NH_3} contributes substantially to the value of $f^{\ddagger}$. Further implications of linear dependence of base catalysed reactions on H_-, in other cases where an A-1 mechanism has to be excluded, will be discussed elsewhere.[23]

Several explanations for the role of a base in hydrazine formation might be suggested. First hydroxide ion as a base might affect the reaction rate by abstracting a proton from chloramine in a slow step. The reaction would in this case be zero order in ammonia, which contradicts the experimental findings. Furthermore, this mechanism would imply an appreciable retardation in the rate when ND_2Cl is present instead of NH_2Cl; this, however, could not be demonstrated (Expt. 4–13). The same arguments apply to the possibility of a slow proton abstraction from ammonia by a hydroxide ion.

Another way which might explain the function of a base is the participation of an OH^- ion in the formation of a cyclic transition state:



The double dashed lines indicate the necessity of accommodating two pairs of electrons in the N-N bond. Such a complex is unlikely, because of the absence of any diminution in rate when ND_2Cl is present; further, the existence of a rapid base catalysed reaction between trimethylamine and chloramine makes this mechanism rather improbable.

The only plausible explanation for the effect of hydroxide ion is that chloramide ion ($NHCl^-$) is formed in a rapid preequilibrium, and this ion is subsequently attacked by ammonia or amine to form the appropriate hydrazine

$$OH^- + NH_2Cl \rightleftharpoons NHCl^- + H_2O$$

$$NH_3 + NHCl^- \xrightarrow{\text{slow}} N_2H_4 + Cl^-$$

A comparison of the relative rates of the reaction of ammonia mono, di- and trimethylamine in the alkaline region (1:50:580:1300), indicates again a *nucleophilic attack* of ammonia or amine.

This mechanism is in accord with all the experimental data: it should not exhibit general base catalysis, it may account for the acceleration on substitution of D for H[24] and the concentration of $NHCl^-$ is expected to show first order dependence on h_-. If $NHCl^-$ is the reactive species in the base catalysed reaction, no base catalysed reaction between dimethyl chloramine and ammonia should be expected. The evidence for the existence of such a reaction (Expt. 6–9) is rather uncertain.

The pK of $NHCl^-$ may be estimated > 18, as no change in the absorption spectrum of chloramine was observed up to $H_- = 17.3$.[9] From $k_b' = 5.6 \times 10^7 x^{-16.300/RT}$ at $H_- = 15.13$ a rate constant $> 2 \times 10^{11} e^{-16.300/RT}$ at 27° can be derived (assuming a small ΔH of ionization). This shows that $NHCl^-$ is over one hundred fold more vulnerable to substitution by ammonia or amines than chloramine. This implies an increased polarisation of the N-Cl bond in $NHCl^-$ compared to NH_2Cl; as it has been suggested by Jander.[25]

It has been suggested[2] that chloramide ions do not react directly with ammonia but decompose in a rate determining step to NH + Cl. The imine molecule in the single state was expected to react in a fast step with ammonia to yield hydrazine. This path would render a rate expression zero order in ammonia and may be thus excluded. A fast preequilibrium $NHCl^- \rightleftharpoons NH + Cl^-$ with a slow $NH + NH_3$ reaction has also to be excluded, since Cl^- has no retarding effect on the reaction rate (Expt. 4–14).

It may be concluded that although the participation of the NH radical in the formation of hydrazine[1–4] could not be confirmed by kinetic measurements, still it was shown that at high alkalinities chloramide ions are actually involved in this reaction, as suggested by Audrieth.[2,3] At lower alkalinities the bimolecular interaction of chloramine with ammonia which was advocated by Sisler[7,8] has been substantiated as a nucleophilic substitution of the S_N2 type on the undissociated chloramine.

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