

Effects of amino acids on solid-state phase transition of ammonium nitrate

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Abstract The purpose of this study was to obtain a better understanding of the effects of amino acids on the solid-state phase transitions of ammonium nitrate (AN). To this end, AN was combined with various amino acids in equimolar ratios and the phase transitions of the resulting mixtures were studied using differential scanning calorimetry (DSC) and in situ Raman spectroscopy. Compositional analysis was also conducted using X-ray powder diffraction (XRD), and the predicted stabilities of various molecular structures were assessed via quantum calculations. DSC and Raman results indicated that L-glycine and L-alanine inhibited the solid-state phase transitions of AN. Both XRD and calculation results suggested that AN reacts with these amino acids to form nitrate salts and that clusters are also generated by interactions between these compounds.

Keywords Ammonium nitrate · Amino acids · Solid-state phase transition · Thermal analysis · DSC–Raman in situ analysis

Introduction

Ammonium nitrate (AN, NH_4NO_3) has been used as an oxidizer in energetic compositions such as gas-generating agents. It also shows promise as a propellant oxidizer because of its high oxygen balance (+20.0 %) and because it is halogen-free like hydrazinium nitroformate and ammonium dinitramide and thus may have applications in green propellants [1–13]. Although AN has the additional advantage of being inexpensive, its use in gas-generating agents and propellants is currently restricted because of its high hygroscopicity and low combustion performance. Many combinations of fuels and additives with AN have therefore been explored in attempts to improve these properties [14–27]. In the present study, we focused on a further challenge of AN: its solid-state phase transition. The phase transition of AN has been extensively investigated [28–38], and as shown in Fig. 1, it has been determined that AN has five stable polymorphic forms between -18 and 125 °C. The transition of phase V (AN_V) to phase IV (AN_{IV}) occurs at -18 °C, while the phase III (AN_{III}) to phase II (AN_{II}) and AN_{II} to phase I (AN_I) transitions take place at 84 and 125 °C, respectively.

The AN_{IV} to AN_{III} transition can occur anywhere within the range of 32 – 55 °C depending on the moisture content and thermal history of the sample. When AN is dried, AN_{IV} transitions directly to AN_{II} at approximately 52 °C, completely bypassing the AN_{III} stage. AN also undergoes an AN_{IV} to AN_{III} transition near room temperature that is associated with a drastic change in the volumes of AN particles. Repeated back and forth transitions between AN_{IV} and AN_{III} near room temperature can therefore lead to cracking in AN compositions, generating unwanted burning behavior in propellants or other formulations [14]. AN compositions meant for use as gas-generating agents in

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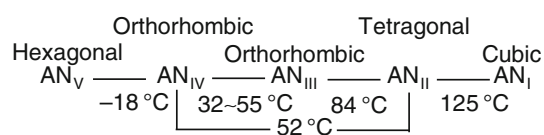


Fig. 1 The phase transition of AN

automobile air bag systems are therefore expected to be phase stabilized over the temperature range from -40 to 107 °C. To inhibit the phase transition of AN at room temperature, one method currently being used is to prepare so-called phase stabilized ammonium nitrate (PSAN) by adding a stabilizer to the AN. Potassium nitrate (KN) is considered the most suitable stabilizer for this purpose because it increases the density and oxygen balance of the resulting PSAN. However, this stabilizer also has disadvantages such as the formation of a solid residue during combustion. PSAN compositions incorporating KN are therefore no longer smokeless, so it would be desirable to identify PSAN phase stabilizers that contain only C, H, N, and O. For this reason, various organic compounds have been investigated as AN stabilizers. Nagayama et al. [28, 29] showed that polyvinyl alcohol with a polymerization degree of 400 and carboxymethyl-cellulose ammonium salt (CMCA) may act as phase stabilizers for AN. Differential scanning calorimetry (DSC) results obtained from AN with CMCA (at a mass ratio of 9:0.3) showed that no endotherms due to phase transitions were observed between 30 and 80 °C. Lang and Vyazovkin [30, 31] prepared samples of AN mixed with polyvinyl pyrrolidone (PVP) at 1:2 molar ratios, and these formulations showed no endothermic transition peaks. Ammonium ions were found to interact directly with the carbonyl oxygen while the nitrate ion centered itself above the pyrrolidone ring as a means of maximizing the proton–nitrate ion interactions. Golovina et al. [32, 33] identified several heterocyclic compounds containing carbonyl, amino, and imino groups that resulted in significant stabilization of the AN lattice. Their studies revealed that certain organic ring structures can affect the phase transitions of AN. However, the inhibitory effect of organic compounds without ring structures on the solid-state phase transitions of AN has not yet been investigated in detail.

In the present study, we selected amino acids as additives because these contain both carbonyl and amino groups and have simple structure that do not contain rings. The purpose of this work was to obtain a better understanding of the effects of amino acids on the solid-state phase transitions of AN. For this purpose, AN was mixed with various amino acids in equimolar ratios and the effects of this combination on the solid-state phase transitions were assessed using DSC and in situ Raman spectroscopy. Compositional analyses

were conducted via X-ray powder diffraction (XRD), and structural predictions were obtained through quantum chemical calculations as a means of determining the most stable molecular structures in such mixtures.

Experimental

Materials

AN, L-glycine (Gly), L-alanine (Ala), L-valine (Val), and L-aspartic acid (Asp) were obtained from Wako Pure Chemical Industries, Ltd. The physical properties of these compounds are summarized in Table 1. AN/amino acid mixtures in equimolar ratios were prepared by wet blending in a mortar following the addition of a small quantity of water. The amounts of mixture and water were 600 and 100 mg. The samples were subsequently dried under vacuum to obtain powder samples. The effects of the mixing method were assessed by also producing AN/amino acid combinations using a powder mixing method without water.

Solid-state phase transitions

The solid-state phase transition characteristics of the various AN/amino acid mixtures were determined by DSC (PerkinElmer DSC8500). During these measurements, an approximately 4 mg quantity of the sample was loaded into an open aluminum pan and subsequently heated from 30 to 180 °C at a rate of 5 K min^{-1} under air condition. The crystal structures of the AN in these mixtures during heating under these conditions were investigated by in situ Raman spectroscopy (KAISER RXN2) in conjunction with DSC (DSC–Raman). Raman spectra were obtained using a 1000 nm semiconductor laser to irradiate the sample in the pan through a glass porthole in the DSC cover. Spectra were acquired at 10 s intervals during heating, using a laser power of 400 mW with an exposure time of 1 s.

Compositional analysis

XRD patterns were acquired using a powder X-ray diffractometer (Rigaku RINT-2500). In these analyses, a 100 mg sample was transferred to a glass plate and diffraction patterns were recorded at room temperature over the 2θ range of 10° – 90° at a scanning rate of 2° min^{-1} .

Predictions of stable molecular structures

The most stable molecular structures in the AN/amino acid mixtures were determined by quantum chemical calculations

Table 1 Physical properties of AN, Gly, Ala, Val, and Asp

	AN	Gly	Ala	Val	Asp
Chemical formula	NH ₄ NO ₃	C ₂ H ₅ NO ₂	C ₃ H ₇ NO ₂	C ₅ H ₁₁ NO ₂	C ₄ H ₇ NO ₄
Molecular weight/–	80	75	89	117	133
Melting point/°C	169	232–236	297	315	270–271
Assay/%	99.0	99.0	99.0	99.0	99.0

performed using density functional theory at the ωb97xd/6-311++g(d,p) level and incorporating the effect of water as a solvent because samples were prepared in the presence of water. The Gibbs free energy values of AN/amino acid mixtures were determined using the CBS-QB3 method. All calculations were conducted with the Gaussian 09 software package [39].

Results and discussion

Solid-state phase transitions

The results of the DSC–Raman analyses are shown in Fig. 2. Figure 2a presents DSC plots obtained from both pure AN and the AN/amino acid mixtures at a heating rate of 5 K min^{−1}. These plots have been smoothed in order to reduce the effect of the Raman laser. In the case of the AN/Gly and AN/Ala mixtures, no endotherms are observed below 120 °C, while a single endotherm is seen at 90 °C for the AN/Val mixture and the AN/Asp sample has generated a single endotherm at 50 °C, just as the pure AN does. It is known that the peak associated with the completely symmetric stretching vibration of the nitrate ion appears at a different position for each AN crystal system [38]. Wu et al. [38] found that the Raman frequencies of this vibrational mode for AN_{IV}, AN_{III}, and AN_{II} were 1044, 1048, and 1054 cm^{−1}, respectively. The temperature-dependent transitions of the nitrate ion symmetric mode in the AN/amino acid mixtures and in pure AN are shown in Fig. 2b. Here, the Raman peak obtained from the pure AN shifts from 1044 to 1054 cm^{−1} at 55 °C due to the solid-state phase transition from AN_{IV} to AN_{II}. AN_{III} is not observed because AN was dried. The AN/Asp mixture exhibits a similar shift of AN. The AN/Gly and AN/Ala specimens, however, do not show a peak position change. In the case of the AN/Val mixture, two transitions are observed: from 1045 to 1047 cm^{−1} and from 1047 to 1054 cm^{−1}, at 55 and 90 °C, respectively. It therefore appears that the AN_{IV} to AN_{III} and AN_{III} to AN_{II} solid-state transitions occur in the AN/Val mixture. These DSC–Raman results demonstrate that both Gly and Ala inhibit the

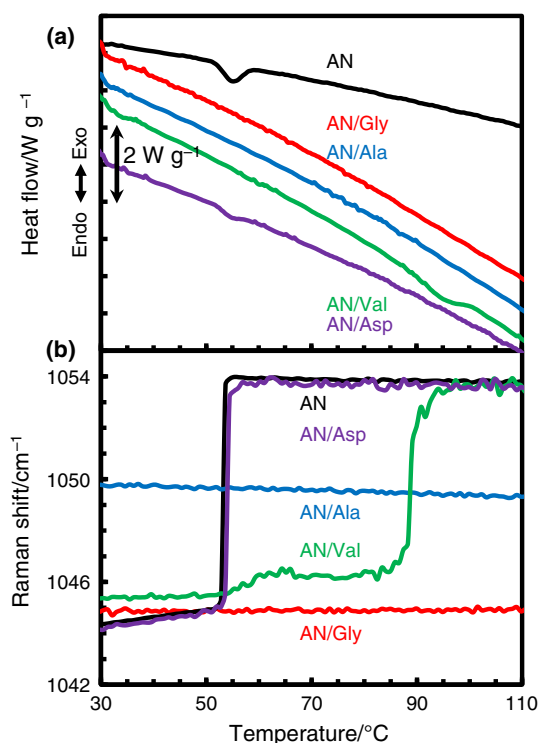


Fig. 2 DSC–Raman results: **a** DSC plots obtained from pure AN and AN/amino acid mixtures (heating rate = 5 K min^{−1}) and **b** temperature-dependent transitions of nitrate ions in pure AN and AN/amino acid mixtures

solid-state phase transitions of AN, and that the AN/Ala mixture is stable and exists in a crystal phase other than AN_{IV} because value of each Raman peak is different.

Compositional analysis

The XRD patterns of the Gly and Ala mixtures, both of which appear to have an inhibitory effect on the solid-state phase transitions of AN, are presented in Figs. 3 and 4. Figure 3 shows that the pattern for the AN/Gly mixture has new peaks appearing at 15°, 20°, 27°, and 35° compared with the patterns of pure AN and pure Gly. For XRD pattern of an AN/Gly mixture prepared without the addition of water by powder mixing, several new peaks are

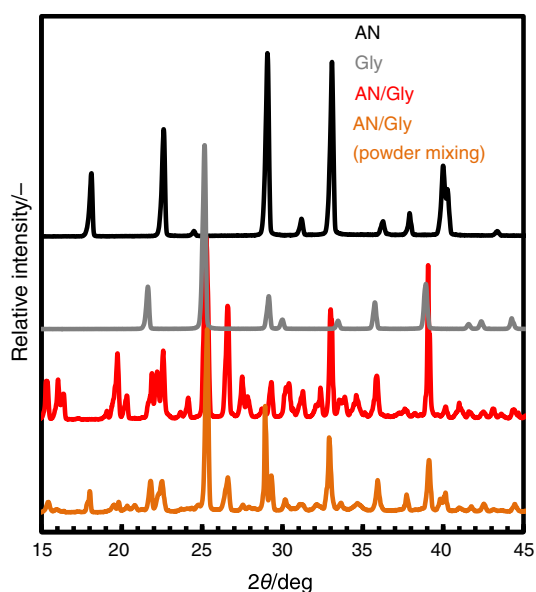


Fig. 3 XRD patterns of pure AN, pure Gly, and an AN/Gly mixtures

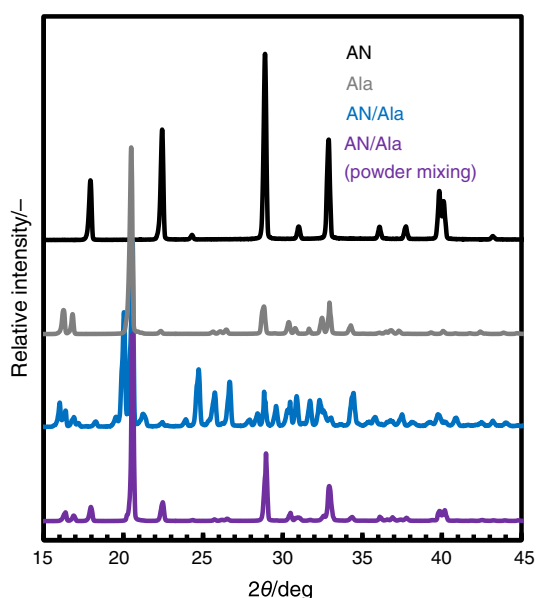


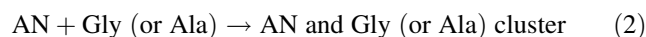
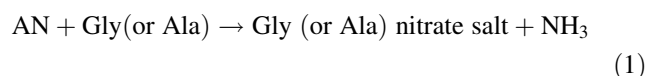
Fig. 4 XRD patterns of pure AN, pure Ala, and an AN/Ala mixtures

present, owing to the generation of a new crystal phase in the mixture, although the intensities of these peaks are lower than those in the AN/Gly mixture pattern. Likewise,

the AN/Ala mixture generates new peaks at 20°, 25°, 26°, 27°, and 30° compared with pure AN and pure Ala. In the AN/Ala mixture prepared by powder mixing, peaks of AN and Ala are observed. These results indicate that new crystal phases different from those in the original pure raw ingredients were formed in the AN/Gly and AN/Ala mixtures. It is believed that these new crystal phases inhibit the solid-state AN transition of these samples in the vicinity of 50 °C. These results suggest that more of the new crystal phase was formed as a result of interionic interaction between AN and Gly or Ala in the presence of water because AN, Gly, and Ala are ion in water. Since neither Val nor Asp are water soluble, these amino acids would not be expected to react with the AN under these experimental conditions. Previous studies of L-glycine nitrate and L-alanine nitrate [40–42] have found that the nitrate ion symmetric stretching vibration generated by glycine nitrate appears at 1044 cm⁻¹ [40], a value that is similar to the peak position obtained from both pure AN and the AN/Gly mixture in this study. In contrast, the nitrate ion peak in the spectrum of the AN/Ala mixture does not appear at the 1041 cm⁻¹ position seen in the case of the L-alanine nitrate spectrum [42]. Therefore, we believe that the AN in these mixtures reacted with the amino acids to form nitrate salts or cluster-like structures which are observed as new crystal phase in XRD patterns of the mixtures prepared by wet blending.

Predictions of stable molecular structures

The results of DSC–Raman and XRD analyses indicate that the formation of new crystal phases, such as nitrate salts or clusters, in some of the mixtures inhibits the solid-state transitions of the AN. Consequently, we developed the following two equations and used these to predict the most stable molecular structures of the AN/Gly and AN/Ala mixtures in water solvent.



These predictions were made based on calculations of the energy differences between products and reactants. Figure 5 shows the results obtained from the structural

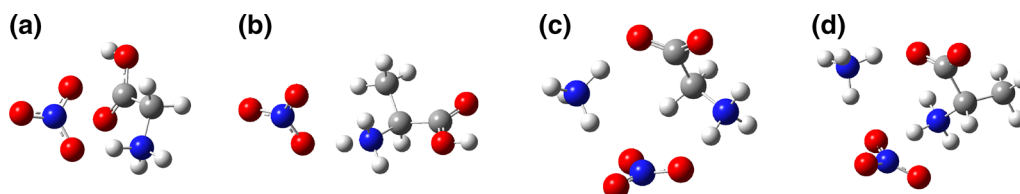


Fig. 5 Optimized structures for **a** glycine nitrate, **b** alanine nitrate, **c** an AN and Gly cluster, and **d** an AN and Ala cluster

Table 2 Stability values obtained from the differences between product and reactant energies

Energy difference (product – reactants)/kJ mol ^{−1}	
Glycine nitrate	−5.319
Alanine nitrate	10.01
AN and Gly cluster	−6.159
AN and Ala cluster	−6.120

optimization of the nitrate salts of Gly and Ala and for clusters of AN with these amino acids, using quantum calculations with density functional theory at the ωb97xd/6-311++g(d,p) level including solvation effects of water because samples were prepared in the presence of water.

The stability values for each product obtained from the difference between the product and reactant Gibbs free energies determined using the CBS-QB3 method are provided in Table 2. Negative value of the energy difference signifies that products are more stable structure than reactants.

In view of the results obtained in the case of the AN/Gly mixture, it appears that both glycine nitrate and AN/Gly clusters may form. Since the Raman spectrum of the AN/Gly mixture is similar to that of glycine nitrate, we can conclude that the Gly reacts with the AN to form both glycine nitrate and AN/Gly clusters in the AN/Gly mixture. In the case of the AN/Ala mixture, we would expect AN/Ala clusters to form rather than alanine nitrate. It seems that glycine nitrate, AN/Gly and AN/Ala clusters formed in the presence of water exist in dried powder samples. Therefore, both glycine nitrate and AN/Gly clusters as well as AN/Ala clusters evidently inhibit the solid-state phase transitions of AN. The inhibition effect of the clusters is believed to derive from intermolecular interactions between AN and the amino acids.

Conclusions

Gly, Ala, Val, and Asp were mixed with AN by wet blending to investigate the effects of these amino acids on the solid-state phase transitions of AN. These mixtures were analyzed using DSC–Raman spectroscopy to determine both the solid-state phase transition behavior and the crystal systems. The AN/Gly and AN/Ala mixtures did not generate endotherms and showed no changes in their crystal structures, indicating the absence of phase transitions. Powder XRD and quantum calculations were used to investigate the compositions and the most stable molecule structures for the AN/Gly and AN/Ala mixtures. The XRD results showed a new crystal phase inhibiting the phase transition of AN was formed in these mixtures and a

comparison with the results obtained from a powder blending mixture determined that both Gly and Ala reacted with AN in the presence of water during the initial preparation of the mixtures. The calculation results showed that both glycine nitrate and AN/Gly clusters were formed in the AN/Gly mixture, while AN/Ala clusters were present in the AN/Ala mixture. These results are not unexpected since both Gly and Ala are soluble in water, while Val and Asp are insoluble. These results lead to the conclusion that water soluble amino acids react with AN to form nitrate salts and/or clusters, both of which have an inhibiting effect on the AN solid-state phase transitions.

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