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Synthesis of Propyl Nitroguanidine (PrNQ)

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1 ABSTRACT

PrNQ is an alkylated analog of the commonly used explosive, nitroguanidine (NQ). The propyl group reduces the melting point yielding a material that is suitable for melt-pour applications while the nitroguanidine portion of the molecule provides the explosive power. In addition, NQ is known for its inherent insensitivity. PrNQ is easily synthesized through the reaction of propylamine with nitroguanidine resulting in the liberation of ammonia. PrNQ has been previously synthesized on the large laboratory scale by scientists at the Army Research Laboratory (ARL) and the Army Research, Development and Engineering Center (ARDEC). As part of this ongoing effort, BAE Systems, Ordnance Systems, Inc. (OSI) has been selected to provide several hundred pounds of PrNQ to ARL for further evaluation in a series of next-generation GP bomb fills. This paper will discuss the synthesis and optimization of PrNQ that was conducted at OSI's Holston facility.

2 INTRODUCTION

The first documented synthesis of PrNQ was reported in 1927 by Davis and Luce. [1] This process employed propylammonium hydrochloride which was first neutralized with hydroxide to give the free amine. The free amine can then be reacted with nitroguanidine (NQ) to yield PrNQ. Scientists at ARL recognized the added cost in both materials and labor associated with the use of propylammonium hydrochloride. As such, they developed a synthesis requiring only propylamine, NQ and water as a solvent (Figure 1). [2]

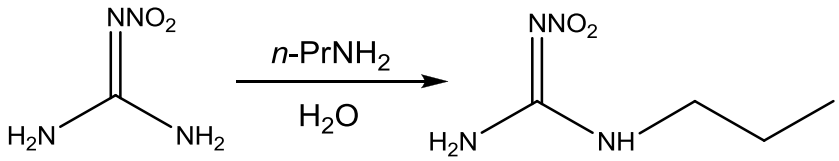

Figure 1. Synthesis of PrNQ

Upon modification of the PrNQ synthesis process, the reaction conditions were optimized by ARL scientists. This optimization of the reaction was intended for the purpose of developing an adequate process that could be used to acquire material for further evaluation. The reaction was then completed on the 200 gram and 600 gram scales.

Once the staff and ARL had scaled up the process, it was transitioned to ARDEC in order to provide larger quantities of material that would be sufficient for performance testing. ARDEC scientists completed multiple reactions on the kilogram scale that resulted in a total of 24+ kilograms of material. During the course of this work, it was noted that several parameters required further optimization. These parameters included temperature, neutralization conditions and recrystallization conditions. At this point, it was also determined that the material needed to be synthesized on a larger scale in order to cost-effectively provide sufficient material for further testing. As such, BAE Systems, OSI was contracted to further optimize and scale up the reaction. To date, approximately 5,000 lbs of analytical pure PrNQ have been generated and delivered for further testing.

3 DISCUSSION

3.1 PrNQ Synthesis Optimization

The optimization of the PrNQ synthesis was broken down into six distinct phases. The first five phases focused on optimization of the PrNQ reaction itself. These phases consisted of optimization of the solvent content, temperature, reagent ratios and quench conditions. Lastly, the crystallization conditions were considered. The results of each of these phases are discussed below.

3.1.1 Solvent Content Evaluation

Upon analysis of the previously developed PrNQ synthesis process, it was clear that the solvent content of the reaction mixture should be evaluated. Through adjustment of the water content, it was determined that the optimal H_2O to NQ weight ratio was three times that of the original process that had been previously developed at ARL (Table 1). This ratio served to increase yield while still providing exceptional product purity. Further increase of the solvent to four times that of the original process caused a reduction in yield and purity.

Table 1. Optimization of Solvent Content in PrNQ Reaction

H_2O:NQ Ratio	Temperature	Yield	Purity
Original	Original	44	100.0
Original	Optimal	46	97.9
Original x 2	Optimal	51	97.4
Original x 3	Optimal	56	98.9
Original x 4	Optimal	52	98.0

3.1.2 Temperature Evaluation

Upon determination of a proper solvent ratio, the temperature of the reaction was evaluated. In order to get a better understanding of the effects of reaction temperature, several iterations were completed at different temperatures and the reaction was sampled each hour. HPLC analysis was used to determine in-situ yields. The purpose of this exercise was to determine how quickly the PrNQ that was generated was reacting further. The PrNQ could either decompose or further react to yield dipropyl nitroguanidine. Although this byproduct could possibly be generated, it has not presently been identified in the reaction solution. The results of testing at the various temperatures (Table 2) indicate that both temperatures A and B are reasonable temperatures for conducting the PrNQ synthesis.

Table 2. Temperature Evaluation for PrNQ Reaction

Temperature	% Yield				
	Dissolution	1 hour	2 hours	3 hours	4 hours
A	71.8	73.5	73.5	67.8	65.1
B	70.0	72.7	62.6	54.6	51.7
C	70.8	59.2	45.3	31.1	25.6

*Note: All times given are post-dissolution, including the total heating time

3.1.3 Reagent Ratio Evaluation

Upon determination of the solvent content and appropriate reaction temperature, the reagent ratio was evaluated. As can be seen from the data (Table 3), the original ratio could be lowered by approximately 25% without a great loss in yield or in purity. This ratio was used for many of the pilot scale batches that were completed. However, further optimization proved that an even lower reagent ratio could be used when the solvent content was adjusted a second time. These adjustments were applied to the final few pilot scale batches.

Table 3. Reagent Ratio Evaluation for PrNQ Reaction

$PrNH_2$:NQ (mol/mol)	Temp.	Yield	Purity
Original	Temp B	56	98.9
Original – 12.5%	Temp A	58	99.5
Original – 25%	Temp A	60	98.7
Original – 25%	Temp B	65	99.1
Original – 37.5%	Temp B	64	94.6

3.1.4 Quench Conditions Evaluation

Two different aspects of the quench conditions were considered. First, the pH of the reaction mixture after the quench was evaluated. In some instances, the pH can greatly affect the amount of product that can be acquired from the reaction solution. For this particular reaction (Table 4) it appears that the pH at quench does not have much effect on the final reaction yield. As such, the optimal pH value for this reaction was determined to be approximately neutral pH. This pH ensures that all of the propylamine in the reaction solution is converted to a salt which eliminates the inhalation hazards associated with propylamine. Also, this pH requires the minimum amount of acid to be used. Next, the acid used during the quench was considered. Consultation with scientists at ARL indicated that only Acid A had been used in their method due to the ready availability of this acid at their location. Acid B and Acid C were both evaluated as quench acids. Testing indicated that Acid C served to increase both reaction yield and product purity, while Acid B lowered the resulting purity. Therefore, Acid C was chosen for use in the pilot scale reactions.

Table 4. Quench Conditions Evaluation

Acid	pH	Yield	Purity
Acid A	6.4	56	ND
Acid A	3.6	57	ND
Acid A	3.1	57	ND
Acid A	1.8	58	ND
Acid A	1.1	56	ND
Acid A	1.1	60	ND

Acid B	~3.0	59	97.6
Acid C	~3.0	63	99.5
Acid A	6.5	56	98.9

3.1.5 Crystallization Conditions Evaluation

As the crystallization conditions provided by ARL employed a cost-effective solvent, there seemed to be little reason to evaluate other solvents. However, adjustment of the solids loading was considered. As can be seen in Table 5, even an increase of 250% of water does not appear to cause a large decrease in the amount of PrNQ that is recovered. This indicates that the crystallization conditions are robust and a small upset will cause only minor decreases in yield.

Table 5. Crystallization Solids Loading Effects for the PrNQ Reaction

Solvent:PrNQ ratio	% Recovery
Original	92
Original x 1.5	88
Original x 2.5	86

3.2 Large Laboratory Scale Production of PrNQ

In preparation for production, a large laboratory scale reaction for PrNQ was completed using a Holston style 18 L still (Figure 2). Upon completion, the reaction solution was was quenched with acid. After the quench, the mixture was cooled to and filtered. The yield of this reaction was 56% and the purity of the PrNQ from this reaction was excellent at 99.9%.

Figure 2. Holston 18 L Still

3.3 Pilot Scale Synthesis of PrNQ

A total of 5,000+ pounds of PrNQ were generated during the pilot scale synthesis portion of this project. All of the PrNQ for this program was generated in the newly commissioned pilot plant at Holston. The facility, which is solely dedicated to research and development activities, is fully functional with three glass-lined, jacketed reactors sized 50, 100 and 200 gallons. Each of these reactors and the corresponding utilities can be remotely monitored and controlled using a Siemens PLC system. The pilot plant is rated for 3,000 pounds of explosive and has a flexible design that can be adapted to endless configurations.

Figure 3. Pilot Plant 200 Gallon Pfaudler Reactor

Figure 4. BAE Systems' Pilot Facility

All reactions and crystallizations for this effort proceeded as planned with no unexpected events. Analytical results for all of the pure samples are given in Table 6 below. Figure 5 depicts crude PrNQ in a Nutsche filter.

Table 6. Analytical Results for Pilot Scale Synthesis

Avg. Rxn Yield	Avg Cryst. Yield	Avg. Purity
69%	87%	99.5%

Figure 5. Crude PrNQ

3 CONCLUSIONS

The PrNQ reaction has undergone extensive optimization. Parameters evaluated during this study include reaction temperature, solvent ratio, reagent ratio, quench conditions and crystallization conditions. In addition, waste solutions from the reaction were also analyzed for handling purposes and this analysis indicated that there were no signification waste handling concerns. Lastly, a total of approximately 5000 lbs of analytically pure PrNQ were synthesized and delivered to ARL for testing.

4 ACKNOWLEDGEMENTS

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