

AD-A071 195

AEROSPACE CORP EL SEGUNDO CALIF IVAN A GETTING LABS
STUDIES OF THE PRODUCTION OF CHLORAMINE IN THE GAS PHASE. (U)

F/G 7/2

JUN 79 C C BADCOCK, D J MILGATEN, E T CHANG

F04701-77-C-0078

UNCLASSIFIED

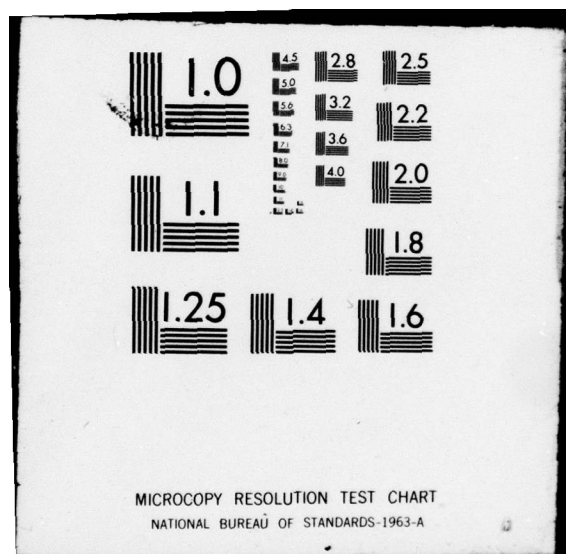
TR-0078(3447)-1

SAMSO-TR-79-42

NL

1 OF 1
AD
A071195





LEVEL

72

DA071195

Studies of the Production of Chloramine in the Gas Phase

Prepared by C. C. BADCOCK,
D. J. MILGATEN, and E. T. CHANG
Chemistry and Physics Laboratory
The Ivan A. Getting Laboratories
The Aerospace Corporation
El Segundo, Calif. 90245

1 June 1979

Final Report

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

Prepared for

SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

DDC
RECEIVED
JUL 13 1979

DDC FILE COPY

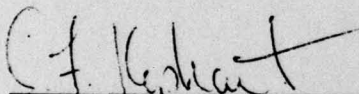
79 07 13 006

This final report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-77-C-0078 with the Space and Missile Systems Organization, Deputy for Space Launch Systems, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by S. Siegel, The Ivan A. Getting Laboratories and S. Lewis, Programs Group. Maj. J. F. Kephart, SAMSO/LV-1 was project officer.

This report has been reviewed by the Office of Information and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

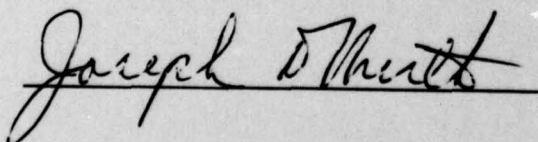
Approved



J. F. Kephart, Maj, USAF

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER



Joseph D. Thurtell

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER 18 SAMSO-TR-79-42	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) 6 STUDIES OF THE PRODUCTION OF CHLORAMINE IN THE GAS PHASE		5. TYPE OF REPORT & PERIOD COVERED 9 Final report	
7. AUTHOR(s) 10 Charles C. Badcock, Donna J. Milgaten, and Elfreda T. Chang		8. PERFORMING ORG. REPORT NUMBER 144 TR-0078(3447)-1	
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 145p.	
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE 11 1 Jun 79	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Space and Missile Systems Organization, Air Force Systems Command, Los Angeles Air Force Station, P.O. Box 92960, Worldway Postal Center, Los Angeles, Calif. 90009		13. NUMBER OF PAGES 43	
15. SECURITY CLASS. (of this report) Unclassified		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chloramine Ammonia Chlorine Hydrazine and derivatives AMMONIA AND CHLORINE			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The gas phase reaction of NH_3 and Cl_2 to produce chloramine NH_2Cl has been studied. The ratio of reactants (NH_3/Cl_2), the effects of diluent gas (N_2), and the temperature of the reactants and reaction zone were investigated in a reactor designed to emphasize changes in the yield. The yield of NH_2Cl and the temperature of the reacted gas stream were the key parameters monitored. The yield can be high when the ratio of reactants is low if diluent gas is used. The molar ratio $(\text{NH}_3 + \text{N}_2)/\text{Cl}_2$ can be lower than			

DD FORM 1473
(FACSIMILE)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

409 944

JOB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

seven based on literature data and that reported here. Except under one set of apparently optimized conditions, it did not matter whether the diluent was added to the NH_3 or the Cl_2 reactant stream. The temperature of the reaction zone and the reactants had little effect on the yield except under the optimized conditions. The temperature of the reacted gases did roughly correlate with yield in the experiments. Highest yields were observed when the reacted gas was cooler than 260°C . The yield decreased as the temperature rose to near 310°C in the gas stream. Emission of light and low yields were observed at higher temperatures. When the reaction zone and reactant gases were heated to 190°C with $\text{NH}_3/\text{N}_2/\text{Cl}_2 = 4/3.4/1$ and N_2 in the Cl_2 stream, yields of 95 percent were observed. A mechanism involving a chain reaction is proposed to explain the chemical kinetics of the system.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

CONTENTS

I.	INTRODUCTION	1
II.	EXPERIMENTAL	5
	A. Reactor and Reactant Delivery System	5
	B. Chemicals	7
	C. Sampling and Analysis	7
	D. Yield Computation	9
	E. Description of an Experimental Run	10
III.	RESULTS	11
	A. Characterization of the Reactor	11
	B. Effects of Reactant Ratios, Diluent Gases, and Temperature	16
IV.	DISCUSSION	25
V.	SUMMARY AND CONCLUSIONS	33
	REFERENCES	37
	APPENDIX	39

Accession For	
NTIS GMA&I	☒
DDC TAB	☐
Unannounced Justification	☐
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	

FIGURES

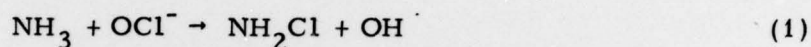
1.	Reactor Schematic	6
2.	Glass Sampler for Analysis of Chloramine	8
3.	Characteristic Temperature Profiles for an Experiment	12
4.	Reactor Characterization	14
5.	The Yield of Chloramine vs the Observed Reaction Temperature	20

TABLES

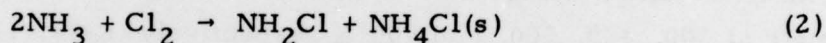
1.	Summary of Chloramine Yields, $\text{NH}_3/\text{Cl}_2 = 8$, Cl_2 Flow Rate = 0.4 or 0.5 l/min	17
2.	Summary of Chloramine Yields, $\text{NH}_3/\text{Cl}_2 = 6$, Cl_2 Flow Rate = 0.5 l/min	17
3.	Summary of Chloramine Yields, $\text{NH}_3/\text{Cl}_2 = 5$, Cl_2 Flow Rate = 0.5 l/min	18
4.	Summary of Chloramine Yields, $\text{NH}_3/\text{Cl}_2 = 4$, Cl_2 Flow Rate = 0.5 l/min	18
5.	Comparison of Adding N_2 Diluent to Cl_2 and NH_3	22

I. INTRODUCTION

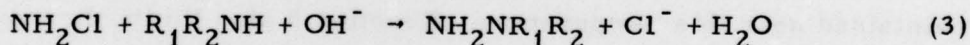
Chloramine NH_2Cl is used in the synthesis of the amine fuels: anhydrous hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine. It can be prepared in solution by the reaction



This is the common practice and is a key part of the Raschig hydrazine synthesis. Preparation can also be accomplished under anhydrous conditions in the gas phase by the reaction (Ref. 1)



The gas phase generation of NH_2Cl provides a possible pathway to the production of higher concentrations of amine fuels in the outflow stream from the reaction

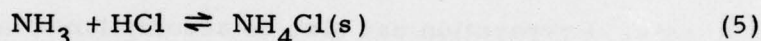
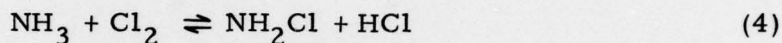


where R_1 and R_2 are CH_3 or H . Higher concentrations of the hydrazine $\text{NH}_2\text{NR}_1\text{R}_2$ would have a significant economic impact. A study of the gas phase reaction 2 to produce chloramine is reported.

The objective in the work reported here was to emphasize the chemical reactions taking place and to minimize, in so far as possible, the physical design and problems associated with the continuous production of NH_2Cl . Most published work has been concerned with the production of NH_2Cl for subsequent use and, therefore, continuous, low production rate runs were used (Refs. 1 through 5). One publication and many patents have dealt with design

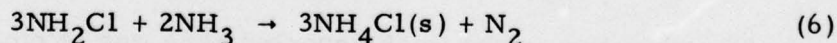
of reactors that produce high yields of NH_2Cl and minimize the plugging of the system by the ammonium chloride produced (Refs. 6 through 11). The most detailed previous report on the parameters affecting the yield of NH_2Cl was that of Sisler, Neth, Drago, and Yaney (Ref. 12).

Chloramine is formed by reaction 2 in what can be viewed as a two step process

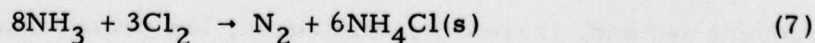


The free energy change ΔG in reaction 4 is 2.04, 1.76, 1.48, and 1.21 kcal/mole at 300, 400, 500, and 600°K respectively (Refs. 13 and 14). The ΔG of reaction 5 is -21.7, -15.0, -8.6, and -2.4 kcal/mole at 300, 400, 500, and 600°K respectively (Ref. 14). Reaction 5 drives the overall process and causes operational problems because of the precipitation of solid NH_4Cl . The condensation of NH_4Cl is not possible under representative conditions near 600°K. This is the reason that in most reported reactors the injectors are maintained near this temperature. Reaction 5 also limits the upper temperature that can be achieved by the overall exothermicity of reactions to near 600°K.

Chloramine can decompose in the presence of NH_3 by the reaction



Alternatively, the reactants can yield the same products by (Ref. 12)



Both of these reactions are significantly exothermic under all conditions; reaction 7 is only a combination of reactions 4, 5, and 6.

The work reported here was performed in a reactor with a large throughput to simulate pilot plant scale operation. No steps were taken to specifically reduce problems of NH_4Cl buildup because the intention was to operate for periods only long enough to permit reaction system stabilization and sample recovery. Although several other points were considered the ratios of reactants and the temperature of the reaction volume were the key variables addressed.

II. EXPERIMENTAL

A. REACTOR AND REACTANT DELIVERY SYSTEM

A schematic of the apparatus is illustrated in Figure 1. The gas flow controlling equipment was constructed of 304 and 316 stainless steel (SS), Viton, Teflon, polyethylene, and glass. All metal parts were maintained with a positive, dry N_2 pressure when not in use to prevent moisture from enhancing the corrosive properties of the reactants. The gases were carried in polyethylene tubing to the annular glass injector. Chlorine was delivered through the central 1.0 mm dia capillary and NH_3 flowed from the annular ring approximately 7 mm in dia. A cross-section of the injector is shown in the inset in Figure 1. The area ratio of the outer to the inner openings was 20.

Reaction took place in a 25-mm ID zone approximately 9 cm long. Temperatures in this zone were measured with a glass-sheathed thermocouple 2.0 cm from the injector face on the axial centerline of the reaction zone (T1, Figure 1). The temperature of the gas stream was monitored at the exit from the reaction zone with another glass-encased thermocouple (T2, Figure 1). The reacted gas stream then flowed into a gravitational precipitator to permit cooling and to remove the larger NH_4Cl particles. The precipitator was a Pyrex glass resin kettle (10 cm dia, 2 l. volume). In later experiments a Teflon baffle was inserted in the precipitator to ensure that the gases flowed in a predictable path and that little dead volume was present. The baffle permitted more reproducible operation. The reacted stream then flowed out through a 2.5-cm tube containing the sample port S to a turbulent water scrubber. Sampling could be performed at the exit from the precipitator or from points closer to the injector.

Temperatures were determined using chromel-alumel (Type K) thermocouples. They were recorded using high input impedance recorders and an Omega electronic ice point reference junction or read from a

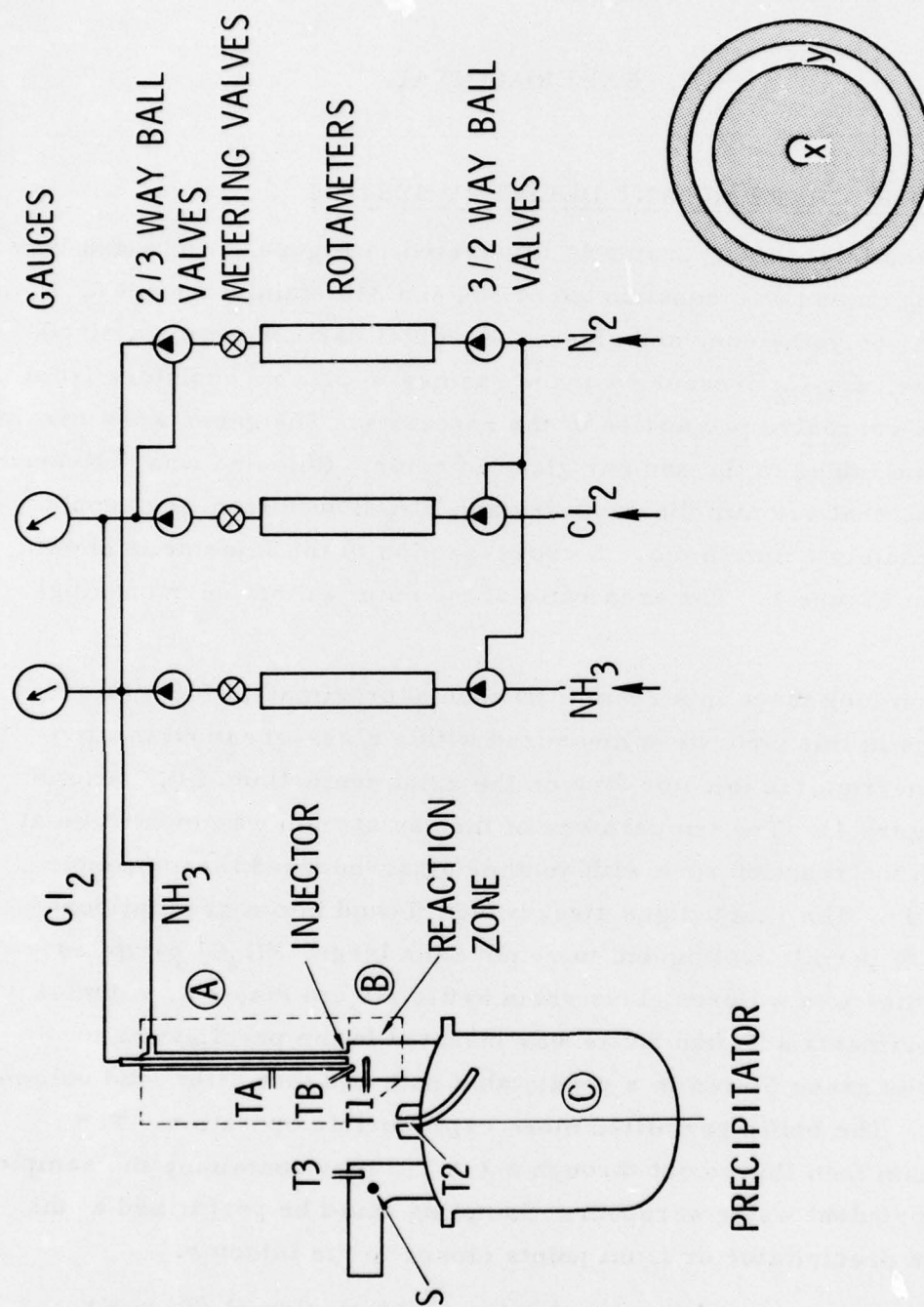


Figure 1. Reactor schematic shows the metering and mixing design and the reactor. A and B are separate heaters for non-ambient experiments. C is a Teflon baffle used in later experiments to assure proper flow. T1-3 and TA, B are thermocouples. S is the sample port. Insert shows an end view of the annular injector. Chlorine entered at X and ammonia at Y. Area ratio Y/X = 20.

multipoint Doric digital temperature indicator with internal reference compensator. Thermocouple probes were inserted into wells in the injector to monitor temperatures of the reactant gases during higher temperature experiments (TA and TB) in addition to temperatures of the reacted gases.

Flow rates of the reactant and diluent gases were measured by the use of rotameters of appropriate capacity. Matheson Gas Products rotameters No. 603 for Cl_2 , No. 604 for NH_3 , and No. 603 for N_2 were calibrated at the delivery pressure of the gases using a Precision Scientific wet test meter with N_2 as the calibrating gas. The flow rate vs ball height curves were converted to the appropriate gases using density and viscosity corrections (Ref. 15). All flow rates were reported at 1 atm and 294°K independent of reactor temperatures.

B. CHEMICALS

Matheson Gas Products anhydrous ammonia and High Purity chlorine and Air Products Extra Dry nitrogen were used without further purification. J. T. Baker Company Dilut-it 0.1 N HCl was prepared using deionized water.

C. SAMPLING AND ANALYSIS (Ref. 16)

A fixed volume sampler was used in all experiments (Figure 2). The reservoir volume was evacuated with an aspirator to permit filling with approximately 125 ml of deionized water. The sample volume was evacuated with a mechanical pump to less than 1 Torr. The sampler was then connected to the sample port of the reactor and the lower high vacuum valve was opened slowly to collect the sample. The valve was shut and the sampler removed from the reactor. The valve separating the reservoir from the sample volume was then opened and the water was drawn in by the dissolution of NH_3 and NH_2Cl . The water and two subsequent rinses were transferred to a volumetric flask and made up to volume.

The NH_2Cl content of the sample was determined spectrophotometrically at 243-243.5 nm. The extinction coefficient of $4.53 \pm 0.06 \times 10^5$

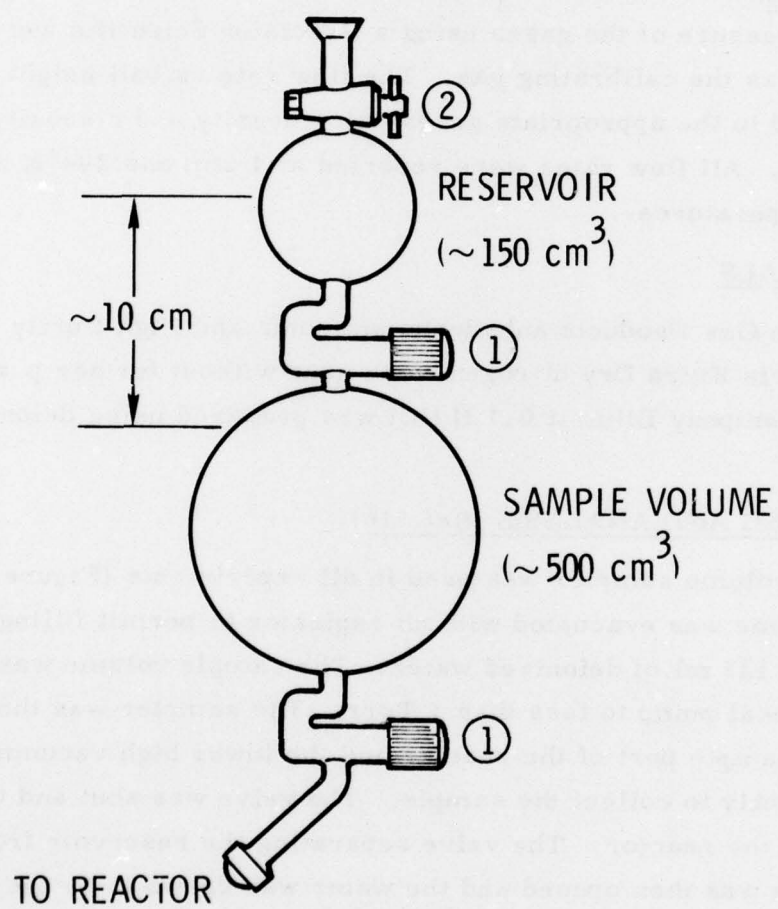


Figure 2. Glass sampler for analysis of chloramine.
High vacuum Teflon stopcocks are ①,
straight-bore Teflon stopcock is ②.

cm^2/mole was in agreement with the value given by Kleinberg, et al. (Ref. 17). Beer's Law behavior was confirmed from $1 \times 10^{-4} \text{ M}$ to $3.8 \times 10^{-3} \text{ M}$ for a 1-cm cell. The ammoniacal, basic solution stabilizes chloramine and limits solution degradation of NH_2Cl to less than 2 percent over 30-min periods. Additional NH_4Cl had no effect on the stability or extinction coefficient. If the NH_3 concentration is low ($\text{pH} < 5$), NH_2Cl can be converted to dichloramine NHCl_2 (Ref. 18). This can be detected spectrophotometrically near 300 nm. Trichloramine NCl_3 can form at $\text{pH} < 0.8$ and would be detected at 340 nm. Neither NCl_3 or NHCl_2 were ever detected in the analytical samples.

The NH_3 content of the sample was determined by titration of an aliquot with 0.1 N HCl using bromcresol green indicator ($\text{pH} = 3.8 - 5.4$ at end point).

D. YIELD COMPUTATION

Computation of the yield requires an assumption about the stoichiometry of the processes occurring in the reaction. Reactions 2 and 6 are assumed to totally describe the stoichiometry when excess ammonia is present. The sampled gases then contain N_2 , NH_3 , and NH_2Cl . The yield can then be computed by determining any two components or one component and the quantity of gas sampled when the initial molar ratio R_i of the reactants is known. Ammonia and NH_2Cl are the easiest and most trouble-free components to determine. The yield is then given by

$$\% \text{NH}_2\text{Cl yield} = \left(\frac{E(R_i - 2.667)}{1 - 1.667 E} \right) \times 100 \quad (8)$$

where E is the moles $\text{NH}_2\text{Cl}/(\text{moles } \text{NH}_2 + \text{moles } \text{NH}_2\text{Cl})$ in the sample. Note that the yield from Eq. (8) is independent of the N_2 content so that diluent gases do not affect the determination of the yield.

Duplicate analyses on samples collected simultaneously indicated a combined sampling and analytical reproducibility of approximately ± 3 percent of the value of the yield.

E. DESCRIPTION OF AN EXPERIMENTAL RUN

The samplers were prepared and all lines of the reactor system were purged with N_2 . If the gases and reactor were to be heated, the heaters were adjusted to the appropriate temperature with N_2 flowing. The flow rate of Cl_2 was set by switching to Cl_2 , then back to N_2 . After the Cl_2 was purged from the system, the NH_3 flow rate was set. If N_2 was to be used, this flow rate was set. The reaction was initiated by switching Cl_2 flow line from N_2 to Cl_2 and starting timers and recorders. The key temperature, T1 in ambient temperature runs or T2 in heated runs, was followed. When this temperature became stable, sampling was delayed until the volume of the precipitator had been swept past the sampling port. The sample valve was then opened slowly to prevent flow perturbations. The time required to withdraw a sample was approximately 30 sec. After the sample had been collected, the reactor was shut down immediately by returning all lines to N_2 purge. A second run could be performed by cleaning the injector tip and the reaction zone of all NH_4Cl and reinitiating the experimental procedure.

III. RESULTS

The experiments performed fall into two groups: (1) characterization of the reactor and miscellaneous experiments and (2) the effects of reactant ratios, diluent gases, and temperature of the reactant zone and of the reactant gases. A summary of all acceptable experiments is given in the Appendix. The reaction is sensitive to both reactor configuration and to adjustable parameters. Therefore, the reactor design will produce characteristic yields under conditions that might produce different yields in another reactor. Furthermore, the intention was to determine trends as a function of various parameters. If a high yield were always observed then these trends could not be established. These parameters were varied under conditions that approximated a production process, that is, high throughput rates with respect to physical dimension. For example, the ratio of the chlorine flow rate to the reaction section diameter (25 mm) was 4 to 50 times that used by Sisler and coworkers (Refs. 1, 6, 12). These conditions resulted in lower yields.

A. CHARACTERIZATION OF THE REACTOR

The ratio of NH_3 to Cl_2 was chosen as 8:1 and the injector and reactor were at room temperature for the reactor characterization. The temperature of T1, Figure 1, was used as the main monitoring parameter during an experiment. Various temperature profiles and significant events are illustrated in Figure 3. A typical acceptable experiment is shown by curve I. Sampling was always performed from the product gas stream that had been formed during the "steady state" portion of the temperature profile extending from A to approximately C. Sampling was performed as illustrated by the sampling period B, B1 which sampled gases reacted during A, A1. The change in temperature was limited to 50°C during a sampling period for a run to have been acceptable and the mean temperatures are reported. Usually temperature variations were less than 30°C .

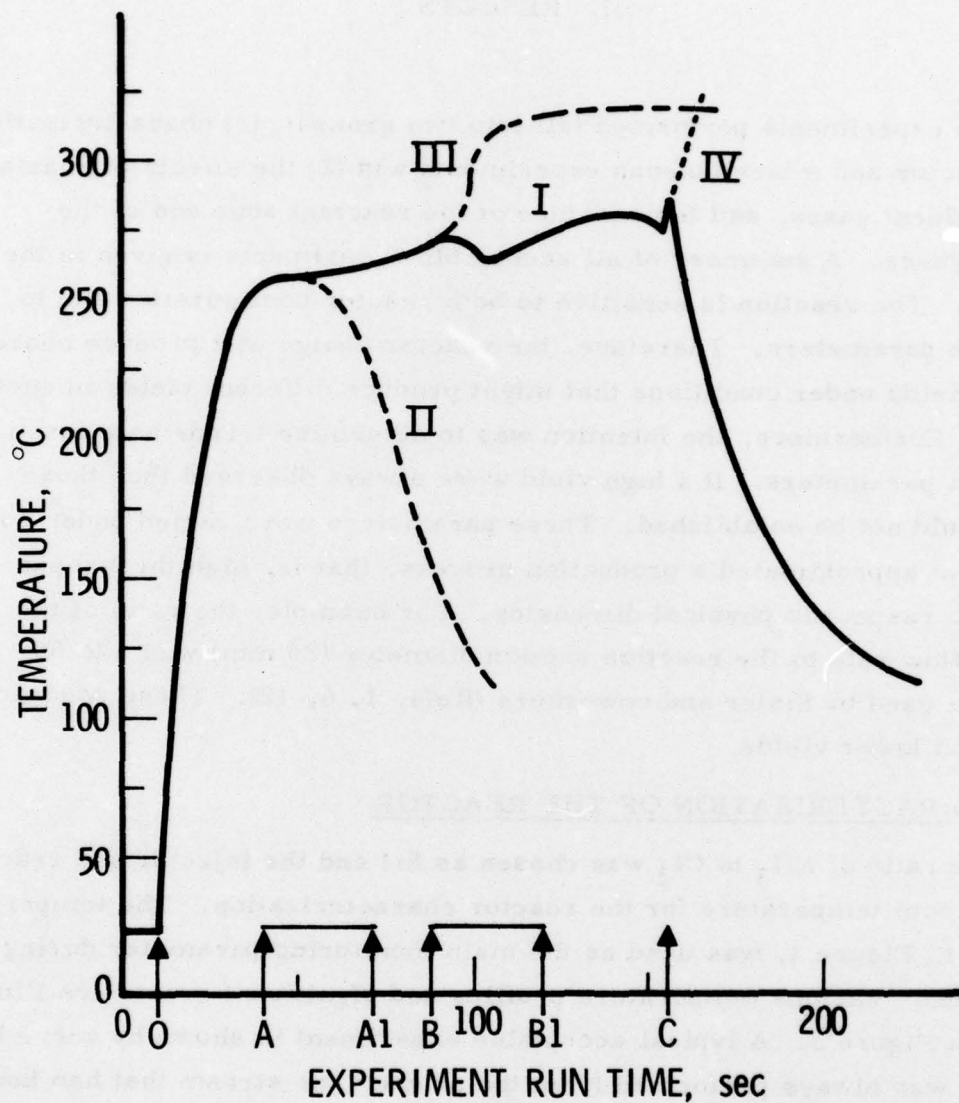


Figure 3. Characteristic temperature profiles for an experiment. Curve I is typical of an acceptable experiment. Curve II indicates plugging of the reactor. Curve III indicates a stable flame (see text) has ignited. Curve IV continues to much higher temperatures. Timing diagram at the bottom of the figure: O, reaction begins (gases switched on at time 0); A to A1, sampling period when sampler is actuated from B to B1; C, gases shut off.

Figure 3 illustrates other temperature profiles that were observed. Curve II is characteristic of early plugging of the Cl_2 jet and termination of the reaction. This behavior was most often observed when the Cl_2 flow was low so that reaction took place within the orifice. Curve III illustrates a characteristic transition to a flame. When the temperature exceeded approximately 310°C , emission of light from the reaction zone was observed. The flame was white to yellow-orange in color and was diffuse with few striations. It was similar to a low pressure flame in a fast flow tube. No central core or cone was detected. This transition to the higher temperature regime could occur at any time during an experiment, but it was generally associated with a flow perturbation. Although sampling was performed after the 2 l. precipitator, the opening of the sampler valve could cause the flame condition if the valve was opened too rapidly. Sampling from the reactor region was not possible because of the flow perturbation that it caused.

The reactor normally ran smoothly, maintaining a relatively constant temperature at T1 until sufficient NH_4Cl had been accumulated to plug the system. In all room temperature runs a cone of glassy NH_4Cl was formed from the injector face around the Cl_2 inlet to the temperature probe T1 by the end of an experimental run. If the reactor was not shut-off, the temperature would climb steeply to greater than 600°C (the Pyrex thermocouple probe would melt). This is shown by curve IV in Figure 3. This indicates that under certain conditions reactions other than those shown in Eqs. (4), (5), and (6) dominate the system. In any event, a flame signaled near zero yields of NH_2Cl and data from these runs are not included in this report.

The flow rate of Cl_2 at constant NH_3 to Cl_2 ratio of 8 was varied to determine if an optimum flow condition existed for the reactor. The acceptable experiment criteria of no flame, relatively flat temperature profile, and a sample only from this flat profile region were used. Figure 4a shows the results of these experiments. The reactor was difficult to operate below 0.3 l/m Cl_2 because it tended to plug or, if it did not plug, a flame

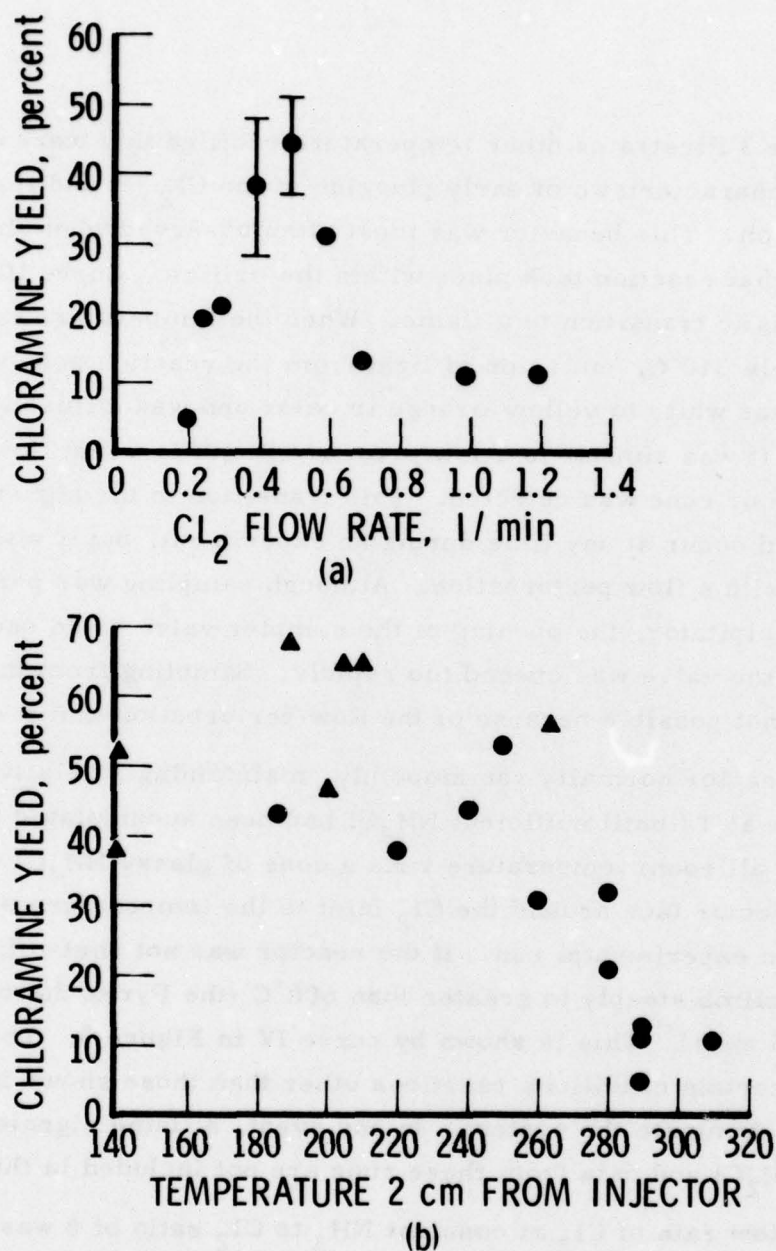


Figure 4. Reactor characterization: (a) The dependence of the yield on Cl_2 flow rate at a fixed $\text{NH}_3:\text{Cl}_2$ ratio of 8:1 with no diluent gas. (b) The correlation between yield of chlormaine and the steady state temperature observed 2 cm from the injector face. The ratio of $\text{NH}_3:\text{Cl}_2$ was fixed at 8:1 but the Cl_2 flow rate varied. ●, no added diluent; ▲, 1.1 to 1.3 moles N_2 added to the Cl_2 stream per mole of Cl_2 .

tended to occur. Plugging was caused by the reaction occurring at a high enough rate to move counter to the gas flow toward the surface of the injector. Sampling from these low flow runs often caused sufficient flow perturbation to cause ignition of a flame. Although high flows ran smoothly, the yields were low. The high flow rates also tended to build up NH_4Cl more quickly and resulted in earlier termination of the runs. Flow rates of 0.4 and 0.5 l/m gave the highest yields and were the easiest flows to manipulate. The average yield of NH_2Cl at a reactant ratio of 8 was 38 ± 10 percent at 0.4 l/m and 44 ± 7 percent at 0.5 l/m or 42 ± 7 percent for both 0.4 and 0.5 l/m. All subsequent tests at all conditions were performed at flow rates of 0.4 or 0.5 l/m of Cl_2 .

The data for the 8:1 experiments at an initial temperature of 24°C , including several experiments with added N_2 diluent in the Cl_2 stream, are plotted in Figure 4b as a function of the temperature at T1. These data contain experiments at differing Cl_2 flow rates but a correlation of higher yields with lower observed temperatures is apparent. The same phenomena was observed under all experimental conditions where the temperatures of the reacted gas stream varied significantly.

Several experiments were performed at higher NH_3 to Cl_2 ratios to verify the trend in yield reported by others (Refs. 1, 6 through 12). These experiments were found to be difficult to execute because the Cl_2 line tended to plug, temperature profiles were erratic, and a flame tended to ignite. Those runs that did appear to be acceptable gave higher yields at a reactant ratio of 20 than at 8. Three acceptable runs at a ratio of 20, no added N_2 , and room temperature initially, gave yields of 71, 106, and 97 percent for an average of 91 ± 18 percent.

The precipitator, the Teflon divider (in the later experiments), and the tubing and samplers were all glass or Teflon and near room temperature. Both clean glass surfaces and surfaces coated with NH_4Cl , as well as Teflon surfaces, were presented to the reacted gases. Stability of NH_2Cl in contact

with these surfaces at room temperature was in question, based upon some assumptions and the report by Prakash and Sisler that walls were maintained above 50°C to prevent decomposition (Ref. 6). This report was in contradiction to a previous study by Sisler, et al. (Ref. 12) that decomposition is undetectable above about 10°C for long glass bead-packed columns. From the analytical studies (Ref. 16), it was shown that NH_2Cl decreases at a rate of less than 0.5 percent of its concentration per minute in 500 cc glass sample bulbs.* Furthermore, examination of data with varying flow rates and residence times in the reactor indicate that no heterogeneous decomposition of NH_2Cl at room temperature was detectable.

A test of contact with 304 SS tubing was performed at 8 NH_3 : 1 N_2 : 1 Cl_2 . Samples were taken simultaneously with a sampler attached to a glass "T" at S and with another connected at the "T" through 3 m of 0.5 cm ID, 304 SS tubing, all at room temperature. The measured yield was 65 percent in the all-glass sample line and 68 percent after the stainless steel tubing.

B. EFFECTS OF REACTANT RATIOS, DILUENT GASES,
AND TEMPERATURE

The data for experiments with NH_3 to Cl_2 ratios of 8, 6, 5, and 4 are summarized in Tables 1 through 4. These are averages and contain reactant temperature dependences imbedded in the yield data. This explains, in part, the ranges of yields observed. The trend at all ratios is for diluent gas to increase the yield. Addition of one part nitrogen to one Cl_2 dramatically increased the yields, even at the relatively high ratio of 8 NH_3 to 1 Cl_2 . Addition of more N_2 had a lesser effect; there appears to be a limit to the efficacy of adding diluent gas. These effects were more dramatic at lower NH_3 to Cl_2 ratios. Adding one part N_2 to Cl_2 at a reactant ratio of 8 increased the yield by approximately 40 percent but adding six parts increased the yield by only 60 percent. At a reactant ratio of 4, one part N_2 increased the yield by 130 percent and 3.4 parts N_2 increased it 215 percent (at 24°C).

* If reproducibility of the analysis and sampling is considered, the effect could not be detected in 15 minutes.

Table 1. Summary of Chloramine Yields^a $\text{NH}_3/\text{Cl}_2 = 8$,
 Cl_2 Flow rate = 0.4 or 0.5 l/min

Ratio N_2/Cl_2 $\text{Cl}_2 = 1$	Initial Temperature °C	No. of Runs	Yield %	Range %	Comments
0	24	6	42 ± 7	31-53	combined N_2 flows delete 38% run N_2 in Cl_2 and NH_3 delete 38% run
	280	1	44		
	All	7	42 ± 7	31-53	
1.1 + 1.3	24	7	56 ± 11	38-68	
		6	59 ± 8	47-68	
	191	1	66		
	240	2	62 ± 11	56-67	
	All	9	60 ± 8	47-68	
6.4	24	1	69		
8.4	24	1	82		

^a The averages and the standard deviations are given when more than two experiments were performed. When two experiments were performed, the uncertainty is given as the difference between the two values. No uncertainty is given if only one experiment was performed or two experiments gave the same value. This applies to Tables 1-5.

Table 2. Summary of Chloramine Yields $\text{NH}_3/\text{Cl}_2 = 6$,
 Cl_2 Flow rate = 0.5 l/min

Ratio N_2/Cl_2 $\text{Cl}_2 = 1$	Initial Temperature °C	No. of Runs	Yield %	Range %	Comments
0	24	1	17		
	220	1	47		
1.1	24	3	58 ± 12	49-72	
2.2	24	2	58 ± 13	51-64	

Table 3. Summary of Chloramine Yields $\text{NH}_3/\text{Cl}_2 = 5$,
 Cl_2 Flow rate = 0.5 l/min

Ratio N ₂ /Cl ₂ Cl ₂ = 1	Initial Temperature °C	No. of Runs	Yield %	Range %	Comments
0	24	2	20 ± 6	17-23	
	230	1	19		
1.1	24	3	48 ± 10	38-61	
	220	1	47		
2.2	24	2	59 ± 5	56-61	
3.4	24	3	58 ± 8	48-63	
6.7	24	1	67		

Table 4. Summary of Chloramine Yields $\text{NH}_3/\text{Cl}_2 = 4$,
 Cl_2 Flow rate = 0.5 l/min

Ratio N ₂ /Cl ₂ Cl ₂ = 1	Initial Temperature °C	No. of Runs	Yield %	Range %	Comments
0	24	1	15	45-50	N ₂ in Cl ₂ and NH ₃
	220	1	22		
	270	1	20		
1.1	24	1	29		
	190	4	46 ± 3		
	220	1	48		
2.2	24	1	61		
	270	1	60		
3.4	24	2	63 ± 2	62-64	N ₂ in Cl ₂ and NH ₃
	190	7	88 ± 9	78-102	
5.6	24	1	68		

The effect of decreasing the NH_3 relative to Cl_2 is not clear. High NH_3 ratios, increased the yield of NH_2Cl , within the limits of the reactor operation, e.g., 20 NH_3 to Cl_2 gave yields near 100 percent. When the ratio was decreased, the yields tended to become constant with no diluent gas for experiments at 24°C . The yield of NH_2Cl was 18 ± 3 percent for all runs at 24°C for reactant ratios of 4, 5, and 6 with no diluent. With the exception of one experiment at an initial temperature of 220°C with a NH_3 to Cl_2 ratio of 6, the yield from experiments with no diluent at all temperatures was 19 ± 3 percent at these three low reactant ratios.

The effect of temperature is both interesting and puzzling. Two temperatures are recorded, the temperature of the reaction zone initially (that listed in Tables 1 through 4) and the temperature at T1 or T2 measured during the flat portion of the temperature profile. Figures 4b and 5a, b show the correlation between the reaction temperature and the yield. Although the data are scattered, the yields were generally higher at lower temperatures. All three figures show a transition from lower to higher yields near 260°C . Although the lower temperatures were generally associated with the addition of diluent gas, Figure 4b shows a similar dependence when no diluent was added.

The initial temperature of the reaction zone had little effect on the reaction temperature as measured at T1 or T2 and, with some exceptions, had little effect on the yields. At higher initial temperatures the reactor was easier to operate because the heated reaction zone did not foul with NH_4Cl . At initial temperatures of 220°C and above, the reaction zone and the injector remained clean and the reactor could be operated continuously until the exit area into the precipitator plugged. The reaction zone did accumulate NH_4Cl slowly at an initial temperature of 190°C .

Table 1 shows that experiments with the reaction zone heated to 240°C and 280°C are indistinguishable from those with a 24°C initial reaction zone temperature. The one experiment at 220°C initial temperature at a reactant

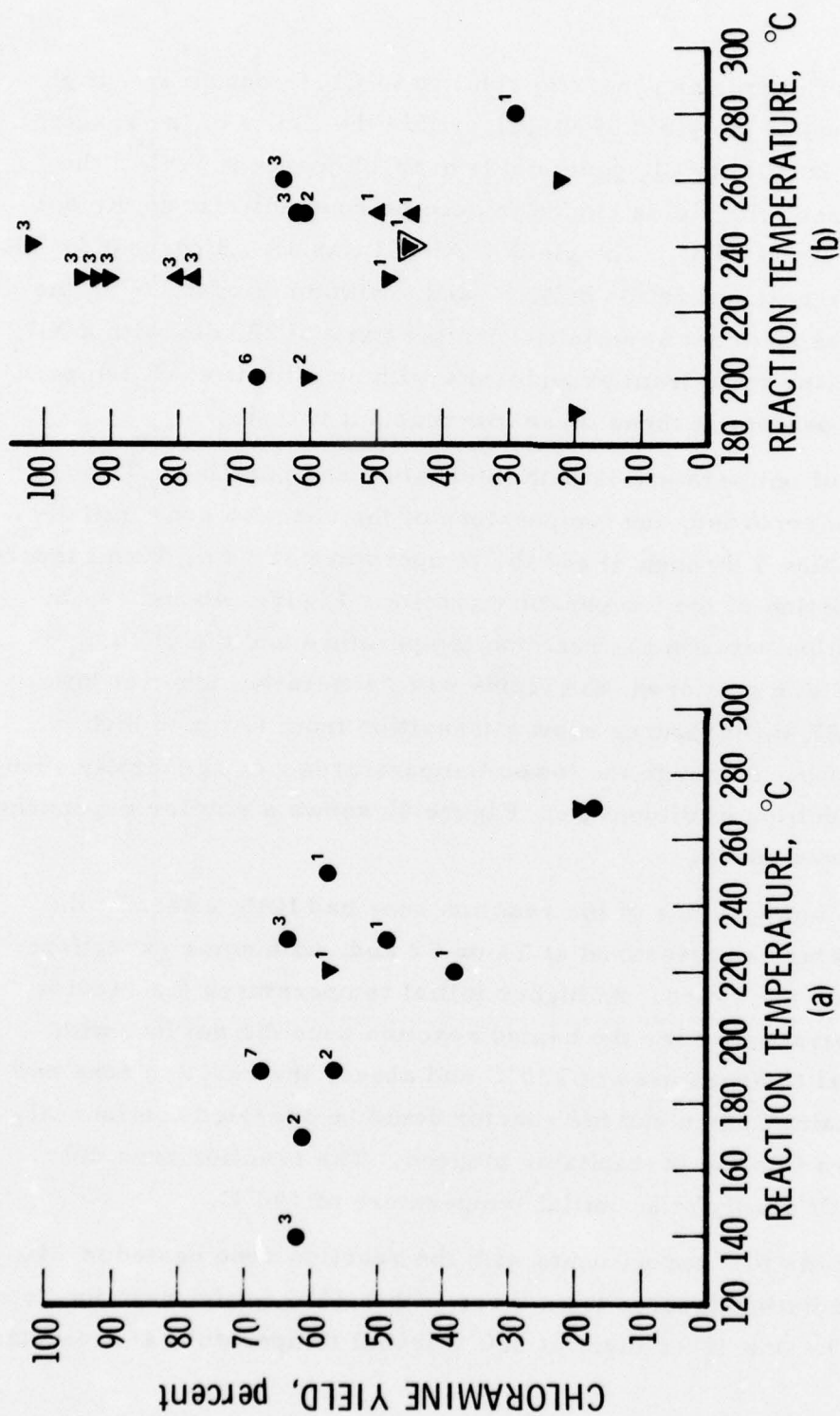


Figure 5. The yield of chloramine vs the observed reaction temperature. ●, initial temperature 24°C; ▼, initial temperature 190, 220-230 or 270°C, N₂ added to Cl₂ stream; ▲, elevated initial temperature, N₂ added to NH₃ stream. Temperatures measured at T1 for 24°C initial temperature and at T2 for all others. Number adjacent to the symbol is the approximate ratio of N₂ to Cl₂. The ratio of NH₃ to Cl₂ is 5 in (a) and 4 in (b).

ratio of 6 with no diluent was exceptional (Table 2). This yield was high when compared to other reactant ratios and a review of the data showed no reason to suspect the experiment. The use of an elevated initial temperature at a reactant ratio of 5 (Table 3) resulted in no apparent change in the NH_2Cl yields. Changes in the yield as a function of temperature were observed at a reactant ratio of 4 (Table 4). The yield of NH_2Cl was the same at 24, 220, and 270°C with no diluent gas. When 1.1 parts N_2 per Cl_2 were added, an increase in the yield was detectable at 190 and 220 deg although at 2.2 N_2/Cl_2 the yield was the same at 24 and 270 deg. The experiments with 3.4 N_2/Cl_2 showed increased yields at 190 deg when compared to the experiments at 24 deg initial temperatures. The data for a reactant ratio of 4 and diluent gas suggest an optimum initial temperature of 190 to 240 deg.

The data summarized in Tables 1 and 4 and plotted in Figure 5b include experiments with the diluent gas added both to the NH_3 stream and to the Cl_2 stream. Table 5 shows that dilution of either the NH_3 or the Cl_2 stream has the same effect on the yields, with the possible exception of the data at NH_3/Cl_2 of 4 with 3.4 N_2/Cl_2 at 190 deg. Experiments testing the effect of addition of diluent gas to either reactant stream were performed under conditions where yields were found to be most reproducible and experiments most convenient. The yield of NH_2Cl at NH_3/Cl_2 of 8 was lower when the diluent was placed in the Cl_2 stream than in the NH_3 stream but both yields were within the standard deviation of all experiments with similar ratios at all temperatures. No difference in the yield was detectable at a reactant ratio of 4 with 1.1 N_2/Cl_2 when the diluent was added to the different reactant streams.

The experiments performed at 190 deg with a reactant ratio of 4 and 3.4 N_2/Cl_2 show a difference in yield when the diluent was added to the different reactant streams. Five experiments were performed with the N_2 added to the Cl_2 stream. The first experiment performed gave a significantly lower yield than the other four (experiment 60, Appendix). Deletion of this

Table 5. Comparison of Adding N₂ Diluent to Cl₂ and NH₃
(Cl₂ Flow rate: 0.5 l/min)

Ratio (Cl ₂ = 1) N ₂ to NH ₃ NH ₃ Cl ₂		Initial Temperature °C	No. of Exp.	Yield %	Range %	Comments
8	- 1.1	240	1	56		Average of all data: 59 ± 8
	1.1 -	240	1	67		
4	- 1.1	190	2	45	45	All runs at 190° and 220°: 46 ± 2
	1.1 -	190	2	48 ± 5	45-50	
4	- 3.4	190	5	92 ± 9	78-102	Delete 78% yield run
			4	95 ± 5	91-102	
	3.4 -	190	2	79 ± 2	78-80	

experiment gave an average yield of 95 ± 5 percent with the diluent in the Cl_2 stream, whereas two experiments with N_2 in the NH_3 stream gave a yield of 79 ± 2 percent. If a yield of 95 percent with N_2 in the Cl_2 stream is used for the temperature comparison in the previous discussion instead of the average of all 190 deg experiments, the yields at 190 deg are even more dramatically different from those at 24 deg.

IV. DISCUSSION

The experiments reported here confirm and extend previously reported observations. The reactor was designed to accentuate reaction parameters rather than optimize them and to provide data from a reactor of minimal size in relation to the flow rates. The data show that the cross-sectional area of the reaction zone in the reactor in relation to the Cl_2 flow is too small for optimum yields but that the necessary increase for optimization is not expected to be more than a factor of two or three.

The effect of diluent gas on the yield of NH_2Cl was demonstrated to be dramatic at low ratios of NH_3 to Cl_2 in agreement with Prakash and Sisler (Ref. 6). Large quantities of diluent are not necessary to produce high yields and the amount of gas necessary is dependent on the reactant ratio and probably on the conditions in the reactor (temperature and pressure) and the reactor design. The data reported here and from Reference 6 indicate that the mole ratio $(\text{NH}_3 + \text{N}_2)/\text{Cl}_2$ need not be much larger than six or seven for near quantitative yields. The data indicate that the effect of diluent gas addition does not depend on the reactant stream to which it is added except in the case of a reactant ratio of 4 at an optimum temperature. This one condition may have resulted from optimum velocity conditions because the reactant velocities varied with temperature although the mass flow rates were the same under all conditions. Comparison of data at different reactant ratios with and without diluent shows that adding N_2 is more effective in increasing the yield than increasing the amount of NH_3 by an equivalent molar amount. This indicates that the role of the diluent is not only that of a coolant or thermal moderator (N_2 is slightly more than half as effective at accepting heat as NH_3) (Ref. 14), but that the diluent affects the kinetics of the reactions taking place.

Chloramine was found to be relatively stable near room temperature in the presence of NH_3 and solid NH_4Cl . The decomposition could barely be detected after 15 min in the glass sampling bulbs nor could any correlation be detected between flow rate through the reactor and precipitator (as opposed to flow from the reactants injector) and the yield. These observations are in agreement with Sisler's earlier work (Ref. 12) but do not confirm his later observation of the necessity to warm the precipitator sections of the reactor (Ref. 6). It does not appear necessary to warm the precipitator sections of a reactor to prevent NH_2Cl decomposition although NH_4Cl precipitation may be affected by wall and gas temperature. Neither the literature nor the work reported here indicate that NH_2Cl is particularly unstable from 24 deg to at least 100°C in the presence of NH_3 .

The temperatures of the reactant stream have not previously been reported and only room temperature and temperatures greater than that at which NH_4Cl can form have been used in the reactor region. Experiments were performed with the reaction zone and reactant gases initially at 24, 190 ± 5 , 230 ± 10 , and $270 \pm 10^\circ\text{C}$. The temperature of the reacted gas stream did not correlate with the heating of the reactor in any direct fashion.

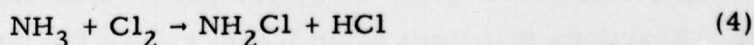
With the exception of experiments performed at a reactant ratio of 4 with diluent gases, the yield of NH_2Cl was found to be independent of the initial temperature of the reaction zone and reactant gases. This is not unexpected because high yields have previously been reported at room temperature (Ref. 12) and at more than 300°C (Ref. 6). The experiments showed that it is possible to prevent significant buildup of NH_4Cl at temperatures lower than the 320°C predicted purely from thermodynamic calculations on NH_4Cl . The reaction zone and injectors remained free of NH_4Cl buildup at all initial temperatures greater than approximately 220°C . The failure to accumulate NH_4Cl was probably the result of the maximum decomposition pressure of NH_4Cl being greater than the NH_4Cl available and of the rates of

particle nucleation being comparable to flow times through the hot reactor section. The high yields at 190 deg with reactant ratios of 4 in the presence of a diluent gas were most probably the result of a combination of both physical and chemical dynamic factors.

The downstream temperature exhibited four different conditions. The most definitive data were those collected at an ambient initial temperature because of the location of the temperature probe, although three of the four conditions were also observable with the probe located downstream of the heated reaction zone. Figures 4b and 5 show two of the conditions observed. At temperatures of approximately 260°C and lower, the yield of NH_2Cl was highest. In the temperature region from approximately 260 to 310 deg the yield roughly increased with decreasing temperature. Near 310 deg, the sublimation temperature of NH_4Cl , the yield was low and the reactions ran smoothly and isothermally; an emission of light was observed. In certain instances where a flame was observed, the temperature continued to increase rapidly to values in excess of 600°C.

To explain the observations, a consistent mechanism for the reactions is necessary. Both homogeneous and heterogeneous processes can be important and must be invoked to explain the observations from the reactor and the mild instability of NH_2Cl in the sampler bulbs. The temperature effects reported here and the high yields above 300 deg observed by others must be rationalized as well as the origin of the light emission (flame). Diluent gas effects and the observed differences between diluents and simply adding more NH_3 must also be included in the mechanism. Suggesting a mechanism is difficult because of the lack of basic kinetic information available on chlorine molecule and atom reactions with NH_3 and ammonia-derived species.

A possible reaction is the direct reaction between the molecular reactants

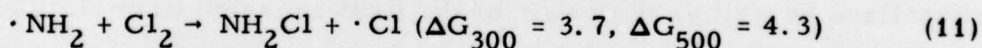
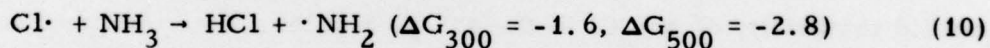


This possibility is rejected because bimolecular reactions between stable species are extremely improbable in the gas phase and require high entropy content transition states. Note that the second step, reaction 5, to produce NH_4Cl is deleted. The reaction is not part of the key pathway although it may drive intermediate equilibrium steps. High yields are observed under conditions where no NH_4Cl can form and it is deleted as a homogeneous reaction species below.

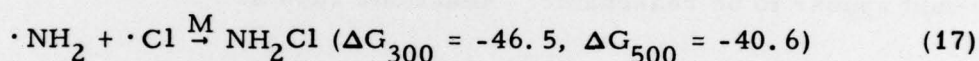
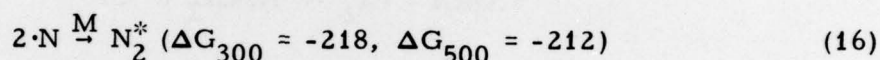
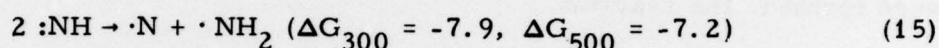
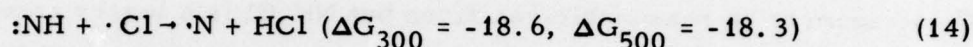
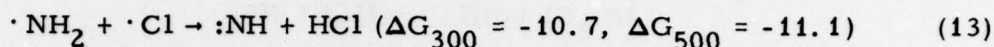
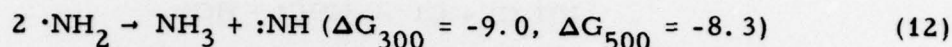
Reactions involving halogen molecules almost exclusively take place by halogen atom reactions in the gas phase. Chloramine can be formed homogeneously by initiating a chain reaction with



The Cl atoms may be formed by photolysis, heterogeneous reaction, or thermal equilibrium reactions; the Cl atom concentration in a one atmosphere gas stream at 400°C is 3.5×10^{12} atoms/cc at equilibrium. The free energies are given in kcal/mole (Ref. 14). After initiation, NH_2Cl and HCl are the products of the chain propagation steps

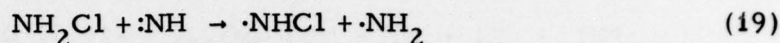
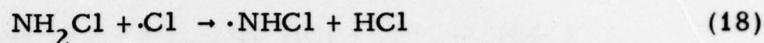


Reaction 11 requires that NH_2 exceed Cl in concentration by more than 100 from the principle of detailed balance. Reaction 10 is driven by the removal of HCl from the system as NH_4Cl at lower temperatures. Under appropriate conditions, e.g., temperatures lower than approximately 320°C and good gas mixing, the Cl and NH_2 concentrations will be very low and the chain lengths (the number of reaction 10, 11 cycles per Cl atom initially generated) will be long. Reactions that limit chain length reduce the yield.

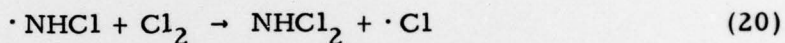


Reaction sequence 12 through 16 limits the chain length and explains the flame that is observed under low yield conditions. Each step is significantly exothermic and the combined process is reaction 7 when proper stoichiometry is applied. Reaction 12 ($k = 10^{11.86}$ cc/mol-sec) (Ref. 19) and even reaction 16 ($k = 10^{11.1}$ at $M = 1$ atm) (Ref. 20) are fast reactions under the conditions of the experiments. Others in this series should be equally fast. The emission of light is from reaction 16, the weak Lewis-Rayleigh afterglow (Ref. 20). It is evident that as the radical or atom concentration begins to increase, the temperature will increase and the reaction rates will increase in a characteristic thermal runaway. Reaction 17 will be improbable at high temperature and it must compete with more probable metathetical reactions. However, the reverse reaction of 17 will become an additional initiation step causing the loss of any NH_2Cl that is formed at high temperature.

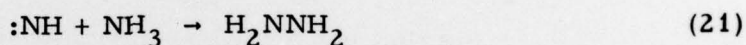
Reactions involving NH_2Cl and radicals or atoms have not been included in the scheme but they should occur.



These seem to be reasonable reactions but NH_2Cl is a lesser component and neither NHC1_2 nor NCl_3 were observed in our experiments.[†] If NHC1 radicals were formed, the reaction



would appear to be reasonable. Reactions such as



were not considered because active nitrogen reactions have shown these to be minor pathways (Ref. 20). It might be expected, however, that hydrazine and hydrogen would be detected in trace quantities if the proposed mechanism is correct.

It is apparent how the proposed mechanism results in extremely high temperatures. In the experiments where a plateau at 310 deg is observed, the temperature is maintained by the NH_4Cl condensation reaction. As more heat is placed in the system by reactions 12 through 16, NH_4Cl solid decomposes to NH_3 and HCl . When these reactions are moderated, condensation of NH_4Cl increases the temperature. Higher concentrations of radicals can eventually overcome this moderation process and thermal runaway results. These conditions will be sensitive to gas flows and mixing in the reactor. Thus, identical temperature conditions can result in high or low yields

[†]Under significantly different conditions of limiting NH_3 in some liquid phase injection experiments, NHC1_2 was observed.

depending on slight pressure (flow) variations because of radical and atom density changes. It should also be emphasized that the downstream temperatures reported in the data are 2 cm or greater from the injector and most probably reflect not the reaction temperature, which may have been higher, but the temperature of a partially cooled gas stream.

The observed increase in yield with decreasing temperatures below 310 deg would result from a decrease in radical concentrations at lower temperatures and therefore longer chain lengths. Lower temperatures would tend to slow reactions 9 through 15 and enhance reaction 17 thus promoting higher yields. At some temperature, e.g., approximately 260 deg in the experimental reactor, reactions 12 through 16 become less significant. The reason yields are not near 100 percent may be that the reacting gases have experienced less favorable conditions upstream. An alternative explanation is that hot NH_4Cl surfaces are particularly effective in decomposing NH_2Cl . This explanation, coupled only with reactions 9, 10, 11, and 17 would explain most of the observations, except the emission of light and the effects of diluent gases.

Considering the proposed mechanism and the operation of a flowing reactor, diluent gas serves three purposes in the reaction scheme. Added gas serves as an inert coolant to partially assist in absorption of heat. Diluents increase the volume of the gas, thus decreasing the residence time of the reacted gases in the hot reaction zone. These two functions are also performed by excess NH_3 . The most important function of the inert diluent in an isobaric flow tube reactor is to decrease the concentration of all reactants. Additional NH_3 in the reacting gases will increase the rate of reaction 10, whereas, an inert diluent would slow this process and reaction 11, as well as greatly decreasing the rate of the bimolecular radical or atom reactions, 12 through 15.

The data and the proposed mechanism indicate that an optimum reaction system can be constructed using ratios of NH_3 to Cl_2 of four or less. A diluent gas must be added and it will be more effective than increasing the NH_3 to Cl_2 ratio by an equivalent amount. A high temperature reactor section enclosing the injectors is required to prevent NH_4Cl buildup in this region but temperatures of less than 300 deg will be sufficient. Variation of this temperature over some range will probably not affect the yield but it may be important to the particle size of the NH_4Cl that is formed downstream. The reactants should be mixed smoothly with steps taken to prevent areas of high temperature or conditions that will generate high radical concentrations. The diluent should be added to the Cl_2 stream because the highest yields were observed in this configuration under optimum conditions of temperature, gas composition, and flow rate. Under these conditions, the diluent diffusion and mixing with the NH_3 probably coupled with the reaction rates in an optimum fashion. The dimensions of the hot reactor section should be such that the reactants and products move through it as rapidly as possible with complete reaction. Back diffusion of products must be restricted to prevent decomposition. The exit from the hot reactor zone into the precipitator should provide rapid cooling to less than 260°C. Again the shape of the exit area may be important to the characteristics of the condensed NH_4Cl . The NH_4Cl removal equipment and the flow lines do not appear to need to be heated so long as the surfaces are passivated (glass walls appear acceptable without passivation) and the residence time to the NH_2Cl use point is less than 15 min.

V. SUMMARY AND CONCLUSIONS

The production of chloramine NH_2Cl by the reaction of NH_3 with Cl_2 has been studied. The ratio of reactants NH_3/Cl_2 , the addition of diluent gas to both reactant streams, and the temperature of the reactant gases and the reaction zone were the parameters varied. The observables were the yield of NH_2Cl and the temperature in or immediately downstream from the reaction zone. The reactor was designed to emphasize the results of the parameterization and not to produce maximum yields.

The temperature of the reacted gases showed a rough correlation with yield. Highest yields were observed when the reacted gases were 260°C or lower, no matter what the reactor temperature was initially. As these gases became hotter, the yield decreased until near zero yields were observed at 310°C . Under some conditions, a flame was observed and the temperature increased to over 600°C . Little dependence of yield upon the temperature of the reactant gases and the reactor section was observed except under one set of conditions. The yield was the same at most reactant ratios and levels of diluent gases at reactant and reaction zone temperatures of 24, 190, 220, and 270°C . The exception was at $\text{NH}_3/\text{N}_2/\text{Cl}_2$ ratio of 4/3.4/1 (N_2 in Cl_2 stream) and a temperature of 190°C . Yields in excess of 90 percent were observed under these conditions, whereas, yields of approximately 60 percent were observed at other temperatures. It was observed that NH_4Cl accumulation in the reactor zone during the course of an experiment ceased at temperatures greater than 220°C . No buildup at all was observed at 260°C or above.

The addition of a diluent was found to be more effective than increasing the NH_3 by an equivalent amount. Thus, yields at $\text{NH}_3/\text{N}_2/\text{Cl}_2$ of 4/3.4/1 were higher than yields at 8/0/1. Diluent gas permitted low reactant ratios to be used. Under the optimum conditions of temperature identified above,

the addition of N_2 to the NH_3 stream produced lower yields than when it was added to the Cl_2 stream. Yields were not dependent on the stream to which the N_2 was added under all other conditions.

A homogeneous gas phase reaction mechanism can be proposed that agrees with the observations made and literature data. Although heterogeneous processes probably occur in the system, they need not be invoked. It is proposed that the reaction is initiated by chlorine atom formation. NH_2Cl is formed in chain reaction with Cl abstracting a hydrogen atom from NH_3 to form HCl and NH_2 ; NH_2 then reacts with Cl_2 to reform Cl and NH_2Cl . Reactions that decrease the yield are those that shorten and interfere with the chain reaction, e.g., atom-atom and radical-radical reactions. High temperatures and flow perturbations can increase radical and atom concentrations and decrease the yield. Light emission from the reaction zone is the Lewis-Rayleigh afterglow from combination of N atoms to produce N_2 . This mechanism does not require NH_4Cl formation for heat production. Diluent gases reduce radical concentrations in an isobaric flow system and extend the length of the chain, whereas, NH_3 interacts directly with the reactions and is less effective than an inert diluent. Variations in yield between seemingly identical experiments are ascribed to variations in these radical and atom concentrations.

The experiments reported here and the proposed mechanism suggest that several parameters can be used to optimize the yield. The ranges over which the yield is insensitive to those parameters can be used to optimize the removal of the NH_4Cl by-product by controlling the particle growth rate and size. The finding that the reactor can be kept free of NH_4Cl at $260^\circ C$ instead of temperatures greater than $320^\circ C$ can result in better growth characteristics for the NH_4Cl . The data show that low reactant ratios can be used if some diluent gas is added. From the work of Sisler and the data presented here, it is estimated that the ratio $(NH_3 + N_2)/Cl_2$ can be 7 or less for

high yields of NH_2Cl . Diluents may be added to either reactant stream with equal effect unless the reaction couples strongly with mixing and flow as it appeared to under one set of experimental conditions. Although the reaction must be run at temperatures that prevent NH_4Cl fouling of the system, the product stream should be cooled to less than 260°C as rapidly as possible after reaction has taken place. Finally, if the mechanism is correct, gas injection and flow design must be optimized to maintain low concentrations of radicals and long chain lengths.

REFERENCES

1. R. Mattair and H. H. Sisler, "The Production of Hydrazine by the Reaction of Chlorine with Anhydrous Ammonia," J. Am. Chem. Soc. **73**, 1619 (1951).
2. H. H. Sisler, F. T. Neth, and F. R. Hurley, "The Chloramine-Ammonia Reaction in Liquid Ammonia," J. Am. Chem. Soc. **76**, 3909 (1954).
3. H. H. Sisler, C. E. Boatman, F. T. Neth, R. Smith, W. Shellman, and R. Kelmers, "The Chloramine-Ammonia Reaction in Pure Water and in Other Solvents," J. Am. Chem. Soc. **76**, 3912 (1954).
4. I. T. Gilson and H. H. Sisler, "The Reaction of Diphenylchlorophosphine with Ammonia-Free Chloramine," Inorg. Chem. **4**, 273 (1965).
5. H. H. Sisler and G. Omietanski, "Trisubstituted Hydrazonium Chlorides," Inorg. Syn. **5**, 91 (1957).
6. H. Prakash and H. H. Sisler, "Preparation of Chloramine by the Gas-Phase Reaction of Ammonia and Chlorine at Low Molar Ratios," Allgem. Prakt. Chem. **21** (4), 123-24 (1970).
7. _____, NEDERLAND OCTROOI No. 66758 (15 November 1950).
8. F. V. Canfield, Z. Reynolds, and L. B. Reynolds, U.S. Patent 2,726,935 (13 December 1955).
9. G. L. Braude, N. Linthicum, and J. A. Cogliano, U.S. Patent 3,038,785 (12 June 1962).
10. _____, United Kingdom Patent 1,149,836 (23 April 1969).
11. H. Clasem and W. Wendel, Ger. Offen. 2,440,225 (4 March 1975).
12. H. H. Sisler, F. T. Neth, R. S. Drago, and D. Yaney, "The Synthesis of Chloramine by the Ammonia-Chlorine Reaction in the Gas Phase," J. Am. Chem. Soc. **76**, 3906 (1954).
13. M. W. Chase (Dow Chemical Co.) Communication to Martin Marietta Corp. (Attn: L. Williams), Subject: Thermochemical Data for Chloramine (27 April 1977).

14. D. H. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed., NSRDS-NBS 37 (June 1971).
15. _____, "Tube Flowmeter Correction Factors - Calculation Procedure," published by Matheson Gas Products.
16. M. Awane and C. Badcock, The Analysis of Chloramine in Gas Streams, ATM 77(2296)-2, The Aerospace Corp., El Segundo, Calif. (16 May 1977). This document presents a complete description of the sampling and analysis studies performed.
17. J. Kleinberg, M. Tecotzky, and L. F. Audrieth, "Absorption Spectrum of Aqueous Monochloramine Solutions," Anal. Chem. 26, 1388-89 (1954).
18. W. S. Metcalf, "Absorption Spectra of Mono-, Di-, and Trichloramines and Some Aliphatic Derivations," J. Chem. Soc. pp. 148-50 (1942).
19. A. F. Trotman-Dickenson and G. S. Milne, Tables of Bimolecular Gas Reactions, NSRDS-NBS9 (October 1967).
20. A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, NY, 161-510 (1968).

APPENDIX

The following tables list all acceptable experiments performed on the reaction of NH_3 with Cl_2 . An acceptable experiment is defined as having the following observed properties:

1. The experiment must not exhibit light emission or a flame prior to or during the sampling period.
2. A flat temperature profile must be observed during the sampling period. This is defined as having a total temperature variation of less than 50°C during this period. (Most experiments had less than a 30°C variation.)
3. The sample must be taken from the gases generated during the period where the temperature profile is relatively flat.

The tables list the temperature at T1 unless otherwise noted. The gas flows are listed at 294°K and 1 atm. The actual flows depend on the temperature. The following factors will convert the flows into mass units.

$$\text{Cl}_2 \text{ (g/min)} = 2.94 \times [\text{Cl}_2 \text{ Flow rate (l/m)}] \quad (\text{A1})$$

$$\text{NH}_3 \text{ (g/min)} = 0.706 \times (\text{NH}_3/\text{Cl}_2 \text{ ratio}) \times (\text{Cl}_2 \text{ Flow rate}) \quad (\text{A2})$$

$$\text{N}_2 \text{ (g/min)} = 0.861 \times (\text{N}_2/\text{Cl}_2 \text{ ratio}) \times (\text{Cl}_2 \text{ Flow rate}) \quad (\text{A3})$$

$$\text{NH}_2\text{Cl (g/min)} = 2.134 \times (\text{Yield}) \times (\text{Cl}_2 \text{ Flow rate}) \quad (\text{A4})$$

The experiment numbers are for reference only and do not reflect the order of experiments. The N_2 diluent was always placed in the Cl_2 input stream except where noted.

SUMMARY OF EXPERIMENTS

No.	Ratio Cl ₂ = 1		Cl ₂ Flow Rate ℓ/m	Temperatures		Yield NH ₂ Cl %	Notes
	NH ₃	N ₂		Initial °C	Reaction °C		
1	8	0	0.3	24	280	21	1
2	8	0	0.6	24	280	32	
3	8	0	0.25	24	160	19	
4	8	0	0.2	24	290	5	
5	8	0	0.4	24	260	31	
6	8	0	0.5	24	220	37	
7	8	0	0.7	24	290	13	
8	8	8	1.2	24	290	11	
9	8	0	1.0	24	310	11	2
10	8	0	0.4	24	260	45	
11	8	0	0.5	24	185	43	
12	8	0	0.5	24	240	44	
13	8	0	0.5	24	250	53	
14	8	1.1	0.5	24	130	52	
15	8	1.1	0.5	24	130	38	
16	8	1.1	0.5	24	200	47	
17	8	1.3	0.4	24	210	65	
18	8	1.3	0.5	24	263	56	
19	8	1.3	0.5	24	190	68	
20	8	1.3	0.5	24	200	65	
21	8	6.4	0.4	24	185	69	3
22	8	8.4	0.5	24	180	82	
23	8	0	0.5	280	190	44	
24	8	1.1	0.5	190	230	66	
25	8	1.1	0.5	240	170	67	
26	8	1.1	0.5	240	210	56	
27	8	0	0.4	24	210	106	

SUMMARY OF EXPERIMENTS (Continued)

No.	Ratio $\text{Cl}_2 = 1$		Cl_2 Flow Rate l/m	Temperatures		Yield NH_2Cl %	Notes
	NH_3	N_2		Initial °C	Reaction °C		
28	20	0	0.4	24	170	97	
29	20	0	0.5	24	120	71	
30	6	0	0.5	24	300	17	
31	6	1.1	0.5	24	210	72	
32	6	1.1	0.5	24	180	49	
33	6	1.1	0.5	24	260	53	
34	6	2.2	0.5	24	180	51	
35	6	2.2	0.5	24	260	64	
36	6	0	0.5	220	280	47	3
37	5	0	0.5	24	230	23	
38	5	0	0.5	24	270	17	2
39	5	1.1	0.5	24	250	57	
40	5	1.1	0.5	24	220	38	
41	5	1.1	0.5	24	230	48	
42	5	2.2	0.5	24	170	61	
43	5	2.2	0.5	24	190	56	
44	5	3.4	0.5	24	140	62	
45	5	3.4	0.5	24	--	48	5
46	5	3.4	0.5	24	230	63	
47	5	6.7	0.5	24	190	67	
48	5	0	0.5	230	270	19	3
49	5	1.1	0.5	220	220	47	3
50	4	0	0.5	24	--	15	
51	4	1.1	0.5	24	280	29	
52	4	2.2	0.5	24	250	61	
53	4	3.4	0.5	24	250	62	
54	4	3.4	0.5	24	260	64	

SUMMARY OF EXPERIMENTS (Continued)

No.	Ratio Cl ₂ = 1		Cl ₂ Flow Rate l/m	Temperatures		Yield NH ₂ Cl %	Notes
	NH ₃	N ₂		Initial °C	Reaction °C		
55	4	5.6	0.5	24	200	68	
56	4	1.1	0.5	190	240	45	3
57	4	1.1	0.5	190	250	45	3, 4
58	4	1.1	0.5	190	250	50	3, 4
59	4	1.1	0.5	190	240	45	3
60	4	3.4	0.5	190	--	78	3
61	4	3.4	0.5	190	240	102	3
62	4	3.4	0.5	190	230	95	3
63	4	3.4	0.5	190	230	91	3
64	4	3.4	0.5	190	230	92	3
65	4	3.4	0.5	190	230	78	3, 4
66	4	3.4	0.5	190	230	80	3, 4
67	4	0	0.5	220	260	22	3
68	4	1.1	0.5	220	230	48	3
69	4	0	0.5	270	190	20	3
70	4	2.2	0.5	270	200	60	3

1. T1 located 5 cm lower in reactor section.
2. T1 not within 50°C range, $\Delta T \sim 70^\circ\text{C}$.
3. Temperature measured at T2 for all heated samples, initial temperature is that of injector at TB.
4. N₂ added to NH₃ rather than to the Cl₂ stream.
5. Reaction temperature not available.