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BASE HYDROLYSIS AND SUPERCRITICAL WATER OXIDATION OF
PBX-9404

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ABSTRACT

Base hydrolysis in combination with hydrothermal processing has been proposed as an environmentally acceptable alternative to open burning/open detonation for degradation and destruction of high explosives. In this report, we examine gaseous and aqueous products of base hydrolysis of the HMX-based plastic bonded explosive, PBX-9404. We also examine products from the subsequent hydrothermal treatment of the base hydrolysate. The gases produced from hydrolysis of PBX-9404 are ammonia, nitrous oxide, and nitrogen. Major aqueous products are sodium formate, acetate, nitrate, and nitrite, but not all carbon products have been identified. Hydrothermal processing of base hydrolysate destroyed up to 98% of the organic carbon in solution, and higher destruction efficiencies are possible. Major gas products detected from hydrothermal processing were nitrogen and nitrous oxide.

INTRODUCTION

In dismantling weapons from stockpile reduction, suitable degradation of the associated high explosive (HE) waste to environmentally acceptable forms is a critical objective within the DOE complex. Currently, open burning is the method of choice for HE disposal and separation of HE and uranium components. Revocation of burning licenses could hinder HE disposal and impact the dismantlement process. Thus, alternate methods are needed as back-ups and, eventually, as replacement techniques.

Base hydrolysis is one proposed alternative method that involves chemical reaction of the HE with sodium hydroxide solution at temperatures of approximately 85 to 90°C. The resulting product mixture is no longer energetic and mostly water-soluble. Explosives such as nitrate esters, nitroaromatics, and nitramines are decomposed under basic conditions (1-5). Nitramine explosives RDX and HMX decompose to form nitrates, nitrites, ammonia, nitrogen, organic acids, formaldehyde, and hexamethylenetetramine. In addition to this, RDX is more readily hydrolyzed than HMX (3,6).

The products from the base hydrolysis of PBX-9404¹ have not yet been fully characterized. In order to properly dispose of the hydrolysis product mixture, it is desirable to obtain a mass balance for the reaction. The primary focus of this work is to identify and quantify the products from the base hydrolysis of PBX-9404.

Secondary processing of base hydrolysis products is needed because some constituents of the process are considered hazardous. Hydrothermal treatment has been proposed as a secondary process of base hydrolysate. In hydrothermal treatment, the hydrolysate is heated to elevated temperatures and pressures (> 200°C, 100 bar) in the presence of an oxidant. Above water's critical parameters (374°C, 221 bar), hydrothermal treatment is known more formally as supercritical water oxidation. The transport properties of supercritical water resemble those of gases, allowing chemical

¹ The formulation for PBX-9404 is 94% HMX, 3% nitrocellulose, 3% chloroethylphosphate, and 0.1% diphenylamine.

reactions to occur without diffusion limitations. Solution densities are also reasonably high in SCWO/hydrothermal systems (0.1 to 0.9 g/cm³), allowing reasonably high waste throughputs (7). Because required organic oxidation temperatures are below 600°C, NO_x gases are not generated (8). In addition, hydrothermal processing/SCWO reactors are totally enclosed treatment facilities, in which gaseous and liquid effluents can be analyzed and retained, if necessary, before their release to the environment. In this work, we will discuss destruction of PBX-9404 hydrolysate in a hydrothermal process reactor. The general term hydrothermal treatment is applied to the 9404 hydrolysate, because the critical parameters of the solution are unknown; that is, even though treatment parameters are above the critical parameters for water, they may or may not be above the critical parameters for the hydrolysate.

EXPERIMENTAL METHODS

Base Hydrolysis Reaction Conditions

The amounts of materials typically used were 10 milliliters of 1.5 normal sodium hydroxide solution per gram of explosive. Base solutions were prepared with reagent grade sodium hydroxide and in-house deionized water. Hydrolysis reactions were normally performed in a round-bottom flask fitted with a condenser. A temperature controller was used to obtain a constant 85 to 90 °C temperature. The temperature was held below the solution boiling point to minimize foaming and to keep the explosive from splashing onto the sides of the reaction vessel. For the on-line mass spectral analysis of gaseous products, the gases were swept with helium into the inlet of the instrument.

Base Hydrolysis Product Analysis

Products from the hydrolysis reactions were analyzed by a number of different methods. Nuclear magnetic resonance (nmr) spectrometry was used to identify the major hydrolysis products. A JEOL GSX-270 multi-nuclear spectrometer was used to obtain proton and carbon nmr spectra. Analyses were performed on the hydrolysis solution with a small amount of deuterated water added to provide a lock signal. Mass spectrometry was used to analyze gaseous hydrolysis products (Extrel residual gas analyzer) and for solid residue analysis (Finnigan-Mat model 8200). Some gas analysis was also performed by Fourier transform infrared spectrometry using a Bio-Rad FTS 40 instrument. Ammonia was analyzed by trapping in dilute hydrochloric acid solution and using a gas sensing electrode for quantitation. Quantitative analysis for inorganic and organic anions was performed with a Dionex ion chromatograph using a conductivity detector. Solid residues from dried hydrolysis solutions were tested for thermal stability by differential thermal analysis (DTA) using a Dupont model 910 thermal analyzer.

Hydrothermal Reaction Conditions

Reactions were carried out from 960 to 1100 bar at 380 to 450°C in a 0.478 cm ID Inconel 625 reactor. A complete description of this reactor and experimental procedures has been provided elsewhere (9,10). The average residence time of reaction was approximately 1 min. Nitric acid and hydrogen peroxide were used as oxidizers for the base hydrolysis effluent. Nitric acid was added to hydrolysate originally treated with 1M NaOH in a molar ratio of 1 mole nitric acid per mole of organic carbon residing in the sample. Hydrogen peroxide was added to hydrolysate originally treated with 1.5M NaOH in a molar ratio of 1 mole hydrogen peroxide per mole of organic carbon.

Hydrothermal Product Analysis

Products from the hydrothermal reactions were analyzed by ion chromatography, gas chromatography, and total organic carbon. Quantitative analyses for inorganic and organic anions, and ammonium were performed with a Dionex ion chromatograph using a gradient eluent, an AS9 column, and a conductivity detector. Gas products were measured using a HP 5890 series II gas chromatograph, using a CarbPLOT column, helium carrier gas, and a thermal conductivity detector. Total organic and inorganic carbon were measured using a Rosemount-Dohrmann DC-190 TOC analyzer.

RESULTS AND DISCUSSION

Qualitative Analysis of Gaseous PBX-9404 Hydrolysis Products by FTIR

Fourier transform infrared (FTIR) spectroscopy was used to identify the gaseous products from the hydrolysis of PBX-9404. Prior to and during the hydrolysis reaction, the mixture was purged with argon to replace air in the vessel. When gas evolution was visible from the mixture, a sample was taken using a gas tight syringe. The gas was injected into an evacuated infrared gas cell for analysis. The infrared spectrum, Figure 1, below, shows nitrous oxide and ammonia as the major infrared-detectable products. Nitrogen is also known to be a product and was analyzed by mass spectrometry (see discussion below).

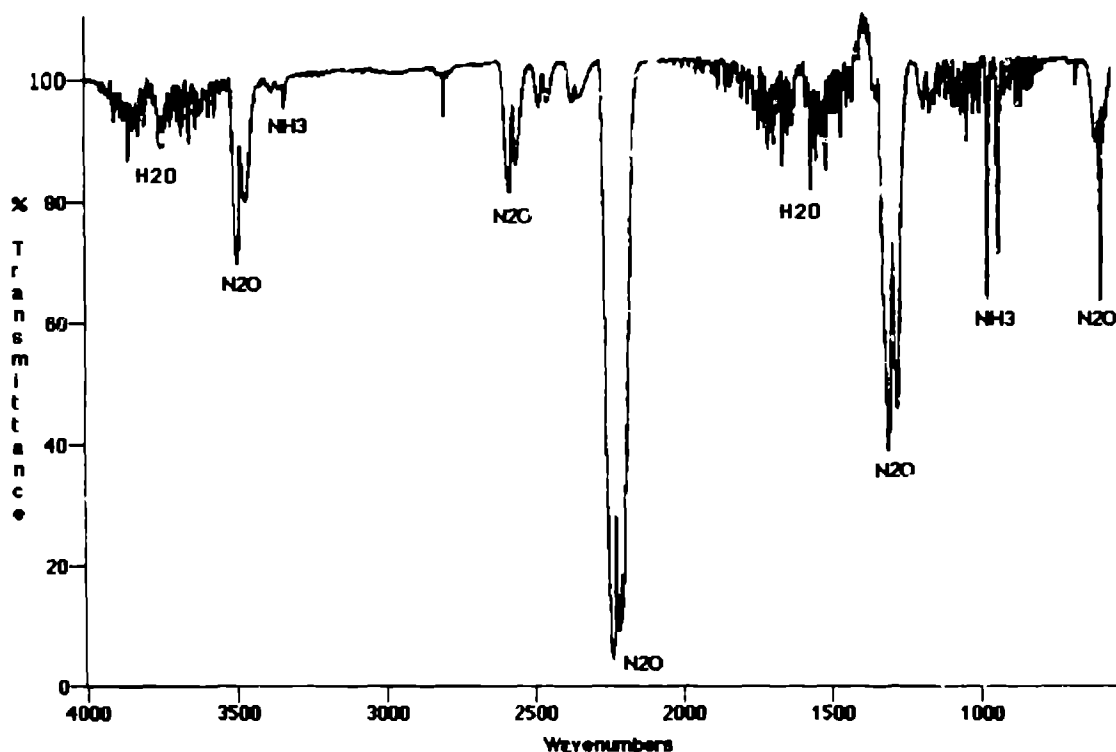


Figure 1. FTIR Spectrum of Gaseous PBX-9404 Hydrolysis Products.

Biotreatment in addition to hydrothermal processing has been proposed as a secondary method for treatment of base hydrolysis effluent. Because the biotreatment of hydrolysate requires neutralization, the gases evolved upon addition of acid to PBX-9404 hydrolysate were also analyzed. Sulfuric acid was added to the hydrolysate and the mixture was put in an ultrasonic bath to drive off the gases produced. The gases were

sampled as described above and found to contain the following: carbon dioxide, formic acid, nitric oxide, and hydrogen cyanide. Although this gas mixture is highly toxic, the neutralization conditions used were a worst case. Concentrated acid was added quickly allowing the mixture to become warm and acidic in pH. Solutions of nitrite, a major hydrolysis product, are expected to produce nitric oxide under these conditions. When neutralization is done by slow addition of dilute acid, very little gas is produced.

Gases produced from pyrolysis of dried PBX-9404 hydrolysate (described below) were also analyzed. The pyrolysis was found to produce nitrous oxide, carbon dioxide, ammonia and carbon monoxide as shown in Fig. 2.

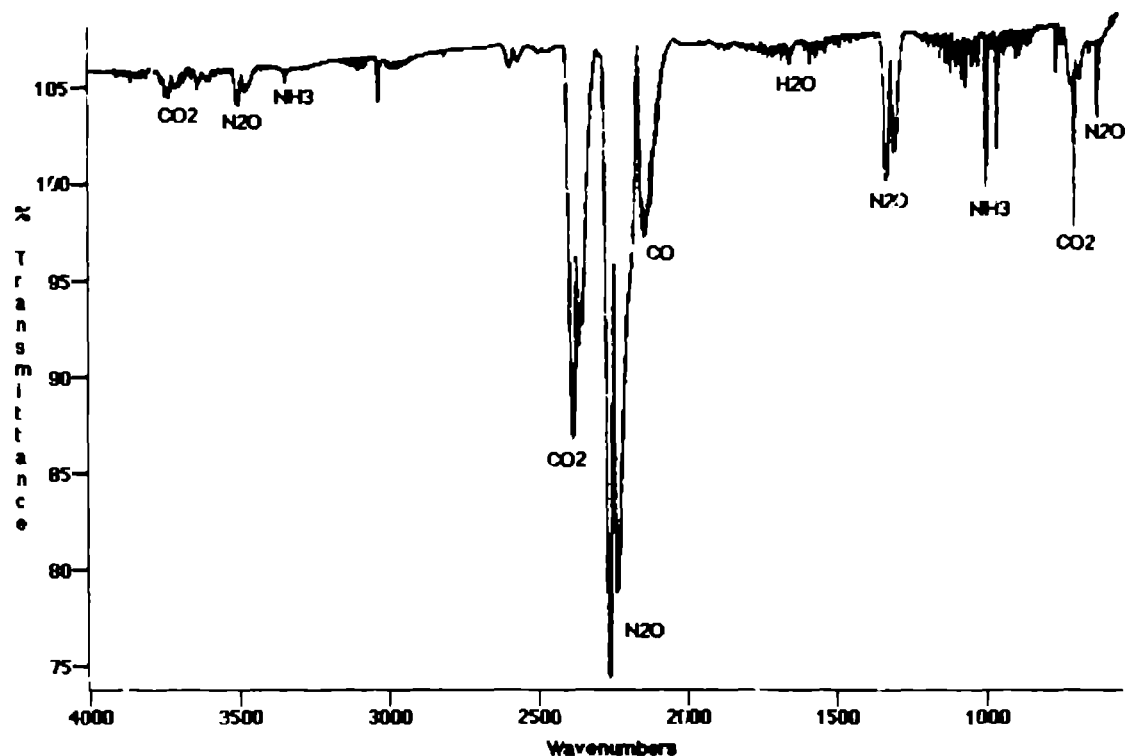


Figure 2. FTIR Spectrum of Gases Produced from Pyrolysis of PBX-9404 Hydrolysate.

Quantitative Analysis of Ammonia from PBX-9404 Hydrolysis

The gaseous hydrolysis products were also analyzed for ammonia content. A dilute hydrochloric acid trap was used to convert the ammonia to ammonium chloride. A one gram sample of PBX-9404 was hydrolyzed and the gases were swept into the trap with argon. Ammonia analysis of the trap solution was then performed with a gas-sensing electrode. It was found that nine millimoles of ammonia were produced from one gram of HE. This represents 35 percent of the nitrogen contained in the PBX-9404.

Analysis of Gaseous PBX-9404 Hydrolysis Products by Mass Spectrometry

Gases were analyzed on-line during a reaction by sweeping them with helium into the instrument inlet as they were produced. Mass/intensity/time/temperature data were collected for masses up to 100 amu over a period of approximately one hour. The reaction was then stopped by cooling in ice and the unreacted material (HMX) was

filtered and weighed. A three-dimensional plot of the data is shown in Figure 3, below. Because no masses above 50 amu were detected, the mass range plotted is 10-50 amu.

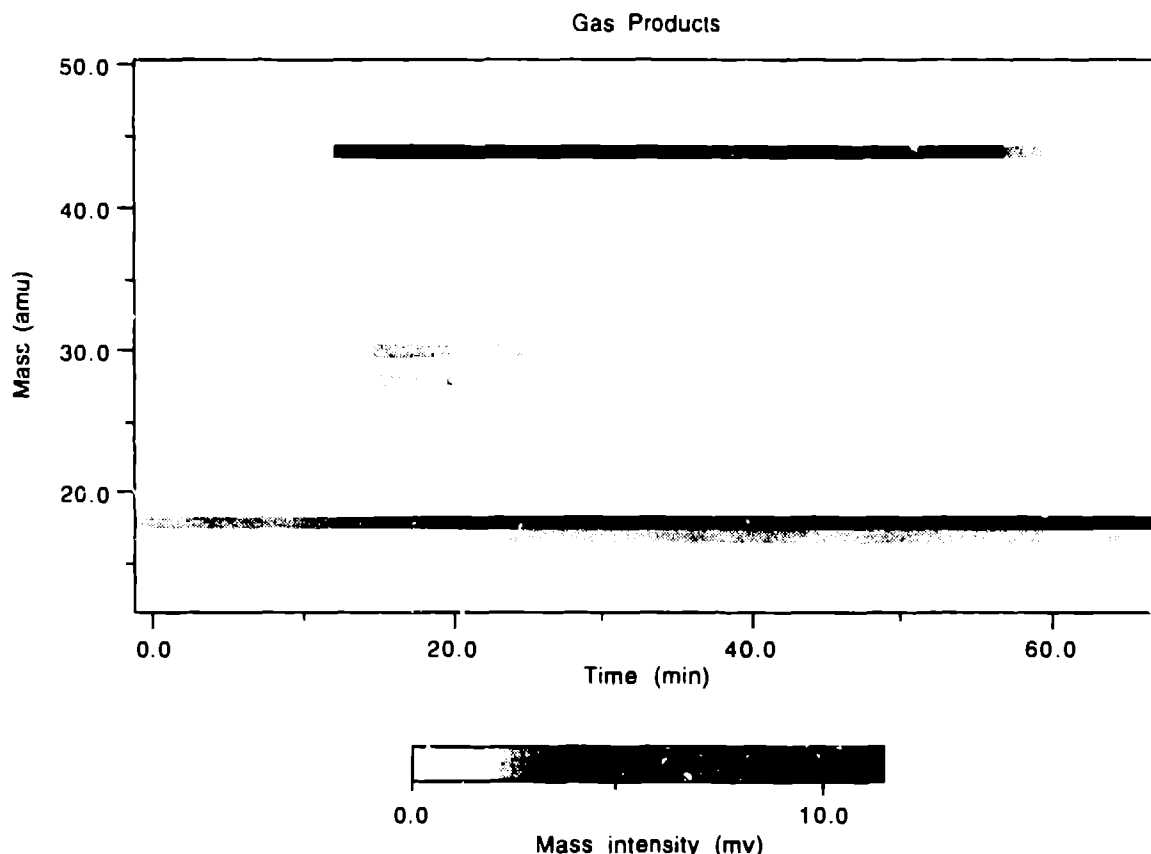


Figure 3. Three-dimensional Plot of Mass-Time-Mass Intensity Data of Gaseous PBX-9404 Hydrolysis Products.

Over the course of the reaction, the only significant masses detected were 44, 30, 28, and 18 through 14. The gases identified from these data are nitrous oxide, nitrogen, and water vapor. Although mass 44 matches carbon dioxide as well as nitrous oxide, the absence of a peak at 12 amu indicates CO_2 is not present. The mass intensity data at 44 and 28 amu were converted to amounts of nitrous oxide and nitrogen. Calibration data were acquired by injecting known amounts of pure N_2O and N_2 into the instrument. The mass spectrum of N_2O includes fragments at 30 and 28 amu, and the intensity due to nitrogen at 28 was corrected for this. Figure 4 is a plot of the rates of N_2O and N_2 evolution versus time of reaction. Also plotted is the temperature profile for the reaction.

Because of the time delay of the gases reaching the detector, the mass spectral data lags the temperature data by 2-3 minutes. As the final temperature of 85°C is reached, the rate of N_2O and N_2 evolution peaks and then gradually declines. When the reaction is quenched in ice, gas evolution ceases abruptly. Integration of the gas evolution curves gives the total amounts of N_2O and N_2 produced. This was found to be 1300 μmoles and 290 μmoles , respectively. Based on the weight of material that reacted, the total nitrogen (N not N_2) consumed in the reaction was 20.9 millimoles. The above amounts of N_2O and N_2 represent 12 and 3 percent of the reacted nitrogen, respectively.

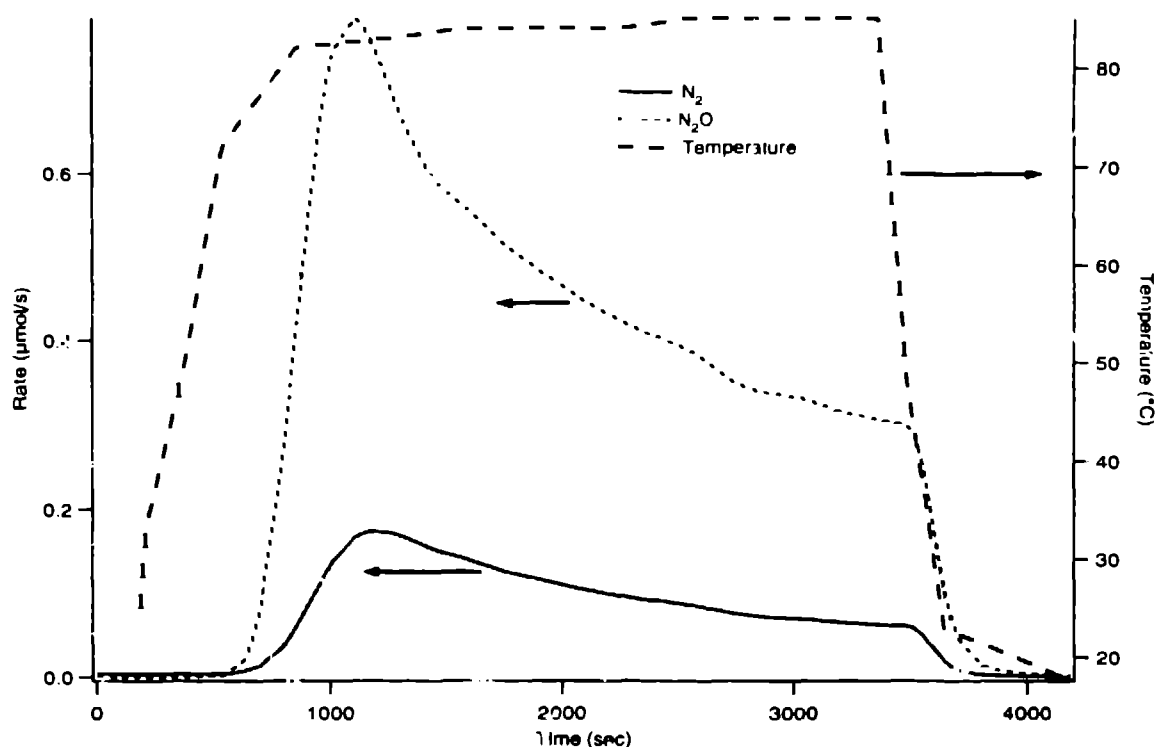


Figure 4. Rates of Nitrous Oxide and Nitrogen Evolution versus Reaction Time

PEX-9404 Hydrolysis Non-gaseous Product Analysis

Because no significant amount of carbon has been detected in the gaseous products, it can be assumed that nearly all of the carbon remains in solution as water-soluble products. The ^{13}C nmr spectrum of PBX-9404 hydrolysate shows the formate ion as the major carbon-containing product. One explanation for the production of formate is the reaction of formaldehyde, the initial product of HMX hydrolysis, with sodium hydroxide. This is known as the Cannizzaro reaction and methanol should be produced in equimolar amount to the formate (11).



An experiment was performed to trap and analyze methanol in the gaseous products. A purge of argon was used to sweep the gaseous hydrolysis products through water that was cooled in ice. The water trap solution was then analyzed by gas chromatography for methanol content. The amount of methanol found represented only one percent of the carbon from the PBX-9404. This means that either the formate is produced by some other mechanism, or the methanol is consumed in a subsequent reaction.

Ion chromatography and ^{13}C nmr spectrometry have shown that approximately one-third of the carbon is converted to sodium formate. The ^{13}C nmr also shows at least fifteen peaks in addition to the formate peak, most of them relatively small, as shown in Figure 5. Many of the peaks are grouped between 50 and 80 ppm chemical shift, some are near 180 ppm, and a couple are near 20 ppm. A nmr experiment called DEPT (Distortionless Enhancement by Polarization Transfer) was performed to determine the

carbon types, i.e., methyl, methylene, methine, or quaternary. The unknown peaks near 20 ppm were found to be methyl carbons, those between 50 and 80 ppm were methylenes, and those near 180 ppm were quaternary carbons. One of the quaternary and one of the methyl carbons may be due to the acetate ion. A peak matching the retention time of acetate was found in the ion chromatographic analysis. Quantitative analysis showed it to represent 13% of the total carbon from the PBX-9404.

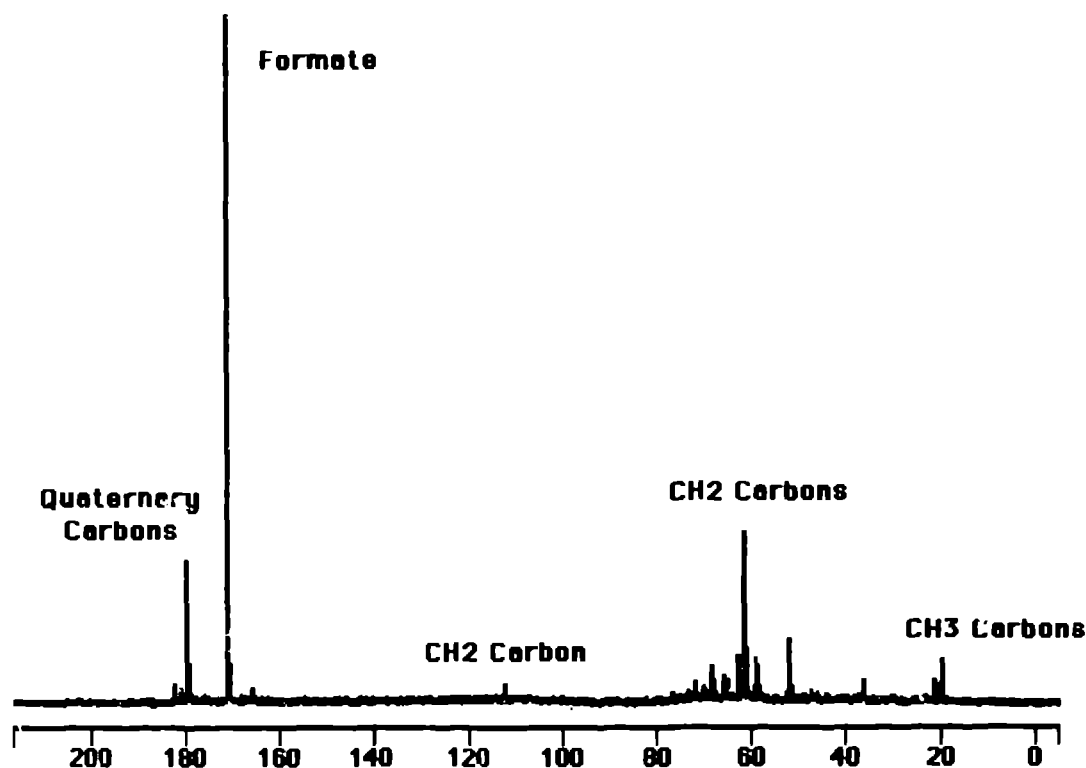


Figure 5. Carbon NMR Spectrum of PBX-9404 Hydrolysate.

In addition to the Cannizzaro reaction described above, formaldehyde may undergo condensation reactions in base solution (11). Condensation reactions of formaldehyde can form hydroxy aldehydes, hydroxy ketones, and sugars. The unidentified ^{13}C nmr peaks of the PBX-9404 hydrolysate have chemical shifts in the region expected for these types of compounds. Some of these materials were obtained or synthesized, and evaluated by nmr as possible products. The following compounds were checked: dihydroxyacetone, 1,4-dioxane, formaloxime trimer, formalin, formamide, glycolaldehyde, glyceraldehyde, glyoxal, methylene bis-formamide, and paraformaldehyde. Of all the materials checked, dihydroxyacetone came closest in nmr chemical shift to the hydrolysis product unknowns, 64.6 ppm. It has not yet been verified that dihydroxyacetone is, in fact, among the hydrolysis products.

PBX-9404 Material Balance

Table 1 shows all of the products that have been identified for PBX-9404 hydrolysis. To date, 47 percent of the carbon, 70 percent of the nitrogen, and 62 percent of the chlorine have been accounted for. Further work is required to achieve a better mass balance.

Table 1. Products from the Hydrolysis of PBX-9404
(Shown as percentage of starting C or N from explosive)

Product	% of PBX-9404
Formate	33 % of C
Acetate	13 % of C
Methanol	1 % of C
Total Carbon	47 %
Ammonia	35 % of N
Nitrite	19 % of N
Nitrate	0.4 % of N
Nitrous Oxide	12 % of N
Nitrogen	3 % of N
Total Nitrogen	70 %
Chloride	62 % of Cl

Hydrothermal Processing Results of PBX-9404 Hydrolysate

Nitric acid oxidation

Nitric acid was initially used as an oxidant for two reasons. The nitrate ion is an effective oxidant for organic matter in hydrothermal systems (12), and the acid itself helps to neutralize the basic hydrolysis solution. In addition, nitrate has been demonstrated to be a considerably more effective oxidant for ammonia than molecular oxygen in supercritical water (13); ammonia removal from the hydrothermal reactor effluent may be necessary for the final disposal.

Reaction conditions for these experiments are shown in Table 3. Oxidation kinetics were studied in three experiments at temperatures from 405°C to 453°C. Total organic and inorganic carbon (TOC and TIC) were measured for the feed solution and effluent samples to determine a material balance on the effluent and to determine organic carbon destruction efficiencies. Gas chromatography (GC) was used to identify gaseous nitrogen and carbon products. The basic pH of the effluent (pH between 9 and 10), compared with the feed solution (12.9) indicated hydroxide was consumed in proton transfer reactions with CO₂ produced from carbon oxidation. No plugging was observed at reactor operating pressures near 1000 bar. Plugging typically occurs at lower pressures and higher temperatures, which favors sodium carbonate precipitation from solution (14).

Table 3. Reaction Conditions for Hydrothermal Processing of 1M Hydrolysate using Nitric Acid as Oxidizer

Reaction Temp (°C)	Pressure (bar)	Residence Time (s)	Effluent pH
405	1111	64	10.0
429	1109	60	9.8
453	1113	57	9.8

Ion chromatography (IC) and TOC/TIC results for these experiments are presented in Table 4. Data in Table 4 indicate that increases in reaction temperature resulted in increased TOC destruction. This fact is also illustrated by acetate and formate concentrations, which monotonically decrease with increases in temperature. Acetate and formate also appear as the majority of the organic carbon remaining after oxidation, representing 93.6% to 114.0% of the measured effluent TOC values. Because TOC values result from a subtraction of TIC from TC values, low TOC concentrations in the

presence of a high TIC background are difficult to accurately quantify. This analytical difficulty, combined with the fact that acetate and formate have long been recognized as refractory carbon reaction intermediates in hydrothermal systems (15), suggests that effluent TOC values might better be derived from acetate and formate concentrations.

As TOC values decrease with increasing reaction temperature, inorganic carbon concentrations increase. The pH of the effluent samples (Table 3) indicate that TIC is present predominately as HCO_3^- , with a significant amount CO_3^{2-} . As discussed previously, these species are formed in rapid proton transfer reactions with CO_2 produced from organic carbon combustion. Ammonium values first increase from the feed solution, and then drop slightly. The initial increase is likely produced from nitrate/nitrite reduction with the organic matter. This behavior has been observed in nitrate/methanol and nitrate/acetate hydrothermal systems (16,17). The subsequent decrease, albeit small, may result from subsequent ammonia reactions with nitrate to form N_2 and N_2O . These reactions have been observed at similar temperature regimes in basic $\text{NaNO}_3/\text{NH}_3$ solutions (13).

Table 4. Total Organic Carbon and Ion Chromatography Results from Nitric Acid Oxidized Hydrothermal Processing of Base Hydrolysate. (All results presented in mg/L)

Reaction Temp (°C)	TOC	TIC	Nitrate*	Nitrite	Ammonium	Formate	Acetate
Feed	5643	169	25771	8019	75	11500	6280
405	1236	3397	18131	7180	596	2940	2700
429	11	5456	9687	8402	704	340	570
453	**	6327	8164	8675	646	0	240

* - Includes HNO_3 addition

** - Below detection limits

Gas products from the hydrothermal processing are reported in Table 5. No oxygen was detected in the gaseous effluent. Significant amounts of hydrogen were evolved at 405°C, but at higher temperatures, less hydrogen and more molecular nitrogen were observed. Hydrogen appears to be produced in early stages of carbon hydrolysis/oxidation, only to be oxidized to water with nitrate/nitrite at higher temperatures. This hydrogen production behavior has also been observed in the hydrothermal treatment of EDTA using nitrate/nitrite oxidizers (9). Nitrous oxide production remained near 10% of the total gas production for all three temperatures; its conversion appeared to reach a maximum at 429°C. Small amounts of hydrocarbon materials, notably methane and ethylene, were also produced, with higher conversions evident at lower temperatures. At 453°C, the only reduced gaseous product present was a trace amount of methane.

Table 5. Gas Products from Nitric Acid Oxidized Hydrothermal Processing of Base Hydrolysate. (All results presented are percentage of total volume of gas produced per liter of solution)

Reaction Temp (°C)	Total gas vol (std cm ³ /L soln.)	N ₂ (%)	N ₂ O (%)	CH ₄ (%)	C ₂ H ₄ (%)	H ₂ (%)
405	2639	48.8	8.2	0.1	0.1	42.9
429	2774	80.1	13.1	0.5	0	6.2
453	2791	87.9	11.6	0.5	0	0

Good mass balances were obtained from the nitric acid oxidation experiments, as shown in Table 6. Also shown in Table 6 are the observed TOC destruction efficiencies. The carbon mass balance is based on the ratio of the known carbon constituents in the effluent to the organic carbon in the feed solution. These carbon constituents include the difference in inorganic carbon between the feed and the effluent. The total destruction efficiency is based on the total organic carbon in the feed compared to the total organic carbon in the effluent and carbon containing gases evolved. As shown in Table 6, the carbon mass balances range from 94 to 114%. Some of these results are larger than 100% because of probable errors in inorganic carbon measurements. As previously discussed, at high inorganic carbon loadings the determination of small levels of TOC is analytically difficult. As a result of this potential error, for the reaction conditions at 429°C and 453°C, DRE's (Destruction Removal Efficiencies) were calculated using acetate/formate concentrations rather than TOC measurements. This prevented the calculation of an artificially high DRE.

Table 6. Carbon Mass Balance and Destruction Efficiency

Reaction Temp (°C)	Carbon Mass Balance *	Total Organic Carbon Destruction Efficiency *
405	94%	78.0%
429	103%	95.3%
453	114%	98.3%

* - See text for explanation of measurements

Destruction efficiencies increased with increasing temperature. Nearly all of the organic carbon was converted to benign products above a reaction temperature of 429°C at 1 minute residence time. Higher destruction efficiencies could be achieved by longer residence times or higher operating temperatures.

Hydrogen peroxide oxidation

Hydrogen peroxide was also used as an oxidant in the hydrothermal processing of base hydrolysate. A more concentrated sample of base hydrolysate (1.5 M NaOH) was used in this experiment, and has been described previously in the experimental methods section. Reactions were carried out at one temperature because of experimental problems with H₂O₂. Hydrogen peroxide reacts with the base hydrolysate at room temperature to form small gaseous bubbles. These bubbles make it difficult to pump the solution at high pressure. One run at 419°C was made before the pump was unable to continue to pressurize the reaction to 1034 bar. Since the time of the initial experiment, a revised experimental setup has been designed to allow the co-pumping of H₂O₂ and hydrolysate at elevated pressures. The pH changed during the reaction from 12.1 in the feed to 9.5 in the effluent. The pressure of the reaction was 990 bar and the residence time was 64 s.

Ion chromatography and total carbon results of feed and effluent ion concentrations are shown in Table 7. Using hydrogen peroxide, nitrate and nitrite were completely reacted, but TOC destruction removal efficiencies were not as effective as with nitric acid. Note that only one temperature was attempted; organic carbon destruction would be more effective at higher temperatures and increased residence times.

Table 7. Total Organic Carbon and Ion Chromatography Results from Hydrogen Peroxide Oxidized Hydrothermal Treatment of Base Hydrolysate. (All results presented in mg/L)

	TOC	TIC	Nitrate	Nitrite	Ammonia	Formate	Acetate
Feed	13180	1490	1357	16383	699	18879	13377
Effluent	5330	8960	0	0	2482	10118	4212

Gas products from the H_2O_2 oxidation experiment were measured by gas chromatography and are presented in Table 8. In contrast to nitric acid oxidized processing, no N_2O was detected, but oxygen was detected in the gaseous products. Significant amounts of hydrogen are evolved at $419^\circ C$. Small amounts of methane and ethylene were also detected, as observed also in the nitric acid oxidation experiments.

Table 8. Gas Products from Hydrogen Peroxide Oxidized Hydrothermal Treatment of Base Hydrolysate. (All results presented are percentage of total volume of gas produced per liter of solution)

Reaction Temp ($^\circ C$)	Total gas vol (std cm ³)	N ₂	N ₂ O	O ₂	CH ₄	C ₂ H ₄	H ₂
419	5805	61.4	0	3.4	5.0	0.7	29.5

Destruction efficiency, or organic carbon conversion, for hydrogen peroxide was not as good as when nitric acid was used as the oxidizer. The destruction efficiency for the one peroxide run was 58%. Since nitrate or nitrite were not present at the end of the reaction (oxidizers themselves), this indicates that not enough oxidizer was added to the feed solution. It is possible that hydrogen peroxide decomposition to molecular oxygen in the feed container resulted in these lower than stoichiometric values. One desirable feature of this reaction is that the nitrogen species are completely converted to gaseous products; this might suggest that a step feed reactor is a favorable reaction scheme, with nitrate/nitrite carbon oxidation in the first reactor segment and oxygen oxidation in the second segment. In this experiment, 92% of the carbon in the feed solution was recovered in the effluent. This mass balance was calculated in the same way as for the nitric acid experiments.

CONCLUSIONS

We have shown base hydrolysis to be a viable alternative to open burning/open detonation disposal of energetic materials. This low temperature chemical treatment method results in nonenergetic and water-soluble products. The gases produced from hydrolysis of PBX-9404 are ammonia, nitrous oxide, and nitrogen. A mass balance of 70 percent has been determined for nitrogen products, and 47 percent for carbon products. More work is needed to identify additional products. If a secondary treatment step is required for the hydrolysis product stream, this can be achieved by hydrothermal processing, biotreatment, or possibly low temperature pyrolysis.

We have also demonstrated that we can process the aqueous effluent of base hydrolysis in a hydrothermal reactor. Destruction efficiencies up to 98% were achieved using nitric acid as an oxidizer. Major gas products detected were N_2 and N_2O at these temperatures, and H_2 at lower reaction temperatures. Nitrate, nitrite, and ammonia were detected in the effluent, and nitrate and nitrite products can be minimized by using less oxidizer. Some acetate was detected in the effluent stream, and formate was detected at lower operating temperatures. For hydrothermal processing using hydrogen peroxide as an oxidizer, lower destruction efficiencies were observed than with nitric acid, but we believe that these destruction efficiencies can be increased with larger amounts of oxidizer and operation at higher temperatures.

ACKNOWLEDGMENTS

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