The Production of Chloramine by Liquid Phase Injection of Ammonia and Chlorine

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1 June 1979

Final Report

APPROVED FOR PUBLIC RELEASE;
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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
This final report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under contract 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 Gentry 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

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FOR THE COMMANDER

[Signature]
**Title**: The Production of Chloramine by Liquid Phase Injection of Ammonia and Chlorine

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**Performing Organization**: The Aerospace Corporation

**Report Date**: June 1979

**Report Number**: TR-79-41

**Abstract**: The results of preliminary experiments on the injection of liquid reactants NH₃ and Cl₂ into a reactor to produce chloramine NH₂Cl are reported. The normal process for the anhydrous production of NH₂Cl introduces the reactants as gases. The direct injection of liquid reactants would be a simplification. Problems with the constancy of reactant delivery and dispersion of liquid reactants caused the observed yields to vary greatly. At NH₃/Cl₂ ratios of 3.3 all of the NH₃ was consumed in two experiments and dichloramine was detected in the analytical solutions. When the ratio was increased to 4.3...
NH₃ was present in all cases and one experiment gave a yield of 60 percent
NH₂Cl. No plugging of the injectors was observed in any of the experiments
and continuous operation appeared feasible. The NH₄Cl product formed in
large flakes that only weakly adhered to the reactor parts. The NH₄Cl settled
out much more rapidly in the liquid injection experiments than in comparable
gas phase injection experiments. The development of this approach should
be considered.
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I. INTRODUCTION

Chloramine \( \text{NH}_2\text{Cl} \) is used in the synthesis of hydrazine, unsymmetrical dimethylhydrazine and monomethylhydrazine. The Raschig synthesis produces chloramine by the reaction

\[
\text{NH}_3 + \text{OCl}^- \rightarrow \text{NH}_2\text{Cl} + \text{OH}^-
\]

in aqueous ammonia-caustic solution. The appropriate amine and additional base are then injected into the reaction stream and flash heating produces the appropriate hydrazine. This reaction requires dilute solutions because of attack by \( \text{NH}_2\text{Cl} \) on the products. A way of increasing the concentration of product in the reaction stream is to produce \( \text{NH}_2\text{Cl} \) under anhydrous conditions in the gas phase. This approach has been developed by Sisler and coworkers (Refs. 1 through 7). Studies of the gas phase reaction

\[
2\text{NH}_3 + \text{Cl}_2 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_4\text{Cl(s)}
\]

and the effects of temperature, diluent gases, and flow rates are contained in a previous report (Ref. 8).

The gas phase production of \( \text{NH}_2\text{Cl} \) on an industrial scale requires the vaporization of large quantities of \( \text{NH}_3 \) and \( \text{Cl}_2 \), and the delivery of these gaseous reactants under high pressure and temperature. The gaseous injectors, reaction zone, and the gases must be further heated to approximately 300° C to prevent fouling of the system by \( \text{NH}_4\text{Cl} \). Previous work has shown that high yields of \( \text{NH}_2\text{Cl} \) are produced at lower temperatures before fouling by \( \text{NH}_4\text{Cl} \) takes place (Refs. 6, 8), and that lower temperatures may increase the yields. An excess of \( \text{NH}_3 \) over the stoichiometric quantity or an additional diluent gas is required (Refs. 1, 6 through 8).
The direct injection of liquid reactants would be preferable on a large scale. The cooling resulting from the vaporization of reactants might permit reactions with smaller excesses of NH_3 and with no gaseous diluent. In addition, the nature of the NH_4Cl product might be advantageously changed. An exploratory investigation of the direct injection of liquid reactants is reported.
II. EXPERIMENTAL

The apparatus, which was adapted from previous gas phase experiments (Ref. 8), is shown in Figure 1. The reactant lines were all 316 or 304 stainless steel (SS) except for polyethylene transfer lines from the flowmeters to the liquid reactant storage tubes. The reactor was a 2 l Pyrex resin kettle. Known amounts of the reactants were condensed in the storage tubes by immersing the tubes in a bath at dry ice temperatures and allowing the reactants to flow into the reservoirs at known flow rates for measured periods of time. After the reactants had warmed to above 0°C, 98 psig (777 kPa) of helium pressure was used to drive the liquids upward through 3 mm tubing to lengths of 0.25 mm ID 316 SS capillary tubing and into the reactor. It was necessary to prechill the lines carrying reactants to assure reproducible delivery times. The insert in Figure 1 shows the injector arrangement. NH\textsubscript{3} flowed from the upper tip downward around the Cl\textsubscript{2} injector. Reacted gases were disposed of in a water scrubber.

The flow rates of both NH\textsubscript{3} and Cl\textsubscript{2} were controlled by varying the length of the capillary tubing. Attempts were made to control the flow rates using constant lengths and variable driving pressures of inert gas with the reactants cooled to 0 to -30°C. Both "vapor lock" and solidification of the reactants in valve orifices prevented the use of this approach. The NH\textsubscript{3} vapor pressure at room temperature is approximately 100 psig and that for Cl\textsubscript{2} is somewhat lower. Therefore, by using a driving pressure of 98 psig and slightly cooling the reactant lines, the liquids could be delivered with predictability. Calibration of the capillaries was performed by observing the time required to deliver known amounts of the reactants. The calibration curves for NH\textsubscript{3} and Cl\textsubscript{2} are shown in Figure 2. The flow rates of the reactants were the slopes of the regression lines through the points. The flow rates were generally reproducible to better than ±15 percent.
Figure 1. Apparatus used for the liquid injection of reactants for the production of chloramine. The reactants were injected through 0.25 mm ID capillary tubing. S is the sampling port. A and B are the metered liquid reactants storage vessels for NH₃ and Cl₂ respectively. They could be immersed in a -78°C bath. Insert is a photograph of the injector with liquid Cl₂ spraying from the lower tip.
Figure 2. Calibration curves for reactant delivered vs. time for 0.25 mm ID capillary tubing. Reactants were forced through tubing with 98 psig of helium pressure. [A] NH$_3$ calibration and regression lines for 2.53 m (▲, --) and 3.3 m (○, ——) long tubes. [B] Cl$_2$ calibration and regression for 1.5 m long tube.
The temperature at T1 was recorded using a glass encased chromel-alumel thermocouple (Type K) and an Omega electronic reference junction. The thermocouple was placed approximately 4 cm below the injector tips.

The sampling and analysis of the effluent gases was performed using an evacuated sampling bulb, water extraction of the gas for NH$_2$Cl and NH$_3$, spectrophotometric analysis of NH$_2$Cl at 243 nm, and titration of NH$_3$. This has been described in detail previously (Ref. 8). Sampling was always delayed until the gas flowing past S (Figure 1) was representative of the reaction. The yield was then calculated from

$$\text{Yield} = \left(\frac{E(R - 2.667)}{1 - 1.667E}\right) \times 100$$

where $R$ is the ratio of the reactants NH$_3$/Cl$_2$, and $E$ is the fraction, moles NH$_3$Cl/(moles NH$_3$ + moles NH$_2$Cl) (Ref. 8) in the sample. In experiments where the quantity of NH$_3$ was very low, NH$_3$ was added to the extraction solution and correction was made for this addition.

The chemicals used were Matheson Gas Products anhydrous ammonia and High Purity chlorine, and Air Products grade "A" helium. J. T. Baker Company Dilut-it 0.1 N HCl was diluted to volume with deionized water and used to titrate NH$_3$ to the bromocresol green endpoint.

In a typical run, the whole system was thoroughly purged with He. The purge was maintained through the capillaries while the reactants were measured and condensed. The reactant storage vessels were loaded separately by first purging the volume with the reactant, then shutting the exit valve, immersing the reservoirs in a -78°C bath, and monitoring the flow for a fixed period of time. Excess NH$_3$ was always added to the reservoir to assure that the experiment began and ended with only an NH$_3$ flow. After each reservoir had been loaded, the gas streams were switched to high pressure He. The lines leading to the capillaries from the reservoirs
and part of the capillaries were then chilled by pouring cold isopropyl alcohol over alumina wool insulation that had been wrapped around the tubing. An experiment was initiated by opening the NH₃ valve to the capillary, waiting until liquid was observed in the reactor, and then opening the Cl₂ valve. Although the reaction would run indefinitely, the Cl₂ quantity limited reaction times to approximately 200 sec. To assure initiation of the reaction at the low temperatures of the liquids, the reactions were run with illumination from several fluorescent tubes. The temperatures were recorded. A sample was collected from the sample port approximately 90 sec after Cl₂ liquid was delivered. Approximately 45 sec were required to collect a sample. After the reaction had terminated and a He flow was re-established, the sample was extracted and analyzed as previously described.
III. RESULTS AND DISCUSSION

The objective of these experiments was to determine if Cl₂ and NH₃ could be reacted by injecting the liquid reactants. The points of importance were the production of NH₂Cl, the nature of the NH₄Cl produced, and the demonstration that the reaction occurred predictably. The last point was of concern because initiation of the reaction could have been delayed if it is a free radical/atom mechanism and an explosion could have resulted. In all cases the reaction initiated and ran smoothly.

A summary of the results of experiments at two different NH₃/Cl₂ ratios is given in Table 1. Chloramine was produced at both reactant ratios in significant quantities although not reproducibly. The scatter in the yield data was the result of several problems. The largest contributor was probably variations in the liquid delivery rates. The reactant ratios and the uncertainties are from the calibrations in Figure 2. These calibrations, however, are based on the integrated flow times for known quantities of liquid and do not reflect the undetectable variations in liquid flow rates during this period. During calibrations, "spurting" of the reactants was observed. The data are reasonable if the flow rate of one or both of the reactants varied because the probability of dropping below the stoichiometric ratio of 2 NH₃ to 1 Cl₂ was less at the higher NH₃ flow rate.

The experiments at the lower ratio of reactants gave indication that less than the stoichiometric ratio was at times present and that decomposition of the products was occurring. In two cases, experiments 1 and 5, no NH₃ was detected in the samples although excess NH₃ should have been present even if all of the NH₂Cl had decomposed by the reaction

\[ 2\text{NH}_3 + 3\text{NH}_2\text{Cl} \rightarrow N_2 + 3\text{NH}_4\text{Cl} \]  (4)
Table 1. Summary of Experiments on the Injection of Liquid Reactants to Produce Chloramine

<table>
<thead>
<tr>
<th>No.</th>
<th>Flow Ratio NH₃/Cl₂</th>
<th>Temperature T1 (°C)</th>
<th>Yield (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.30 ± .36</td>
<td>--</td>
<td>--</td>
<td>NH₂Cl detected, no NH₃ detected</td>
</tr>
<tr>
<td>2</td>
<td>3.30 ± .36</td>
<td>70</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.30 ± .36</td>
<td>70</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.30 ± .36</td>
<td>70</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.30 ± .36</td>
<td>80</td>
<td>(25)</td>
<td>NH₂Cl detected (est. yield), no NH₃, detected NHCl₂</td>
</tr>
<tr>
<td>6</td>
<td>4.29 ± .53</td>
<td>(105)</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4.29 ± .53</td>
<td>(180)</td>
<td>35</td>
<td>Temperature was unstable and rising</td>
</tr>
<tr>
<td>8</td>
<td>4.29 ± .53</td>
<td>(70)</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

Dichloramine NHCl₂ was detected in experiment 5 in at least minor amounts by the ultraviolet absorption of the analysis solution near 310 nm (Refs. 8 through 10). Chloramine was reasonably concentrated in this sample, but no NH₃ was present. Under these conditions, the pH is quite low and NHCl₂ may have formed in the water solution rather than in the reactor (Ref. 10).

The temperature below the injector was stable at the lower reactant ratio. The temperature at the higher ratio was rising during the entire reaction period and sometimes reached as high as 200°C. The temperatures given in the table are averages during the sample period. The use of liquid reactants did appear to lower the temperature of the reaction when compared with similar temperature probe positions and flow rates in gas phase injection experiments (Ref. 8).
Experiment 6 shows that acceptable yields of NH₂Cl are possible by this technique. It is clear that for this approach to be practical, the mechanical problems of liquid delivery and injector design must be attacked. An additional problem may be that cold NH₄Cl particles may promote decomposition (Ref. 6). The evaporation of the liquid reactants on NH₄Cl particles could result in subambient temperatures.

The reaction of NH₃ with Cl₂ has been proposed to occur by a free radical/atom chain reaction. The generation of Cl atoms

\[ \text{Cl}_2 \rightarrow 2 \text{Cl} \quad (5) \]

would initiate the process and a chain reaction would produce NH₂Cl.

\[ \text{NH}_3 + \text{Cl} \rightarrow \text{NH}_2 + \text{HCl} \quad (6) \]

\[ \text{NH}_2 + \text{Cl}_2 \rightarrow \text{NH}_2\text{Cl} + \text{Cl} \quad (7) \]

Reactions of NH₂, NH, and Cl with each other would then cause chain termination and lowered yields. High radical and atom concentrations would decrease the chain lengths and the yields of NH₂Cl. The evaporating droplets of reactants in the liquid injection case could provide high local concentrations of radicals with disproportionate ratios of Cl to NH₂. This could cause higher temperatures and decreased yields. The greatest dispersion and mixing of the reactants would appear to be beneficial. The use of a small jet of diluent gas would perform this task and perhaps increase the yields as was the case in the gas phase injector experiments (Ref. 8).

The most encouraging observations from these experiments were the nature of the NH₄Cl solids and the operation of the reactor. Although NH₄Cl was blown all over the reactor and tended to hang on any surface, the density of the particles was such that most of it settled to the bottom of
the reactor immediately. Generally, the NH₄Cl was flake-like with larger, more granular crystals than the material in gas phase experiments.

Figure 3 shows photographs of the NH₄Cl that adhered to the injectors. These deposits were fluffy and easily removed. Note that Figures 3A and 3B show no glassy deposits although they are in the immediate area of the mixing of reactants. There was also a difference in the appearance of the NH₄Cl between the higher and lower reactant ratio experiments. The flakes of NH₄Cl were larger in the experiments with higher reactant ratios and had a definite 'wet' appearance. Most significantly, mild vibration of the reactor tips caused the deposit to fall away as shown in Figure 3C. A thin, adherent, dust-like coating of NH₄Cl covered all internal parts of the reactor but no heavy buildups were observed.

All experiments ran smoothly; flow variations during the reaction could not be observed due to the NH₄Cl cloud. No plugging of the injector tips occurred at any time during the experiments. Consecutive experiments were performed by purging with He and cleaning the reactor to permit observation of the next experiment. No tip cleaning was ever necessary. This is in contrast to the gas phase studies at room temperature (Ref. 2), where the injector frequently plugged and the reaction zone and injector required careful cleaning between experimental runs (Ref. 8). The liquid injection reactor appeared to be capable of continuous operation with no more than occasional vibration to free the injector of nonadherent NH₄Cl buildup.
Figure 3. Photographs of the NH₄Cl buildup on the liquid injector assembly. 
[A] at the termination of an experiment. 
[B] NH₄Cl formation removed from the injector, viewed from the top. Note the fluffy appearance and the openings where the liquids were expelled. 
[C] The injector tips after mild vibration were clean of NH₄Cl.
IV. SUMMARY

The reaction between NH$_3$ and Cl$_2$ to produce NH$_2$Cl was found to be feasible when the reactants were injected as liquids. The reaction probably still occurs in the gas phase. The NH$_4$Cl produced was more readily separated from the product gas stream with liquid reactant injection than in gas phase injection experiments in the same reactor. The NH$_4$Cl was less adherent and mild vibration would remove buildup from the injectors. No plugging of the injectors was ever observed.

The yields were variable and not very high in the experiments at reaction ratios of NH$_3$ to Cl$_2$ of 3.3 and 4.3. At the lower reaction ratio all NH$_3$ was consumed in two experiments. One experiment at the higher ratio gave a yield of NH$_2$Cl of 60 percent. The low yields and the complete consumption of NH$_3$ indicate that variations in the delivery rate were occurring and that dispersion of the liquid droplets was insufficient.

The advantages of liquid reactant delivery and the observations made in this work indicate that chloramine production by this technique is an attractive alternative to gas phase reactant injection. The problems of flow variation could be corrected easily on a larger scale unit and reactant dispersion could be improved by the use of a diluent gas jet.
REFERENCES


