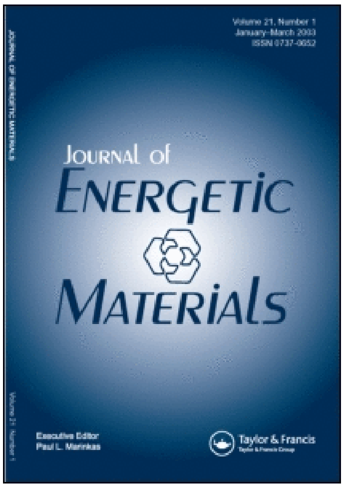

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HYDROLYSIS OF THE ENERGETIC MATERIALS PRESENT IN A COMPOSITE MODIFIED DOUBLE BASE SOLID ROCKET PROPELLANT*

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ABSTRACT

The aqueous hydrolysis of the nitroglycerin (NG), nitrocellulose (NC), and HMX present in CYH, a composite modified double base solid propellant, was successfully performed using either sodium hydroxide (NaOH) or ammonia (NH_3) as hydrolyzing agents. The rate of hydrolysis was faster for NaOH compared to NH_3. For both hydrolysis agents the rate of hydrolysis of NG was the fastest, followed by NC and then HMX. It was determined that 4 parts of NaOH were required to hydrolyze the energetic ingredients in 10 parts of CYH. A similar determination was not made for NH_3.

The original set of experiments were done on a small scale (0.030-10 grams of propellant) with laboratory glassware. Later experiments involved the hydrolysis of larger amounts of propellant (200 grams), again using laboratory glassware. The last set of experiments were accomplished with a small scale glass reactor (4 liters) with up to 900 grams of propellant per run. In addition, exhaustive chemical analysis yielded useful information about the hydrolysis products. The combined data was used to design a reactor for the hydrolysis of 4,000 lbs of CYH propellant.

* This work was performed in conjunction with and under a subcontract to General Atomics (prime contractor to the Air Force, Armstrong Laboratory, Tyndall AFB Large Rocket Motor Disposal program sponsored by the Joint Ordnance Commanders).

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INTRODUCTION*

Past efforts have examined the hydrolysis/decomposition of energetic materials such as NG, NC, and HMX with a variety of hydrolysis agents.[1] The bulk of this work was done with individual ingredients on a very small scale. The CYH propellant examined in this study contains AP (10.8 wt%), HMX (10.8 wt%), NC (21.6 wt%), NG (29.6 wt%), aluminum (19.8 wt%), triacetin (5.3 wt%), 2-NDPA (1.0 wt%), and resorcinol (1.1 wt%).[2] CYH propellant is a composite modified double base (CMDB) propellant used as the predominant formulation in Minuteman II, Stage III motors, which were produced by Hercules Corporation for the Air Force. The purpose of the propellant hydrolysis was to hydrolyze the NG, NC, and HMX in the propellant to give an inert mixture of compounds which would be amenable to normal waste treatment methods. Two of the hydrolysis agents tested were aqueous sodium hydroxide (NaOH) and aqueous ammonia[3] (NH_3).

The SRMD Program is proposed to produce size-reduced CYH propellant from the washout of Minuteman II, Stage III motors with high pressure liquid nitrogen. Earlier work on cryogenic size reduction of CYH propellant has demonstrated that the bulk of the propellant is reduced in size to coarse sand by this process, with a few larger pieces also present.[4] For the current study, CYH propellant was ground in a metal mill with a mesh screen which allowed passage of the propellant once it was reduced to the desired size.[5] Most of the hydrolysis studies of this report were performed with CYH propellant ground to 10 mesh (approximately 0.1 inches in diameter), a size similar to coarse sand.

* This work was performed in conjunction with and under a subcontract to General Atomics (prime contractor to the Air Force, Armstrong Laboratory, Tyndall AFB Large Rocket Motor Disposal program sponsored by the Joint Ordnance Commanders).

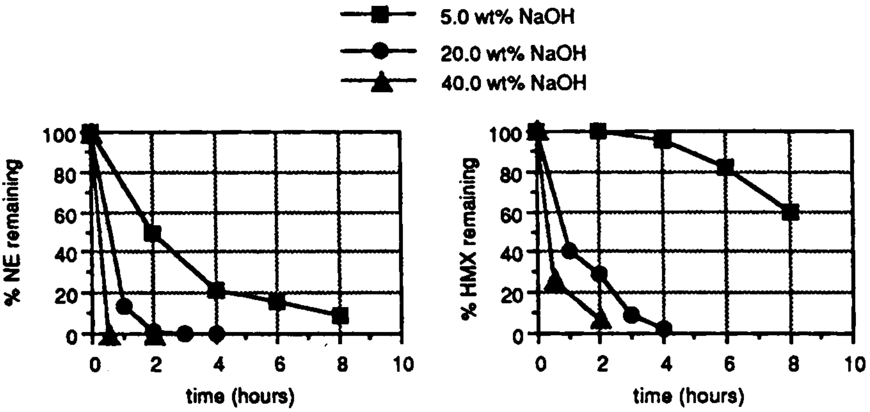
RESULTS AND DISCUSSION

Rate of Hydrolysis

This set of experiments attempted to measure the rate of hydrolysis of the energetic ingredients in CYH with different hydrolysis agents. The rate of hydrolysis experiments were designed to give the rate of hydrolysis of NG, NC, and HMX present in ground (10 mesh) CYH propellant at a certain concentration of hydrolysis agent and at a set temperature. The 10 mesh, ground propellant was used as a model of cryogenic washout propellant. An excess of hydrolysis agent was used in the experiments, so that at the end of the hydrolysis, the concentration of hydrolysis agent would remain essentially unchanged.

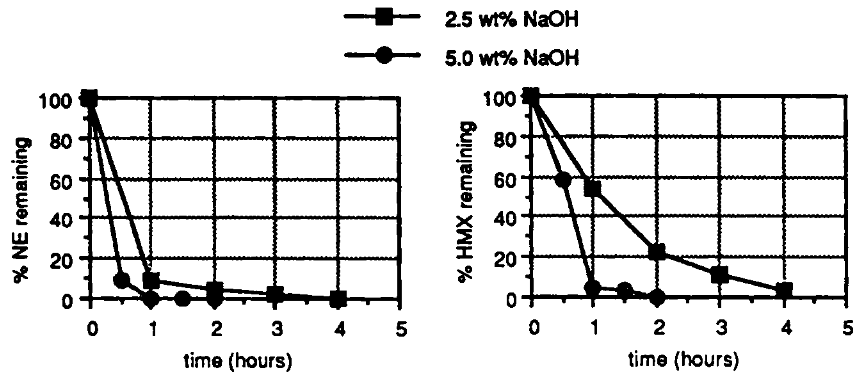
The first hydrolysis agent tested was NaOH. Experiments were performed by the addition of 1.0 grams of ground (10 mesh) CYH propellant to 50 grams of the hydrolysis solution in a 125 mL Erlenmeyer flask which had been previously heated to the desired temperature. The flask was equipped with a septum and thermometer. The mixture was stirred with a magnetic stir bar and the temperature was maintained to ±1.0°C, by constant heating with a silicone oil bath controlled by a Therm-O-Watch controller. For some of the experiments, at higher concentrations of NaOH and/or higher temperatures, the exotherm upon addition of the propellant raised the initial temperature of the mixture several degrees, but this higher temperature was only maintained for several minutes. Some foaming was also observed when an initial exotherm occurred. After heating and stirring for a set time period, the mixture was filtered and the solids obtained analyzed for remaining NG and NC (as nitrate ester (NE)) by FTIR analysis [6,7] and remaining HMX by ^1H NMR analysis. [8] The data obtained from the FTIR and NMR analyses are presented in Figure 1.

FIGURE 1. Plots of the Rate of Hydrolysis of Ground (10 Mesh) CYH Propellant with Aqueous NaOH



Percent of Nitrate Ester (NE) Remaining With NaOH Hydrolysis of 10 Mesh CYH Propellant at 50°C

Percent of HMX Remaining With NaOH Hydrolysis of 10 Mesh CYH Propellant at 50°C



Percent of Nitrate Ester (NE) Remaining With NaOH Hydrolysisof 10 Mesh CYH Propellant at 80°C

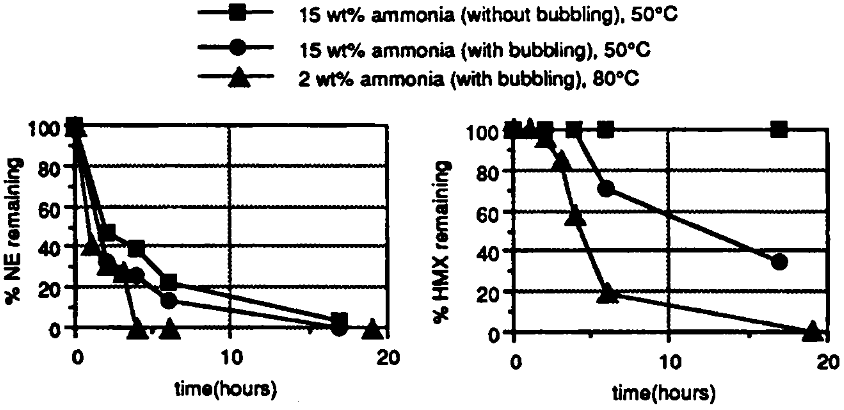
Percent of HMX Remaining With NaOH Hydrolysis of 10 Mesh CYH Propellant at 80°C

All three energetic ingredients of interest (NG, NC, and HMX) were hydrolyzed using NaOH. ^{1}H NMR analysis of the solids obtained at the end of the experiments gave a qualitative indication of the amounts of NG and NC present. These data indicated that the NG was hydrolyzed at a faster rate than the NC. The FTIR analysis gave only quantitative information on the total amount of NE present in the sample. The results indicate that HMX was hydrolyzed more slowly than NG and NC, as expected based on previous hydrolysis work on these materials. The rates of hydrolysis appear to be proportional to the concentration of NaOH for all three ingredients. The rates of hydrolysis at 80°C appear to be much faster than the rates at 50°C, even at lower concentrations of NaOH. At much higher concentrations of NaOH (40 wt%) the 50°C rate is similar to the 80°C rates at 2.5 and 5.0 wt% NaOH.

The next hydrolysis agent tested was aqueous NH_3. The rate experiments were performed in the same manner as for NaOH, with 1.0 grams of ground (10 mesh) CYH propellant in 50 grams of hydrolysis solution. The only difference was that ammonia gas was bubbled through the mixture during hydrolysis for most of the tests. No self-heating of the mixtures was observed in any of the experiments.[9] The results are presented in Figure 2. The rates of hydrolysis with NH_3 were slower than with NaOH. The HMX was hydrolyzed very slowly with overnight periods required for complete hydrolysis. At 50°C, the use of bubbling ammonia lead to minor increases in the rates of hydrolysis compared to use of dissolved ammonia only. At 80°C, the rates for NG and NC hydrolysis were very similar to the rates at 50°C, while the rate of hydrolysis of HMX was noticeably faster. The NH_3 concentration was limited by the solubility of ammonia gas in water at the temperature of the hydrolysis. At 50°C the maximum solubility of NH_3 in water only is 17 wt% while the concentration at 80°C is 3 wt%.[10] No attempt was made to study what effect changing the bubbling rate of ammonia had on the hydrolysis rates. In the experiments with bubbling ammonia approximately the same bubbling rate was used each time.

In summary, the rate studies demonstrate that the NG, NC, and HMX present in ground (10 mesh) CYH propellant can be readily hydrolyzed with aqueous sodium hydroxide at 50-80°C. Aqueous ammonia will perform the same hydrolyses at 50-80°C, but the reactions proceed more slowly, especially for HMX.

FIGURE 2. Plots of the Rate of Hydrolysis of Ground (10 Mesh) CYH Propellant with Aqueous Ammonia



Percent of Nitrate Ester (NE) Remaining With Ammonia Hydrolysis of 10 Mesh CYH Propellant at 50°C and 80°C

Percent of HMX Remaining With Ammonia Hydrolysis of 10 Mesh CYH Propellant at 50°C and 80°C

Ratio of CYH Propellant to Hydrolysis Agent

One important aspect of the hydrolysis of the energetic materials present in CYH is the amount of hydrolysis agent required per amount of propellant. As was demonstrated earlier in the rate studies, aqueous NaOH and aqueous NH_3 can both be used to successfully hydrolyze the NG, NC, and HMX present in CYH propellant. Both hydrolysis agents were examined in the following experiments.

Using the same experimental set up as before, 10 grams of ground (10 mesh) CYH propellant was hydrolyzed by addition (in small portions) to a solution of NaOH in 30 mL of water at 80°C. The amount of NaOH was varied systematically in a series of experiments. After reacting overnight, the mixtures were filtered as before and the solids analyzed for unreacted NG, NC, and HMX. The results are presented in Table 1. No NG or NC was present in any of the solids. Only HMX remained. Interestingly, the amount of HMX left actually started increasing when more than 4.50 grams of NaOH was employed.

A similar result has been reported by Los Alamos National Laboratory (LANL) in the NaOH hydrolysis of HMX-based explosives and has been attributed to a "salting out" effect which greatly diminishes the already low solubility of HMX in water.[11]

The bulk of the solids obtained in these experiments is presumably alumina trihydrate ($Al_2O_3 \cdot 3H_2O$). This compound is formed by the reaction of aluminum powder with water to give aluminum trihydroxide ($Al(OH)_3$), which precipitates from the mixture as $Al_2O_3 \cdot 3H_2O$ when the pH drops due to consumption of the NaOH.[11]

TABLE 1. Hydrolysis of 10 Gram Batches of Ground (10 Mesh) CYH Propellant With Different Amounts of NaOH in 30 mL of Water at 80°C

wt of NaOH (g)	time (hrs)	wt of solids (g)	% HMX left	pH of filtrate
.350	16.0	7.178	41.2	11.0
3.75	16.0	5.811	25.3	12.4
4.00	22.0	5.630	1.6	12.7
4.25	21.0	5.378	2.0	-
4.5	21.0	4.930	0.4	13.2
5.00	20.0	4.300	0.8	13.4
7.00	23.0	1.447	6.7	>13.4
8.00	23.0	0.450	7.5	>13.4

Based on the starting amount of aluminum in the propellant, 5.72 grams of $Al_2O_3 \cdot 3H_2O$ should be formed from the hydrolysis of 10 grams of CYH propellant. The quantities of solids obtained with 3.75 and 4.00 grams of NaOH bracket this value. At higher pH's, substantial amounts of $Al(OH)_3$ would react with the excess NaOH present to form sodium tetrahydroxyaluminate ($NaAl(OH)_4$)[12] and not precipitate from solution as $Al_2O_3 \cdot 3H_2O$. This appears to be occurring since the amount of solids decreases at higher NaOH loadings. This reaction is reversible if the $NaAl(OH)_4$ present is neutralized with an acid. This acid treatment gives $Al_2O_3 \cdot 3H_2O$, water, and the sodium salt of the acid. Another reaction affecting the amount of solids present is the reaction of $Al(OH)_4^-$ with itself to form higher molecular weight compounds, which may not be soluble in water, even at higher pH's. This reaction starts to occur to an appreciable extent at concentrations of $Al(OH)_4^-$ greater than 1.3 M[12] (dissolved aluminum concentration > 3.4 wt%). The maximum dissolved aluminum concentration possible in these experiments was 4.1-4.6 wt% which implies the reaction of $Al(OH)_4^-$ with itself was probably occurring. Therefore, even at higher loadings of NaOH, not all of the solids would be expected to dissolve completely.

From these results it appears, that by reacting 10 parts of CYH with 4 parts of NaOH, all of the NG and NC, and greater than 98% of the HMX present is hydrolyzed. Larger amounts of NaOH (up to 5 parts) will decrease the amount of HMX, but dissolve some of the $Al_2O_3 \cdot 3H_2O$ formed. Even larger quantities of NaOH (7-8 parts) give increasing amounts of HMX but decrease further the amount of solids formed.

Experiments were also performed using aqueous NH_3 with the same experimental set up. Different amounts of ground (10 mesh) CYH propellant were combined with 30 mL of water at 80°C and ammonia bubbled through the stirred mixtures. After stirring overnight the solids collected were analyzed for NG, NC, and HMX. As noted before, no self-heating was observed in these tests with bubbling ammonia. In all but one of the experiments little if any HMX hydrolysis was observed. In the one successful experiment, all of the NG, NC, and HMX in a mixture of 7.5 parts of ground CYH and 30 parts water were hydrolyzed by bubbling ammonia through the mixture at 80°C for 21 hours. The weights of solids obtained were lower than the amounts expected from the complete conversion of aluminum to insoluble $Al_2O_3 \cdot 3H_2O$. The three experiments run for 21 hours all gave essentially the same ratio of solids to original weight of propellant

(0.38-0.40), while the one experiment run for 17 hours gave a smaller ratio (0.33). A maximum ratio of 0.57 is possible, based on the complete conversion of aluminum powder to $Al_2O_3 \cdot 3H_2O$. Presumably, the very low concentration of ammonium hydroxide present is only slowly catalyzing the aluminum/water reaction and the solids obtained are actually aluminum particles coated with aluminum oxide. At much longer reaction times, a higher ratio of solids to propellant is obtained, which approaches the maximum value possible. It is surprising that all of the HMX was hydrolyzed when 7.5 grams of CYH was used while essentially none of the HMX was hydrolyzed in two different attempts with 10 grams of CYH.

Three factors may be the cause of differences in the rate of HMX hydrolysis with bubbling ammonia at the same temperatures. First, the rate of bubbling of ammonia, although nominally the same in each experiment, may have differed enough to give different rates of HMX hydrolysis. Second, the higher loadings of propellant gave greater concentrations of salts in the hydrolyzed mixture and decreased the amount of HMX dissolved in the solution and available for hydrolysis (the same effect is postulated to occur with NaOH). Third, the higher concentrations of salts decreased the solubility of ammonia gas in the mixture, leading to slower rates of hydrolysis.

Chemical Analysis of Hydrolyzed Propellant Samples

The solids and liquid fractions obtained during the preparation of the one gallon sample of CYH propellant hydrolyzed with NaOH were analyzed in some detail. The results from these analyses are present in Table 2. The ^{13}C NMR analyses[13] were done for the five identifiable compounds present. The amount of perchlorate (ClO_4^-) present (4,773 ppm) was close to the expected value of 4,573 ppm. HPLC analysis gave only trace amounts of HMX in the liquid fraction and trace amounts of NG in the solid fraction. No NC was detected by GPC in either the liquid or solid fractions. The amount of aluminum in the solids (35.4 wt%) was close to the expected value of 34.6 wt%. The amount of aluminum in the liquid portion was very low as expected. The presence of carbon and nitrogen in the solids indicate that a small amount of partially hydrolyzed NC may be present.

In Table 2 the amount of solids in the liquid portion of the hydrolyzed CYH sample was determined to be 4.56 wt%. Adding up the weights of all the solids identified in the analyses predicts a solid content of 2.78 wt%. This discrepancy implies that unidentified compounds present in the sample make up a significant portion of the hydrolyzed propellant. This supposition if further corroborated by comparing the amount of sodium added at the start of the hydrolysis (as NaOH) to the amount at the end of the process (determined from all identified sodium salts). The amount of sodium added would predict a concentration of 12,100 ppm while the salts identified in the mixture give a sodium concentration of 7,100 ppm.

Because of the exhaustive analysis of this sample, it is possible to attempt the determination of what fraction of the original propellant may have been lost to gaseous products. The elemental composition of CYH propellant is given in Table 3 along with the amounts of the elements present in 200 grams of CYH and the amount of these elements found during the analysis of the UT sample. These values indicate that a significant portion of the carbon and nitrogen was lost due to the formation of gaseous decomposition products. However, it is also possible that the unidentified compounds present may make up a significant portion of this missing balance.

TABLE 2. Chemical Analysis of Hydrolyzed Propellant Sample Prepared With 200 Grams of CYH Propellant, 80 Grams of NaOH, and 600 mL of Water (Sample Diluted to One Gallon)

constituent	analytical method	liquid portion	solid portion
glycerol acetate formate bicarbonate oxalate	13C NMR	2,600 ppm 1,500 ppm 2,000 ppm 1,000 ppm 680 ppm	N/A N/A N/A N/A N/A
nitrite nitrate	ion chromatography	4,766 ppm 3,418 ppm	N/A N/A
perchlorate	ion-selective electrode	4,773 ppm	N/A
NG HMX	HPLC	< 0.02 ppm 3.2 ppm	121 ppm <0.02 ppm
NC	GPC	<0.015%	<0.011%
aluminum	ICP	127 ppm	49.4%
C H N	elemental analysis	N/A N/A N/A	2.97% 2.55 % 0.39%
wt% solids	(evaporated 50 mL)	4.56%	N/A
pH	pH meter	10.0	N/A
density	weight 100 mL	1.02	N/A

TABLE 3.The Amount of Selected Elements in 200 Grams of CYH and the Percent Remaining in the One Gallon UT Sample

element	grams in 200 grams CYH	grams remaining	% remaining
carbon	32.4	13.3	41%
nitrogen	27.4	9.04	33%
aluminum	39.6	37.2	94%
chlorine	6.6	6.93	105%

* Weight percent is based on the concentration of the compounds identified in the liquid and solid fractions of the sample compared to the original weight in the propellant before hydrolysis.

amount of aluminum in the liquid fraction was very low as expected. The elemental analysis of the solid fraction indicated that partially hydrolyzed NC may be present, as before. In Table 5 the amount of solids in the liquid portion of the hydrolyzed CYH sample was determined to be 2.50 wt%. Adding up the weights of all the solids identified in the analyses predicts a solid content of 2.08 wt%. This discrepancy implies that unidentified compounds present in the sample make up a portion of the hydrolyzed propellant.

TABLE 5. Chemical Analysis of the Hydrolyzed Propellant Sample Prepared With 200 Grams of CYH Propellant, Bubbling NH_3, and 800 mL of Water (the Sample was Diluted to One Gallon)

constituent	analytical method	liquid portion	solid portion
glycerol acetate formate bicarbonate oxalate	13C NMR	1,600 ppm 270 ppm 1,600 ppm not detected 1,740 ppm	N/A N/A N/A N/A N/A
nitrite nitrate	ion chromatography	1,400 ppm 4,722 ppm	N/A N/A
perchlorate	ion-selective electrode	4,476 ppm	N/A
NG HMX	HPLC	4.7 ppm 9.2 ppm	242 ppm <0.02 ppm
NC	GPC	<0.059%	<0.012%
aluminum	ICP	11.3 ppm	44.4%
C H N	elemental analysis	N/A N/A N/A	6.20% 2.32 % 1.93%
ammonium	(calculated from the amount of ammonium salts)	4,170 ppm	N/A
ammonia	(calculated from known solubility of ammonia in water)	1.3%	N/A
wt% solids	(evaporated 50 mL)	4.56%	N/A
pH	pH meter	10.0	N/A
density	weight 100 mL	1.02	N/A

An experiment at LANL was performed on the hydrolysis of 0.52 grams of CYH propellant with 20 mL of 2M NaOH (containing 1.6 grams of NaOH) at 93°C (refluxing solution) for 0.5 hours.[1f] Analysis of the hydrolyzed solution by IC gave the concentrations of acetate, formate, nitrite, and nitrate. These values along with the percentages of the elements remaining is given in Table 4. The overall fraction of carbon recovered is 44 % and for nitrogen it is 45 %. The carbon number is in agreement with the value in Table 20, while the nitrogen value is much higher. The different conditions of this hydrolysis experiment compared to the conditions of the one gallon sample preparation may have lead to the differences observed.

TABLE 4. Ion Chromatography of Hydrolyzed CYH and Weight Percents of Elements Remaining in Hydrolyzed Propellant

anion	concentration	% carbon of original	% nitrogen of original
acetate	3400 ppm	34%	-
formate	1500 ppm	10%	-
nitrite	3690 ppm	-	32%
nitrate	2100 ppm	-	13%

The solid and liquid fractions obtained during the preparation of the one gallon sample of CYH propellant hydrolyzed with aqueous NH_3 were also analyzed in some detail. The results from these analyses are presented in Table 5. The method of analysis for each test was described earlier for the NaOH hydrolyzed sample.

In the ^{13}C NMR analysis, the amounts of glycerol and carboxylate salts were lower than observed for the NaOH hydrolyzed sample discussed earlier. The perchlorate concentration (4,476 ppm) was close to the expected value of 4,573 ppm. HPLC analysis gave very trace amounts of NG and HMX in the liquid fraction and a trace amount of NG in the solid fraction. No NC was detected by GPC in either fraction. The amount of aluminum in the solids (33.6 wt%) was close to the expected value of 31.9 wt%. The

As before, because of the exhaustive analysis of this sample, it is possible to attempt the determination of what fraction of the original propellant may have been lost to gaseous products. The elemental composition of CYH propellant is given in Table 6 along with the amounts of the elements present in 200 grams of CYH and the amount of these elements found during the analysis of the UT sample. These values, at first glance, indicate that a significant portion of the carbon was lost due to the formation of gaseous decomposition products. The truth is clouded by the fact that many unidentified carbon-containing compounds were present in the ^{13}C NMR spectrum. For the nitrogen, the presence of some of the ammonium ions present in solution may have come from the nitrogen originally present in the CYH propellant, thus lowering the apparent amount of nitrogen recovered. An additional point is that the NH_4NO_2 present would be unstable to prolonged heating in water[14] and would decompose to gaseous products, thus lowering the amount of nitrogen still present.

TABLE 6. The Amount of Selected Elements in 200 Grams of CYH and the Percent Remaining in the One Gallon UT Sample

element	grams in 200 grams CYH	grams remaining	% remaining
carbon	32.4	11.2	35%
nitrogen	27.4	10.63	39%
aluminum	39.6	41.7	105%
chlorine	6.6	6.1	92%

* Percentage is based on the concentration of the compounds identified in the liquid and solid fractions of the sample compared to the original weight in the propellant before hydrolysis.
** Only nitrite, nitrate, and ammonium (from the AP) were counted as soluble nitrogen compounds (see text).

Small Reactor Studies

Further hydrolysis studies of CYH propellant were performed using a small hydrolysis reactor. The reactor was a 4 liter glass kettle (140 mm X 337 mm), containing stainless steel heating/cooling coils. It was equipped with a condenser on the vent tube to condense water vapor, a NaOH injection system, an ammonia recycle system, and an internal sparge ring for agitation. The system also included a deluge system (with containment around reactor) to stop an uncontrolled exotherm. The sparger used nitrogen for NaOH hydrolysis and ammonia gas for NH_3 hydrolysis. The top of the reactor was stainless steel with ports for heating/cooling coils, thermocouple, pH meter, NaOH solution addition, solids sampling, vent line, emergency deluge, and sparger. The experiments were run remotely with computer control and monitoring.[15]

The first set of experiments was done with 30 micron aluminum powder and water at 175°F (79.4°C), using NaOH as the catalyst to adjust the pH to 12. This testing was performed to demonstrate control of the large exotherms observed in the hydrolysis of CYH propellant with aqueous NaOH. These exotherms are predominantly associated with the reaction of the 30 micron aluminum powder in CYH propellant with water.

The reaction of 100 grams of aluminum powder and 2000 mL of water (catalyzed by NaOH) was completed in several hours at 175°F with minimal exotherms observed. The reaction was scaled up in runs of 200, 300, and 400 grams of aluminum powder in 2000 mL of water, with progressively larger exotherms observed (the reaction of 400 grams of aluminum powder corresponded to the hydrolysis of 2000 grams of CYH). All of the exotherms observed in this series of reactions were easy to control using the cooling coils of the reactor. Additionally, both the sparging with nitrogen and the condenser on the vent line absorbed large quantities of heat.

The weights of the solids obtained at the end of each aluminum run correlated very well to the weight of $Al_2O_3 \cdot 3H_2O$ expected from the reaction of the aluminum with water. The loss of water (due to reaction with the aluminum) was also observed and an extra 1500 mL of water were added to the 400 gram run which had become a thick slurry during the reaction.

The hydrolysis of CYH propellant using aqueous NaOH was performed next. These experiments and the results obtained are summarized in Table 7. In experiments # 1, #2, #3, #5, and #6 ground (10 mesh) CYH propellant was used. Experiment #4 employed four 1.125 inch diameter blocks. Experiments #7, #8, and #9 were done with propellant chips. In experiment #3 a loose seal let most of the water evaporate during the night. The remaining liquid was diluted with approximately 500 mL of water. In experiment #4, the computer crashed and the emergency deluge went on briefly, adding extra water to the mixture. The volume was reduced some by letting water evaporate overnight. At the end of experiment #9, the mixture was a sludge with no liquid present. Water (1,650 mL) was added for work up. In experiments #1, #2, #5, and #6 the total weight recovered was increased by the rinse water used to transfer the mixture out of the reactor. In experiments #7 and #8 the total weight recovered was reduced by not rinsing the reactor.

The results obtained indicated that the hydrolysis of 10 parts of CYH propellant with 8 parts of NaOH at 175°F in water resulted in complete hydrolysis of the NG and NC in 24 hours or less. The hydrolysis of the HMX was almost complete in the same time frame. At very high loadings of propellant in water, the amount of HMX remaining started to increase. Additionally, small amounts of unreacted propellant were also present. The optimum conditions for hydrolysis were at a loading of 1 part propellant and 2 parts water (experiment #6).

The increase in the boiling point of water by the presence of dissolved salts was a concern for the hydrolyzed propellant. This is because the boiling off of the water during an uncontrolled exotherm was considered a safety measure to keep the temperature below the decomposition temperature of the propellant. A sample from run #6 was boiled in a beaker on a hot plate with a measured solution temperature of 106°C (223°F). Distilled water by the same test gave a solution temperature of 95°C (203°F).

TABLE 7. Hydrolysis of CYH Propellant With Aqueous NaOH in the Small Reactor

experiment	#1	#2	#3	#4	#5	#6	#7	#8	#9
CYH added (g)	50	100	100	165	200	500	700	900	900
water added (mL)	2000	2000	1000	1000	1000	1000	1000	1000	900
NaOH added (g)	40	80	80	400	160	400	560	720	720
water (NaOH) (mL)	60	120	120	600	240	600	840	1080	1080
total initial wt (g)	2150	2300	1300	2165	1600	2500	3100	3700	3600
rxn time -175°F (h)	24	6	24	24	4	16	17	7.5	14.5
end volume (mL)	2170	2450	780	2910	1520	2070	1870	1840	2860
density (g/mL)	1.10	1.04	1.14	1.17	1.16	1.30	1.45	1.54	1.37
wt of liquid (g)	2387	2548	889	3408	1763	2691	2712	2834	3918
NVR of liquid (g)	573	243	250	1108	546	1476	2027	1924	1753
solids (g)	0.04	2.8	0.72	3.19	4.28	15.2	30.7	105	87.7
total wt (g)	2387	2551	890	3408	1767	2706	2742	2939	4006
HMX in solids (g)	ND	0.31	0.01	2.33	2.7	1.2	10.7	49.6	11.4
unreacted CYH	NO	NO	NO	NO	NO	NO	YES	YES	YES

The last NaOH hydrolysis was performed with a 645 gram block of propellant that was mostly CYH propellant with a layer of DDP propellant on one end of the block. The block was irregularly shaped with rough dimensions of 5.375 inches by 2.5 inches by 1.75 inches. The block was combined with 1,200 mL of water and 25 mL of Trans-10, an anti-foam agent. The hydrolysis was performed by the addition of 950 mL of 40% NaOH. The total reaction time was 36.75 hours at 175°F. The DDP portion of the block was the last part to be hydrolyzed. The hydrolyzed mixture was filtered to give 3,320 mL of liquid with a density of 1.26. A total of 11.43 grams of solids were obtained which contained 0.53 grams of HMX. The solids also contained some unidentified organic compounds by proton NMR.

The last set of experiments involved the hydrolysis of CYH propellant with aqueous ammonia. This was achieved by bubbling ammonia through a mixture of the propellant in water at the desired operating temperature of 175°F. The CYH propellant employed was ribbon material which had been shaved from a large block. Two operating procedures were employed with equal success in terms of the rate of hydrolysis. The first method involved continuous sparging of the mixture with ammonia. The second method utilized an air compressor which would recirculate the ammonia through the mixture. Once the pH of the mixture had dropped significantly, indicating consumption of ammonia, a short sparging period was used to replenish the ammonia and the recirculation process continued. The results from these experiments are presented in Table 8. In the first experiment the mixture was inadvertently saturated with ammonia at a lower temperature during a cool down period of the hydrolysis. Upon warming to 175°F a large volume of ammonia gas was released from the mixture, causing a major portion of the mixture to siphon out of the reactor. This incident points out a significant concern during hydrolysis with ammonia gas. The high solubility of ammonia in water, relative to other gases causes this problem.

In the second experiment, due to the bulky nature of the ribbons of propellant, the mixture was a tight mass of propellant covered with water. This appeared to slow the rate of hydrolysis. After 18 hours a significant amount of propellant was left. The hydrolysis was stopped once no propellant ribbon was visible in the mixture. Analysis of the mixture indicated that essentially all of the HMX remained. No NG or NC was observed in the solid portion of the mixture. In the third experiment, the pH probe was removed to increase the void volume of the reactor. A sparger with a higher flow rate was also employed. This allowed for movement of the ribbons during the reaction. The hydrolysis was run with a constant purge of ammonia. A sample removed after 18.5 hours indicated that all of the NG and NC had been hydrolyzed. After 37 hours the hydrolysis was stopped and the mixture analyzed. As with the first experiment, all of the HMX remained.

TABLE 8. Hydrolysis of Propellant With Aqueous Ammonia in the Small Reactor

experiment	#1	#2	#3*
CYH added (g)	536	536	536
water added (mL)	1970	1800	1600
Trans-10 antifoamer added (mL)	0	1	10
total initial wt (g)	2506	2337	2146
rxn time -175°F (h)	NA	44.5	37
end volume (mL)	NA	2042	1135
density (g/mL)	NA	1.01	1.07
wt of liquid (g)	NA	2062	1214
solids (g)	NA	193.5	249.5
total wt (g)	NA	2255.5	1463.5
HMX in solids (g)	NA	[58.1]	[59.9]
unreacted CYH	YES	NO	NO

* Water was lost from the mixture due to a poor seal. The collected filtrate was diluted with water to give 1,135 mL of liquid.

The next idea tested was that of isolating the solids from the aqueous ammonia hydrolysis of CYH propellant, which contain HMX, and then resubmitting the isolated solids to ammonia hydrolysis in fresh water. This approach had worked previously in the preparation of the one gallon sample of hydrolyzed CYH propellant. The remaining solids (after removing samples for testing) obtained from test #3 of Table 8 were washed and dried to give 210 grams of a fine brown powder which contained 25 wt% HMX by NMR analysis. Thirty grams of this material in 240 mL of water was treated with bubbling ammonia at 90°C. Samples of the mixture were withdrawn periodically and analyzed for HMX. After 20 hours, no HMX remained. The experiment was repeated two more times with the same results obtained. The reaction was scaled up to 120 grams of solids in 960 mL of water in the small reactor. After 20 hours no HMX remained. These results demonstrate that this two step method of hydrolyzing CYH propellant with aqueous ammonia is very repeatable.

Further experiments were performed to examine to what extent the solids and liquids present in the hydrolyzed propellant needed to be separated in order to hydrolyze the HMX. A batch of hydrolyzed CYH propellant was prepared by bubbling ammonia through 400 grams of ribbon propellant and 2,000 mL of water at 90°C in the small reactor. An unwashed solids sample was obtained by allowing the mixture to stand for several hours and then decanting off most of the liquid. The remaining residue was divided into two parts. The decanted liquid contained 70 grams of wet solids and 1720 mL of liquid. The remaining residue contained 200 grams of wet solids and 180 mL of liquid. The solids in the decanted liquids and the solids in the remaining residue had approximately the same weight percentage of HMX. Half of the remaining residue was used as a sample of unwashed solids. This sample consisted of 100 grams of wet solids and 90 mL of liquid. Fresh water (1,500 mL) was added to the sample for the second hydrolysis step. The hydrolysis of the HMX present was completed in 19 hours at 90°C. The other half of the solids from remaining residue was washed with 1,000 mL of water to give 70 grams of washed, wet solids. These solids were submitted to ammonia hydrolysis at 90°C for 28 hours with almost complete hydrolysis of the HMX. The solids present, upon analysis, gave 1 wt% HMX present. Trans-10 was added as an anti-foam agent before starting the experiment.

These results indicated that the all of solids present in the hydrolyzed propellant would not settle upon standing. However, if the majority of the solids were isolated by decanting off most of the liquid (with some solids present), then the remaining material could be used with fresh water to give successful HMX hydrolysis. The last experiment with washed solids, which gave almost complete HMX hydrolysis, indicated that the antifoaming agent Trans-10 may actually inhibit the HMX hydrolysis to some extent.

Another experiment was conducted to further understand what the limits of successful HMX hydrolysis are when using dilution of the original mixture. For this experiment, 600 grams of combined flakes and 1/4 inch blocks of CYH propellant were hydrolyzed in 1,200 mL of water at 90°C for 15 hours with bubbling ammonia in the small reactor. Analysis of the solids by NMR indicated 27 wt% HMX with no NG or NC present. The percentage of HMX indicated that it had not been hydrolyzed to any significant extent. The mixture was diluted with 1,200 mL of water and resubmitted to hydrolysis to see if the 1:1 dilution with water was sufficient to allow HMX hydrolysis to proceed. Samples were withdrawn periodically and analyzed for HMX. The results are presented in Table 9. They show that the HMX hydrolysis was completed in less than 38 hours.

TABLE 9. Hydrolysis of HMX (With Ammonia) in Concentrated Hydrolyzed CYH That Was Diluted 1:1 With Water

time (hours)	wt% HMX in solids
0	27%
15	5.4%
19	2.4%
23	1.5%
38	0%

In summary, isolated solids from the hydrolysis of CYH propellant with aqueous ammonia often contain unreacted HMX, due to the variable nature of HMX hydrolysis using ammonia. However, treatment of the isolated solids with ammonia in fresh water does give reproducible HMX hydrolysis in 20 hours at 90°C. Finally, the hydrolysis of the NG and NC present in CYH propellant can be performed with ammonia to give a concentrated mixture which still contains HMX. Dilution of this mixture, followed by additional ammonia sparging at 90°C, leads to complete HMX hydrolysis.

CONCLUSIONS

The aqueous hydrolysis of NG, NC, and HMX in CYH propellant can be accomplished using sodium hydroxide (NaOH) as the hydrolysis agent. NG is hydrolyzed first followed by NC, and finally HMX. The rate of hydrolysis is proportional to the concentration of NaOH. At 80°C (176°F) the hydrolysis of ground (10 mesh) CYH propellant can be completed in 2-4 hours by using 2.5-5.0 wt% NaOH. The hydrolysis of 1.125 inch cubes of CYH propellant can be completed in 24 hours at 80°C (176°F) using 20 wt% NaOH. The combination of 4 parts of NaOH, 10 parts of size reduced CYH propellant, and 30 parts of water at 80°C (176°F) for 22 hours gives complete hydrolysis of the NC and NG, and greater than 98% hydrolysis of the HMX. This procedure gives 5.6 parts of fine solids, which are mostly hydrated alumina. The use of larger amounts of NaOH gives less solids, but more unreacted HMX. The identified hydrolysis products in the liquid fraction (resulting from the combination of 4 parts of NaOH and 10 parts of CYH propellant in water at 80°C) are glycerol, sodium acetate, sodium formate, sodium bicarbonate, sodium oxalate, sodium nitrite, sodium nitrate, and sodium perchlorate. The solid fraction appears to be mostly hydrated alumina with a small amount of water-insoluble organic compounds also present.

The aqueous hydrolysis of the NG, NC, and HMX in CYH propellant can also be accomplished using ammonia (NH_3) as the hydrolysis agent. The same order of hydrolysis of NG, NC, and HMX is observed as above. The rate of hydrolysis can be increased if ammonia is bubbled through the mixture. At 80°C (176°F) the hydrolysis of the NG and NC in ground (10 mesh) CYH propellant can be completed in 4 hours by bubbling ammonia through a 3 wt% aqueous ammonia solution. Complete hydrolysis of the HMX requires an additional 13 hours. The hydrolysis of 1/2 inch cubes of CYH propellant can be completed in 24 hours at 80°C (176°F) by bubbling ammonia through a 3 wt% aqueous ammonia solution.The hydrolysis of the HMX in CYH propellant with aqueous ammonia is very slow, unless ammonia is bubbled through the solution. The rate of hydrolysis is slower and irreproducible at greater initial weight fractions of propellant. The hydrolysis of HMX in CYH propellant with ammonia can be accelerated if the hydrolyzed propellant mixture is diluted, after the NG and NC have been hydrolyzed. In theory, the hydrolysis of CYH propellant with aqueous ammonia should require 1.4-2.1 parts of ammonia to 10 parts of CYH. The identified hydrolysis products in the liquid fraction (resulting from the hydrolysis of CYH propellant with bubbling ammonia in water at 80°C) are glycerol, ammonium acetate, ammonium formate, ammonium oxalate, ammonium nitrite, ammonium nitrate, and ammonium perchlorate. The solid fraction appears to be mostly hydrated alumina with a small amount of water-insoluble organic compounds also present.

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Croce; Y. Okamoto, J. Org. Chem., *44*, 2100 (1979).

2. Chemical Propulsion Information Agency (CPIA) Manual, M2. Unit No. 1045, October, 1964.

3. Aqueous solution of ammonia are commonly referred to as "ammonium hydroxide", although the predominant compounds present in these solutions are ammonia (NH_3) and water and not ammonium hydroxide (NH_4OH). This is due to the fact that the NH_3/water reaction only proceeds to a very small extent. For a 15 wt% solution of NH_3 in water at room temperature, 14.94 wt% is NH_3 and 0.06 wt% is NH_4OH. For a 30 wt% solution of ammonia the values are 29.88 wt% and 0.12 wt%, respectively. Both calculations are from pH measurements of the respective solutions. This implies that only 0.4% of the ammonia present is in the form of NH_4OH.

4. W. P. Creedon; M. H. Spritzer, "Cryogenic Size Reduction of Solid Propellant," General Atomics, San Diego, CA, CEL-TR-92-30, 1992.

5. Grinding was performed under the supervision of Dr. Mike Lesley of the Analytical Department, using a Wiley mill with small pieces of propellant at ambient temperature.

6. Samples of the solids were triturated in THF and the resulting THF solutions analyzed by FTIR. The absorbance at 1650 cm^{-1} was used to determine the wt% of nitrate ester present by comparison to standard solutions of nitrate ester, which were prepared by trituration of known weights of CYH propellant. A similar procedure is described in reference 7.

7. (a) H. M. Rosenberger; C. J. Shoemaker, Anal. Chem. *31*, 1315 (1959) (b) H. Levitsky; G. Norwitz, Anal. Chem. *34*, 1167 (1962).

8. The analysis of the wt% HMX in a solid sample by ^{1}H NMR was performed as follows. A weighed sample of the solid (ca. 0.020 g) was combined with a weighed amount of 1,1,2,2-tetrachloroethane (TCE) in 1.0 mL of d_6-acetone, and the mixture allowed to stand for at least two hours. The mixture was then filtered and the filtrate analyzed by ^{1}H NMR. Comparison of the integration of the TCE and HMX peaks gave the wt% HMX present in the original sample. Duplicate analysis of the same sample and extraction for longer periods of time gave essentially the same values.

9. The heat of solvation of ammonia in water is exothermic and produces .29 kcal of heat per mole of ammonia (see reference 14, p. D-102). This self-heating was not observed in the experiments performed.

10. The solubility of ammonia in water was calculated, based on tables of temperature versus the vapor pressure of mixtures of ammonia and water. The values for 50°C and 80°C were extrapolated from known values at 120°F (48.9°C) and 180°F (82.2°C), assuming a vapor pressure of 12.6 psi (the average barometric pressure at the Wasatch Division of Thiokol at Promontory, Utah).

11. F. A. Cotton; G. Wilkinson, "Basic Inorganic Chemistry," John Wiley & Sons, New York, 1976, p. 248.

12. See reference 11, p. 251.

13. The ^{13}C NMR analyses were performed with an internal standard of dimethylformamide (DMF) and a much longer pulse delay than normal. This should give a reasonable quantitative analysis for the compounds present, although no work was performed to establish the accuracy of the measurements.

14. "Handbook of Chemistry and Physics, 56th Edition," R. C. Weast, eds., CRC Press, Cleveland, OH, 1975.

15. The software employed was CRISP, supplied by Square D, Inc.