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Investigation and Characterization of Water-Recrystallized Croconic Acid

by Sarah Isert and Jennifer A Ciezak-Jenkins

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14. ABSTRACT A high-pressure phase of croconic acid is being investigated as a novel energetic material. When pressed at high pressures (>5.5 GPa), as-received croconic acid transforms into a β -phase that is recoverable to ambient conditions. This phase has a higher density and heat of combustion than the as-received material. Rectangular crystals, which are darker than the original powder, can be observed in the recovered material and are thought to indicate formation of the β -phase. When croconic acid is recrystallized from water at ambient conditions, similar appearing crystals are observed. We performed experiments to investigate the plausibility of recovering the β -phase croconic acid from water recrystallization as an alternative to the high-pressure synthesis. Thermal analysis, bomb calorimetry, X-ray diffraction, and Raman spectroscopy were performed on water-recrystallized croconic acid to determine whether or not it is the β -phase. We found that the water-recrystallized material is not the β -phase and at present high pressures is still required for β -phase formation.					
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1. Introduction

Although current energetic materials provide good and reliable performance, game-changing weapons for the future will require a new class of energetic materials. For example, a 40% increase in impetus is desired for the next generation of gun propellants to substantially increase the muzzle velocity.¹ These “disruptive energetics” will revolutionize range and muzzle velocity of weapon systems. In addition to increased power, novel energetic materials should be less sensitive than currently used materials while being environmentally friendly and inexpensive to synthesize.

A material that shows promise in the novel energetics arena is croconic acid (CA),* a solid bright-yellow compound based off a 5-membered carbon ring (Fig. 1a).² First synthesized in 1825,³ it was recently discovered that CA has the highest spontaneous polarization observed in organic ferroelectrics at room temperature to date.⁴ This quality is thought to be due to the unique hydrogen bonding networks; one network links molecules in a sheet and the other in pleated strips,² as shown in Fig. 1b.

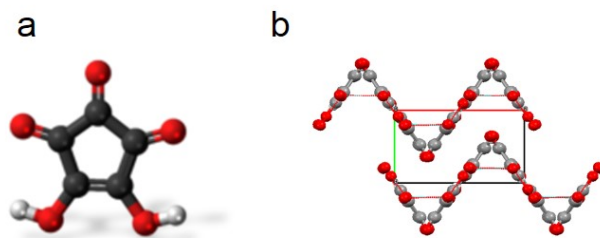


Fig. 1 a) Molecular structure of CA. b) Extended structure of CA, showing the hydrogen bonding network between neighboring molecules.

Previous work done at the US Army Research Laboratory has shed some light on other characteristics of CA, including experimentally determining its heat of combustion⁵ and density,⁶ as well as further research into sensitivity,⁷ spectroscopy, and thermal properties such as melting and decomposition temperature.⁵ These studies included subjecting CA to very high pressures. At pressures between 5.5 and 6.8 GPa, CA undergoes an irreversible phase change.⁶

The phase change includes density and volume changes, but is not accompanied by new diffraction peaks or modifications in the Raman spectrum peak distribution, indicating that a chemical change does not occur. The increase in density is thought to be due to the collapse of the hydrogen bond networks and the onset of pressure-induced polymerization. The high-pressure polymorph is recoverable to ambient

*The molecular formula for croconic acid is $C_5H_2O_5$.

conditions and is called the β -phase (the as-received [AR] material is also known as the α -phase).

Bomb calorimeter testing of the β -CA indicated a heat of combustion almost 80% higher than that of the α -CA. The high heat of combustion and low sensitivity make β -CA a very interesting material from the disruptive energetics point of view. However, at present it is difficult to make large amounts of β -CA, as the current synthesis method can only produce 50 mg of material per day. A proposed alternative synthesis method is recrystallizing CA from water, as the recrystallization leads to crystals similar in shape and color to those seen in the recovered β -CA. If the water-recrystallized (WR) material is indeed the β -phase, synthesis will be greatly simplified. This report describes characterization tests of the AR and WR CA. Computational predictions of impetus for β -phase CA are discussed.

2. Methods

2.1 Pressing

The AR CA was pressed in a VX-5 Paris-Edinburgh cell. The press and anvils (tungsten embedded in stainless steel) were examined for cracks before each use. For a pressing cycle, the CA (about 50 mg) was measured into the disposable stainless steel gaskets as they were sitting on the anvil. The press was then loaded to 9 GPa remotely using a manually operated hydraulic pump. Ramp-up time was about 10 min with a 30-s rest period every minute to allow the system to equilibrate. The material was pressed at 9 GPa for 24 h. At that point, the press was gradually unloaded over a period of 10 min. The pressed CA was recovered, usually in small pellets. A new cycle was then initiated. Figure 2 shows the large-volume press used in the material synthesis.



Fig. 2 Large-volume press used in β -CA production

2.2 Water Recrystallization

Because of concerns about the ability to mass-produce β -CA using the large-volume press, we wanted to explore alternatives to synthesizing β -CA via pressing. While recrystallizing CA from water for another test, the resulting crystals were observed to be similar in shape and color to crystals seen on the surface of the pressed CA. As it is thought from other experiments that the darker crystals are β -phase CA, we decided to investigate water-recrystallization as a possible low-pressure route to the β -phase.

To make the WR material, 5 g of CA were dissolved in distilled water, and the water was then evaporated off using a hot plate at 50 °C. Complete evaporation of the water took 7–10 days and produced large orthorhombic crystals. The crystals were stored in a desiccator until they were used. Upon crushing, the darker crystals took on a more yellow hue, indicating that the dark color is at least partly a particle size effect.

2.3 Standard Analytical Tests

Standard analytical tests were used to characterize the CA, including differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), bomb calorimetry, X-ray diffraction, and Raman spectroscopy. A TA Instruments Q500 and TA Instruments Q2000 operating under Universal Analysis software were used for the TGA and DSC measurements, respectively. The DSC and TGA tests were used to find melting and decomposition temperatures. The DSC samples were run between 40 and 400 °C in sealed aluminum pans with pinhole lids to allow gaseous

decomposition products to escape. The TGA samples were run in open aluminum pans between 40 and 350 °C.

Bomb calorimetry (Parr Instrument Company, Model 6200 Isoperibol Calorimeter) was performed in oxygen. Pellets of layered CA and benzoic acid were tested in Inconel crucibles with 5–10 experiments performed per material to ensure reproducibility. Bomb calorimetry was used to find the material heat of combustion; from this information, heat of formation can be calculated and used in thermochemistry codes.

The Raman spectroscopy was performed with a dichroic micro-Raman system in a backscattering geometry using a 1064-nm continuous wave Coherent diode laser. An IsoPlane SCT320 spectrograph with an air-cooled PIXIS 400BR eXcelon CCD and the LightField software (Princeton Instruments) were used to collect the software Raman spectra. Collection times of 1 s with a laser power of 7 mW were typical. The sample was not observed to react with the laser. The spectra obtained were compared against the library spectrum for CA. These experiments were performed to see if any peak shifts were visible between the as-received CA and the water recrystallized or pressed CA that might indicate a chemical change.

2.4 Computational

In addition to experimental studies, computational techniques were used to predict the effect on impetus of adding CA to gun propellants. For this study, Cheetah 8.0⁸ was used, with data from the bomb calorimetry experiments and previously conducted density experiments⁶ supplying inputs for the code.

3. Results

3.1 Computational Results

The heat of combustion of β -phase CA was previously found to be on average 4374 cal/g via bomb calorimetry. For comparison, the heat of combustion for 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX) is 2285 cal/g. The heat of formation was calculated from the heat of combustion and along with the density (2.1 g/cc) was used in thermochemical calculations. We also desired to see the effect of adding the CA to an existing propellant as an energetic additive, and performed a series of computations where different percentages of JA2 were replaced by CA. For reference, the composition of JA2 is given in Table 1. The resulting impetus was calculated and the results of these computations are shown in Fig. 3. The loading density used in the calculations was 0.25 g/cc.

Table 1 JA2 reference propellant formulation (from Reference 9)

Constituent	wt% of total
Nitrocellulose (NC) (13.4% N)	59.5
Nitroglycerin (NG)	14.9
Diethylene glycol dinitrate	24.8
Ethyl centralite	0.7
Magnesium oxide	0.05
Graphite	0.05

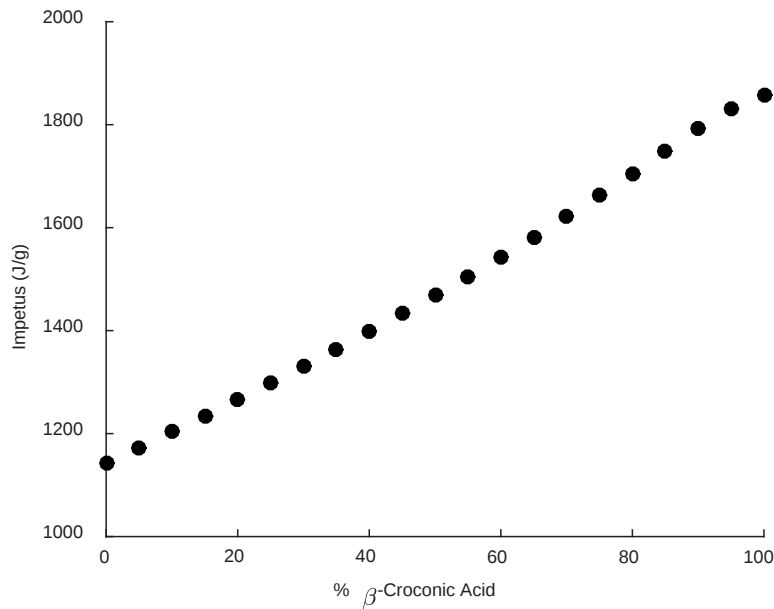
**Fig. 3 Impetus of CA/JA2 propellant. For CA percentages less than 100% the propellant balance is JA2.**

Figure 3 clearly shows that the impetus of a JA2/β-CA propellant increases as more β-CA is present in the propellant. From these results it would appear (due to the high heat of combustion of β-CA) that the ideal propellant formulation would be close to 100% CA with only enough binder present to ensure good mechanical properties. However, impetus is not the only consideration for a propellant. Two other important characteristics of a propellant are flame temperature and oxygen balance. Other parameters like carbon monoxide/carbon dioxide (CO/CO₂) ratios and chemical species present in the propellant flame gases are also important, but were not investigated in this study.

Gun barrel erosion can, in general, be reduced by using propellants with low-flame temperatures.¹⁰ The high-temperature fluctuations that the gun steel is subjected to with every firing can cause the microstructure of the surface to change, and the steel becomes harder and more brittle. Chemical species from the combustion gases can

diffuse into the steel and alter its chemical properties¹¹ and are another major cause of gun barrel erosion.¹² An increase in temperature is not exactly proportional to an increase in gun barrel erosion; the chemical composition of the propellant and associated phenomena like heat conduction and chemistry effects on the gun barrel come into play, and in some propellants erosion is more dependent on chemical species than temperature.

Figure 4 shows calculated flame temperatures of β -CA/JA2 propellants as a function of composition. Predicted temperatures for these propellants, even at moderate CA inclusion percentages, are high and problematic for traditional gun barrel designs. Flame temperatures as low as possible to minimize gun barrel erosion are required, but adding CA produces the opposite effect. Additionally, it is known that propellants producing more CO/CO₂ are more erosive than those that produce large amounts of nitrogen gas (N₂), unless flame temperatures are low. The combination of high flame temperatures and large amount of CO/CO₂ production raises the specter of a CA-based propellant being highly erosive.

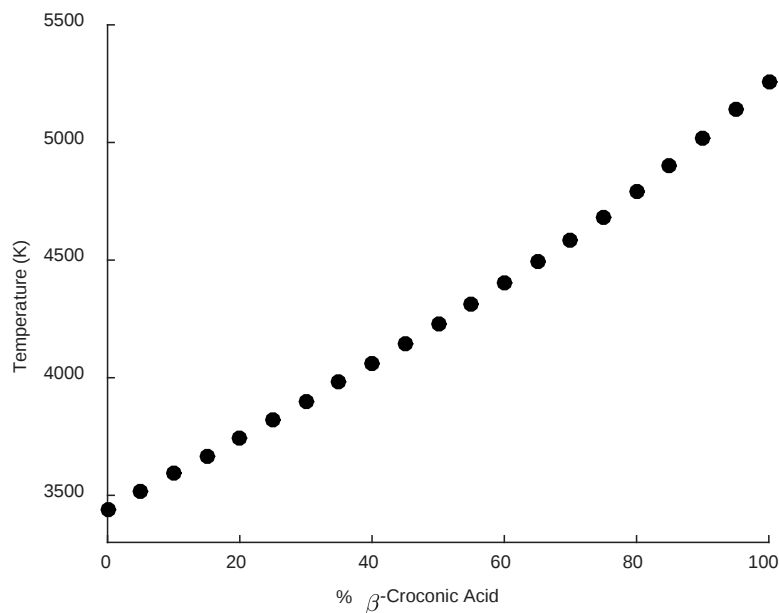


Fig. 4 Temperature as a function of added CA percentage in a JA2 propellant

Another factor that limits the amount of CA that can be added to a propellant is oxygen balance. Oxygen balance is the ratio of the number of oxygen atoms a molecule contains compared to the number of oxygen atoms it needs to completely oxidize the carbon to CO or CO₂, the hydrogen to water, and any metal to metal oxide. A positive oxygen balance indicates a molecule contains excess oxygen, and a negative oxygen balance indicates a molecule requires more oxygen to be in the balanced state. Many propellants and explosives operate in the negative oxygen balance or CO-balanced regime. However, if the oxygen balance is too negative, the propellant will not burn cleanly and will leave behind solid carbon.¹³

The char-free oxygen balance threshold varies with propellant type, composition, and operating pressure; for example, the threshold for an NC/NG-based propellant was found to be around -60% depending on exact propellant formulation and combustion pressure.¹⁴ Another report stated that condensed phases, typically solid carbon, tend to appear when the oxygen/carbon atomic ratio is less than 0.9.¹ Croconic acid itself has an oxygen balance of about -67%. The addition of JA2 (oxygen balance ~ -27%) will increase the oxygen balance somewhat (Fig. 5). Assuming the oxygen balance requirements for noncharring combustion are similar to that of a typical double-base propellant, the maximum allowable percentage of CA in a JA2-based propellant that would limit char formation would be about 82%. Propellants with larger percentages of CA would theoretically have a high impetus (impetus at 55% β -CA is about 1500 J/g), but residual char and temperatures well above 4000 K (according to the calculations) could limit their usability in guns.

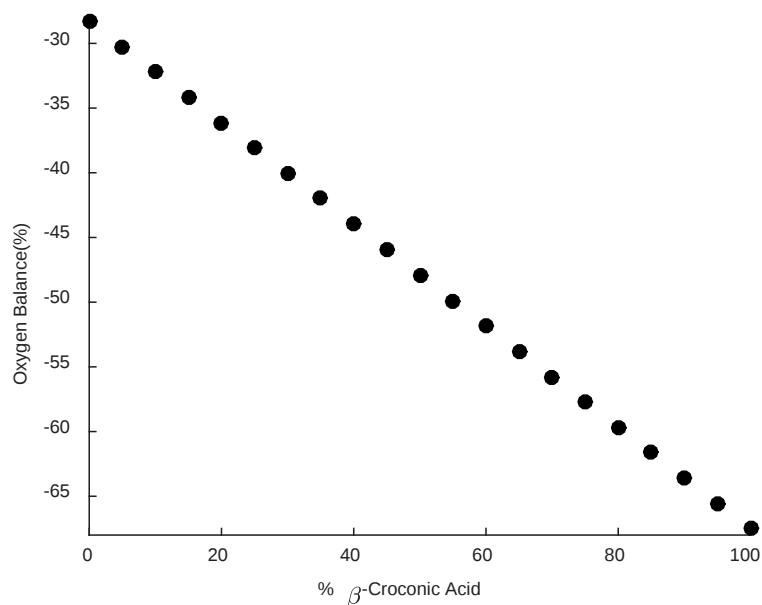


Fig. 5 Oxygen balance as a function of percent added CA in a JA2-based propellant

3.2 Experimental Results

3.2.1 Pressing AR CA

As previously reported, when CA is pressed it undergoes a density change from 1.9 g/cc to 2.1 g/cc,⁶ and the heat of combustion increases by about 80%. This new high-pressure phase is known as the β -phase, while the original material is known as AR CA or the α -phase. Both the α - and β -phases are insensitive to friction, impact, and electrostatic discharge (ESD) stimuli, and do not display any peculiar sensitivities.⁷ It was found in diamond anvil cell experiments that the CA transitions from a yellow to a yellow-red color under the influence of pressure.⁶ Similar results were seen in the large-volume press. Figure 6 shows the outer surface of a pressed AR CA pellet. There are many small, dark crystals visible on the pellet surface. Crystals of similar sizes, shapes, and colors are visible on the interior surface of the pellet.

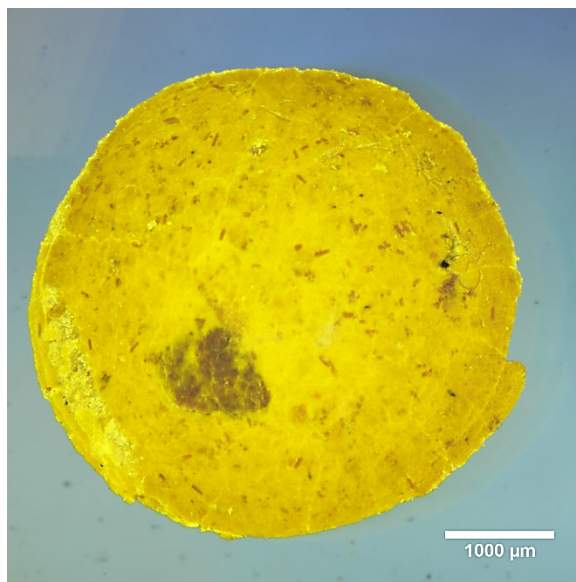


Fig. 6 Pressed AR CA pellet, outer surface

Previous experiments showed that pressures between 5.5 and 6.8 GPa are required to induce polymerization.⁶ The high pressures involved limit what equipment can be used for the synthesis. The polymerization pressures were found in a diamond anvil cell; however, due to the kinetic factors controlling the transition time at larger volume, it is necessary to overdrive the pressure in the large-volume cell in an effort to in push the transition to completion in a reasonable timeframe. Hence we press the CA at 9 GPa. The high pressures required can typically only be achieved using small anvil diameters and therefore small sample sizes. The average amount of material produced in the large-volume cell is 50 mg/cycle; since a cycle is 24 h it

takes 20 working days to produce a gram of material, and a year's output (assuming a 5-day work week and no breaks) would be 13 g. Obviously other methods would be needed to produce the material in production quantities.

The long press cycle time is disadvantageous; however, the amount of time needed to press the material before it is converted to the β -phase has not yet been characterized. The long press time may not be necessary, and in that case, the output could be increased. However, if 24 h is close to the optimum time, or if an even longer time would be better, there would be an even more pressing need to move to another synthesis method.

3.2.2 Water Recrystallization of CA

A proposed non-pressure method of synthesizing β -CA was recrystallizing α -CA in water. When CA is recrystallized in water, crystals similar in color and shape to those visible on the surface of the pressed AR CA are observed. The WR CA was tested using bomb calorimetry to determine if it was a higher-energy form of CA or even the β -phase. Raman spectroscopy on the WR CA was performed to see if it was still CA or if it had undergone a chemical change (to a hydrate, for example) as part of the recrystallization process. Finally, we pressed the WR CA in the large volume press and used bomb calorimetry to investigate the difference in heat of combustion between the pressed WR CA and the β -CA.

Recrystallization changes the CA morphology. The AR powder (Fig. 7a) is composed of small, irregularly shaped yellow particles, while the WR material (Fig. 7b) is darker in color and visibly crystalline. Yellow powder considered to be CA dust is visible on the WR material. Throughout this study we noticed that the color may be in part a particle size characteristic. When the CA was in larger crystals it was a dark red-orange in color, compared to the yellow of the small particle size CA.

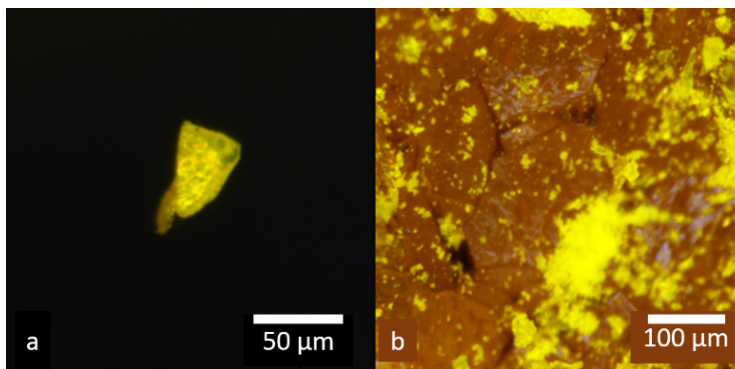


Fig. 7 Comparison between a) AR and b) WR CA. The former is clearly smaller and yellow-colored. The WR material is darker in color and larger.

3.2.2.1 Pressed WR CA Compared to Pressed AR CA

When subjected to standard pressing conditions, the pressed WR CA pellets looked different than the pressed AR CA pellets (Fig. 8). The exterior of the WR CA pellets was more uniformly dark in color, but the darker color is generally not attributable to clearly defined crystals, unlike the pressed AR CA pellets. The pellet interiors also differed. While the AR CA pellet interiors were typically lemon yellow in color with some pockets of darker crystals, the WR CA pellet interiors showed large amounts of dark marbling. A thick dark band was also visible around the perimeter of the WR CA pellet interior; though a similar band is visible in the AR CA pellets, it is not as pronounced.

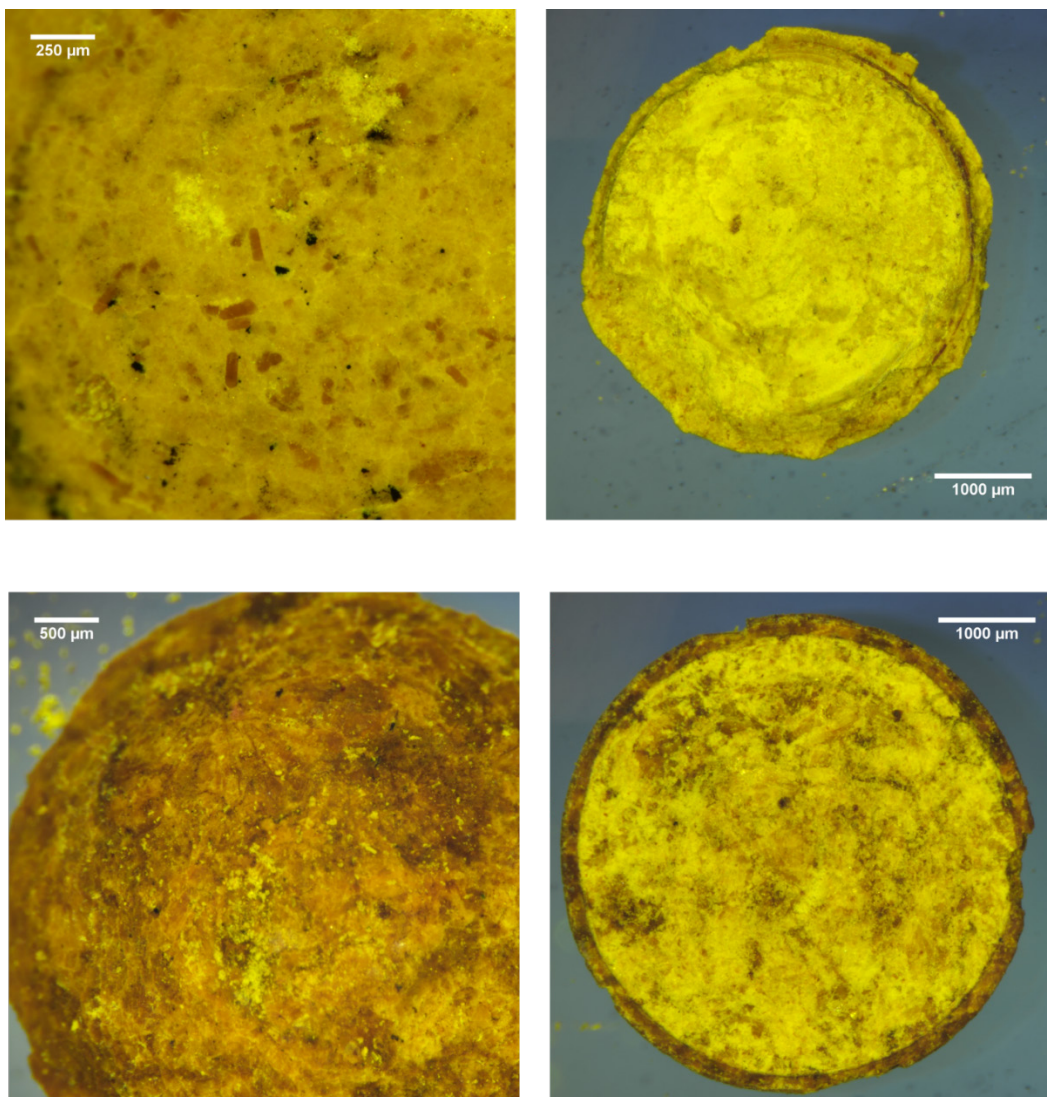


Fig. 8 Comparison between pressed AR CA (top) and WR CA (bottom). Images on the left show the outer surface of the pellet and images on the right, the pellet interior.

3.2.2.2 WR Pellet Reaction

Under the same unloading conditions as the AR CA pellet, the WR CA pellets tended to react when pressure was released. A loud report was followed by a puff of CA emanating from the press. When the press was opened the pellet appeared to be partially reacted to a greater or lesser degree. An example of a partially reacted pellet on the press is shown in Fig. 9a, and the interior of a different partially reacted pellet is shown in Fig. 9b.

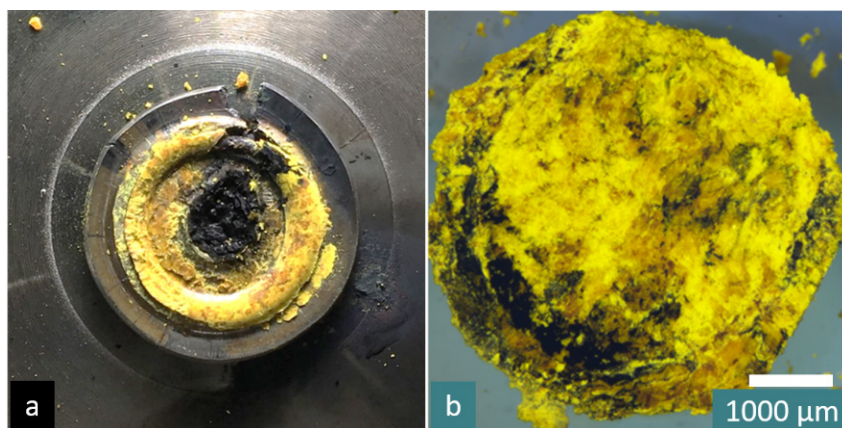


Fig. 9 WR CA a) on the press and b) pellet interior

In Fig. 9a one can see a reacted core surrounded by unreacted material. The inner gasket is distended, with the distension pointing to about the 1 o'clock position. The outer gasket is broken at about the 12:30 position; however, such breaks commonly occur regardless of the material being pressed. The center of the pellet is almost completely charred. Such complete reactions were rare; most reactions were partial as seen in Fig. 9b. For partial reactions, while there are black sections of char, the pellet remains mostly unchanged. Microscopic examination of the pellet interior showed that the char appeared in areas with high concentrations of dark crystals. In some cases one could see where the char was extending into the dark areas indicating that the latter are a precursor to the former.

As the WR CA reacted on the press when the AR CA did not, we also wondered whether or not the percentage of β -CA was higher or if the WR CA, when pressed, had transformed into a different material. Raman spectroscopy, X-ray diffraction, bomb calorimetry, and thermal tests were performed to investigate chemical transformations, heat of combustion, and decomposition onset temperature, respectively.

3.2.3 Raman Spectroscopy and X-ray Diffraction

Because the pressing was not expected to cause any chemical changes, the reaction of the WR CA on the press encouraged testing to see if recrystallization in water produced CA or promoted the formation of another material such as a hydrate. The Raman spectrum of the WR CA showed several slightly shifted peaks and changes in peak magnitude compared to the AR CA, as shown in Fig. 10. No indications of added water were seen in the WR CA Raman spectrum indicating that the WR material is not CA hydrate or an inclusion compound. X-ray diffraction on the AR CA and WR CA was collected at the X-ray Crystallography Center at the University of Maryland and is shown in Fig. 11. Although subtle changes are observed in the patterns such as peak splitting and intensity changes, these suggest a change in the local molecular ordering (such as a modification to the hydrogen bonding sublattice) rather than a distinct phase change. This is supported by the Raman data.

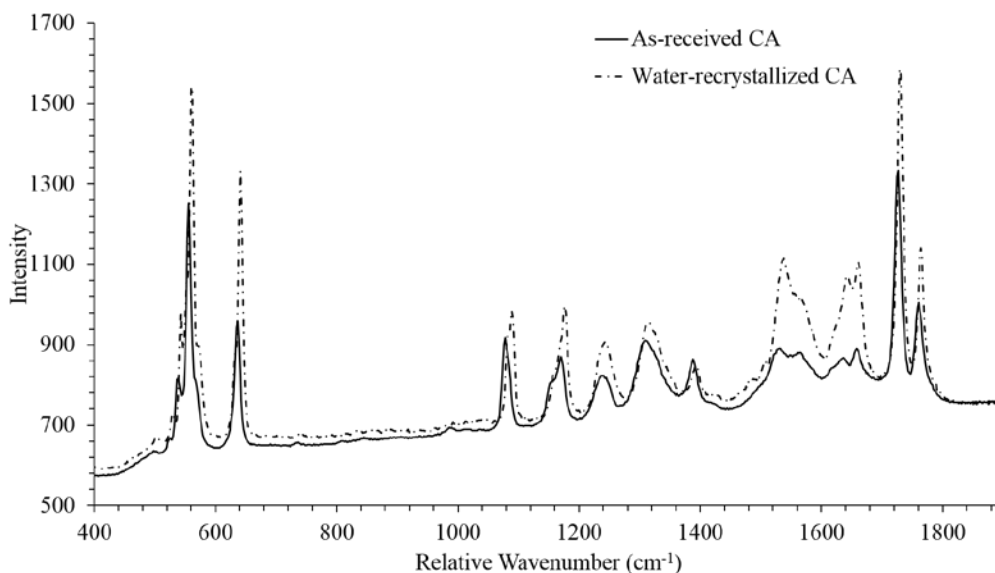


Fig. 10 Raman spectra of AR CA and WR CA

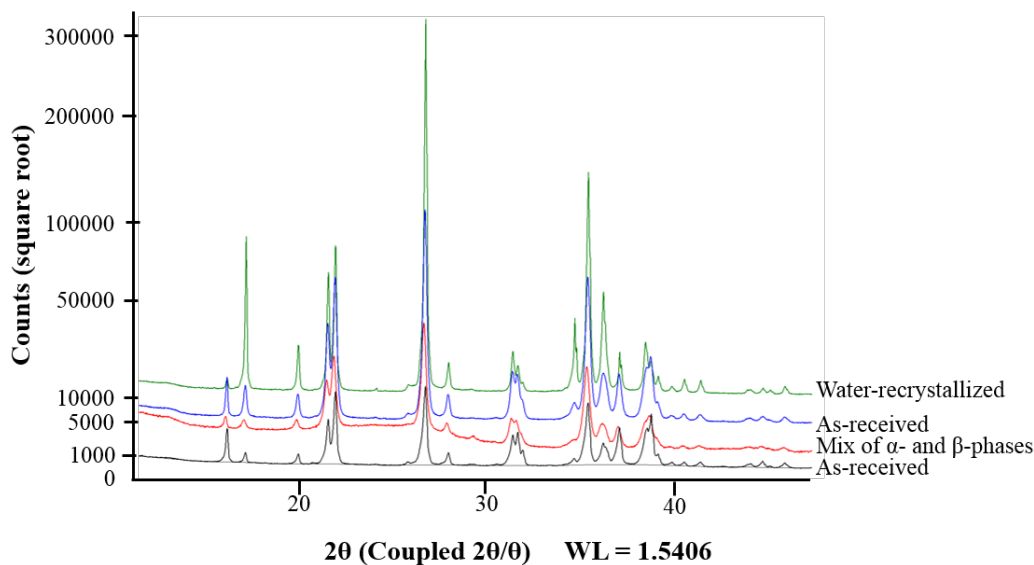


Fig. 11 X-ray diffraction results for AR, WR, and pressed (mix of α - and β -phase) CA

3.2.4 Bomb Calorimetry

Bomb calorimetry was performed on both the pressed and unpressed WR CA. The results were compared with those previously found for RDX and both α - and β -CA. No difference was found in the heat of combustion between WR CA powder and α -CA powder, and while the pressed WR CA had a higher heat of combustion than the unpressed WR CA powder, the difference (while statistically significant) was about 6% between the heats of combustion compared to an 80% difference between the α - and β -CA heats of combustion. Heats of combustion for all materials tested are shown in table form in Table 2 and graphically in Fig. 12.

Table 2 Heats of combustion of various forms of CA. Heat of combustion of RDX is included for comparison

Material	Average heat of combustion (cal/g)
RDX	2243 ^a
α -CA powder	2416 ^a
Water-recrystallized CA powder	2374
Pressed water-recrystallized CA	2514
β -phase CA	4374

^aSee Reference 5.

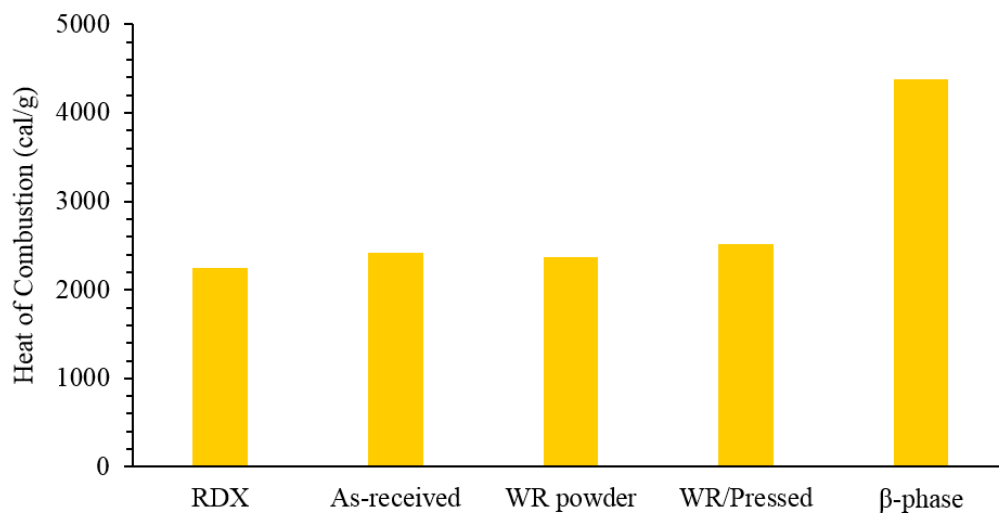


Fig. 12 Heats of combustion of tested materials

The similar heats of combustion between the α -CA powder and the pressed WR CA pellets were a surprise, because the WR CA pellet reacted on the press where the AR CA pellet did not, and an increased percentage of β -CA in the pressed WR CA had been thought to be the cause. Thermal tests (DSC and TGA) did not indicate a lower decomposition temperature for the pressed WR CA compared to the pressed AR CA. So why would the pressed WR CA pellet react where the pressed AR CA did not? And why did pressing the WR CA not result in the high heat of combustion that was achieved by pressing the AR CA?

A possible answer to both questions could be due to powder grain morphology. The AR CA powder, as shown in Fig. 7, contains very small, nonuniform particles. The WR CA powder, on the other hand, has large particle sizes. It is thought that the transition between the α -phase and the β -phase requires the formation of a transient “amorphous phase”, similar to a solid melt. Indications of an amorphous phase is shown in Fig. 11 where β -phase material (red trace) shows a higher background from low angle to about 27° in 2-Theta. While it is difficult to quantify because of the offset patterns, this broad background is typical of an amorphous sample. The small particle size of the AR CA powder means less energy is required for the transient stage to form. On the other hand, the larger crystals of the WR CA powder hinder the formation of the transient phase as the particles are large and require large amounts of energy for the transition. It is possible that the slight heat of combustion increase in the pressed WR CA powder is due to the transformation of the loose powder to the β -phase.

A similar theory can also start to explain why the WR CA pellets react upon depressurization. The large WR CA crystals begin to elastically deform and

plastically flow resulting in the formation of voids and stress concentrators between the crystals if they do not powderize. If the pressure is released rapidly enough, the elastically deformed crystal “springs” back toward its initial shape, releasing energy from the deformed bonds in the process. This may cause hotspots and charring in the area surrounding the deformed crystal, which fits in with the observation that the black areas are often near observed crystal structures. If enough energy is released to partially react the area, gas formed from this reaction may be the cause of the distended inner gaskets.

A large number of alternative mechanisms have been suggested in the literature for hot spot formation, many of which apply to materials that are being compressed. While the reaction of the WR CA occurs on decompression, it may be that compression is occurring somewhere in the pellet, such as on crystal boundaries. Hot spot formation methods that could apply in these cases include adiabatic compression of trapped gas spaces, cavity collapse, viscous or plastic heating of the surrounding matrix material, friction between impacting and sliding crystal surfaces, heating at crack tips, or heating at dislocation pileups.¹⁵

After several WR CA pellets had reacted the press unloading time was increased, and the pellets did not react. In this case, as pressure is slowly released, the crystals more gradually release the energy from the distortion and there is no appreciable hot spot formation. The reduced incidence of hot spots means the CA crystals are less likely to decompose into carbon and gas, and there is therefore no charring and no reaction on the press. At this point it is difficult to know what exactly is causing the hot spot formation, if hot spots are indeed what are causing the partial reaction of the CA pellets. However, the main point of interest for the current study is that there are other possible reasons besides the presence of β -CA for why the WR CA is more reactive.

4. Conclusions

Several conclusions can be drawn from the results of this study. First, our attempt to create β -CA at ambient pressure by recrystallizing the material from water was not successful. Additionally, pressing crystals of WR CA to form the β -phase was not successful, as shown by the bomb calorimeter data. The β -CA has a higher heat of combustion than the α -CA, whether the α -CA is AR CA, WR CA, or pressed WR CA. Further research into synthesis of β -CA is needed, but the fact that we can make a material with a very high heat of combustion from an inert, commercially available material is promising.

5. References

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List of Symbols, Abbreviations, and Acronyms

AR	as-received
CA	croconic acid
CO	carbon monoxide
CO ₂	carbon dioxide
DSC	differential scanning calorimetry
ESD	electrostatic discharge
N ₂	nitrogen gas
NC	nitrocellulose
NG	nitroglycerine
RDX	1,3,5-Trinitroperhydro-1,3,5-triazine
TGA	thermal gravimetric analysis
WR	water-recrystallized

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