JOURNAL OF SOLID STATE CHEMISTRY 39, 154–160 (1981)

Mechanoformation of Ammonium Perchlorate–Potassium Perchlorate Solid Solutions

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Received December 4, 1980; in revised form March 18, 1981

Ammonium perchlorate–potassium perchlorate mixtures, upon pelletization, form a series of homogeneous solid solutions as manifested by X-ray powder diffractograms. Scanning electron microscopic studies throw light on the mechanism of the solid-solution formation. Solid solutions of ammonium perchlorate–potassium perchlorate have also been obtained by a modified cocrystallization technique. The thermal and combustion behavior of the solid solutions have also been studied, using the DTA technique and the Crawford strand burner.

Introduction

The interest in the synthesis of high-energy oxidizers for solid propellants resulted in the synthesis of complex metal perchlorates like $NH_4B(ClO_4)_4$, $NO_2B(ClO_4)_4$, $NH_4Al(ClO_4)_4$, $NO_2Al(ClO_4)_4$, $(NH_4)_3AlClO_4$ (*1*). Recently $Al(ClO_4)_3 \cdot 6N_2H_4$(AlPH) (*2*) has been synthesized which in principle could be used effectively as an oxidizer. Though the heats of formation and thermal reactivities of the complex metal perchlorates and hydrazine complexes are best suited for propellant applications, their incompatibility with other ingredients of the propellant and sensitivity to shock pose several problems as regards their applications in solid propellants.

Another approach to obtain an oxidizer with high heats of formation would be the synthesis of solid solutions with the existing metallic or nonmetallic perchlorates. Metal perchlorates form solid solutions at high temperatures (*3*). Such solid solutions are: $LiClO_4$–$NaClO_4$, $NaClO_4$–$Ca(ClO_4)_2$, $LiClO_4$–$Ca(ClO_4)_2$, $Ba(ClO_4)_2$–$Ca(ClO_4)_2$, $KClO_4$–$Ba(ClO_4)_2$, and $KClO_4$–$Ca(ClO_4)_2$. But solid solutions involving a nonmetallic perchlorate like NH_4ClO_4 (*AP*), which is the workhorse oxidizer of solid propellants, have not been synthesized. The reasons could be that *AP* does not melt and decomposes to 100% at a temperature much lower than the melting point of any metallic perchlorate. Recently, Lengelle *et al.* (*4*) observed an increase in the pressure exponent of a propellant, when 10% of $KClO_4$ (K*P*) coprecipitated with 90% *AP* was used as an oxidizer instead of pure *AP*. (Pressure exponents of propellants containing *AP* and 90% *AP* coprecipitated with 10% K*P* are 0.35 and 0.73, respectively.) They do not give the details of the coprecipitation tech-

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0022-4596/81/110154-07$02.00/0

nique and the effect of K*P* on the thermal behavior of *AP* is also not known. Attempts to coprecipitate K*P* with *AP* in this laboratory resulted in K*P* crystallizing first. An X-ray diffractogram of the coprecipitated substance indicated that it is a physical mixture of *AP* and K*P*. This is because of the wide difference in the solubilities of *AP* and K*P* in water (giving rise to crystallization of K*P* initially).

While the solubility of K*P* restricts the formation of solid solutions by cocrystallization from an aqueous medium, the decomposition behavior of *AP* leaves K*P* alone at high temperatures, posing a threat to the synthesis of *AP*–K*P* solid solutions. Synthesis of solid solutions of *AP*–K*P* would therefore have to wait for newer techniques or concepts. One such concept has been successfully translated into practice in the case of the KCl–KBr mixtures with the application of pressure to the two ingredients (*5*). The object of the present work is to explore the possibility of obtaining solid solutions by applying pressure to *AP*–K*P* mixtures.

Experimental

AP and K*P* used in the present work were reagent grade materials obtained from Veb Laborchemie, Apolda, and Riedel-Hannover, respectively. The powders (as received) were ground and passed through a 400 ASTM sieve ($<37\ \mu m$). The average particle sizes of *AP* and K*P* were found to be 11 and 24 μm, respectively.

The powders were thoroughly mixed in the desired ratio, and a pellet was made using a hydraulic press. A predetermined pressure was applied in an identical manner on a fixed weight, i.e., on 20 g of the sample to make a 5-cm-diameter cylindrical pellet. Applied pressure was 1500 kg/cm^2 with an uncertainty of 10 kg/cm^2. The pressure was maintained for 5 min on the sample.

For cocrystallization of *AP*–K*P*, the required quantity of K*P* was dissolved in hot water. The temperature of the water was maintained at around 70°C. To the K*P* solution, the required amount of *AP* was added and stirred thoroughly. The solution was heated almost to dryness, then was dried at room temperature. The moisture-free sample was ground to $<37\ \mu m$. (Mere grinding of *AP* and K*P* powders together does not give a solid solution.) The standard procedure adopted for coprecipitation is to take *AP* and K*P* in the desired ratio and dissolve in water. It is heated till all of the solid completely dissolves, and is then cooled. When cocrystallization was attempted in this manner, K*P* crystallized out first, as indicated earlier.

Burning rates of the inhibited strands were measured in a conventional Crawford strand burner at 60 kg/cm^2 nitrogen pressurization and hot-wire ignition. Strand dimensions were $L \times 5$ mm $\times$ 5 mm, where L varies from 28 to 44 mm. Each burning rate was an average value of at least five different strands prepared under identical conditions. The uncertainty in the burning rate lies within ± 0.3 mm.

Differential Thermal Analysis (DTA) of the samples was carried out in air on a home-made apparatus. The DTA assembly was housed in a tubular quartz furnace which was programmed to a constant heating rate of 10°C/min. Platinum cups were used as holders for the sample and for the reference, which was powdered, ignited alumina. The DTA curves were recorded on an "Omniscribe" two-pen recorder with an amplifier in circuit. In each case 52.5 mg of the sample was taken. Each experiment was carried out at least twice to ensure reproducibility. The uncertainty in the peak temperature was ±1°C. Some experiments were carried out on an automatic Universal DTA-02 (East Germany) instrument and demonstrated close agreement in the shapes and peak temperatures of the DTA curves.

X-Ray diffractograms were taken on a Philips unit with a vertical goniometer arrangement. The patterns were recorded with a copper tube run at 30 kV and 20 mA, a nickel filter was used. The diffraction peak profiles were obtained by step-scanning ($\frac{1}{4}$°/min) and taking the number of counts for 4 sec. The peaks thus obtained were recorded on a recorder at a very high chart speed. In the case of the pelletized samples, the 5-cm-diameter pellet was broken into two pieces and one piece was used for obtaining the diffractogram. In the case of powders, ground powders (<37 μm) were taken as such for X-ray studies.

Surface structural studies were undertaken with a Cambridge Stereoscan—150 model scanning electron microscope (SEM). Samples were coated with gold prior to examination under SEM.

Results and Discussion

In the X-ray diffractograms of *AP*-K*P* pressed compacts (Fig. 1) the individual reflections of *AP* and K*P* were present in 20 and 40% K*P* compacts but not in 50, 60, and 80% K*P* compacts. The number of reflections that were present in compacts containing 50% or more of K*P* was equal to that of either of *AP* or K*P* reflections, with 2θ values inbetween those of *AP* and K*P*.

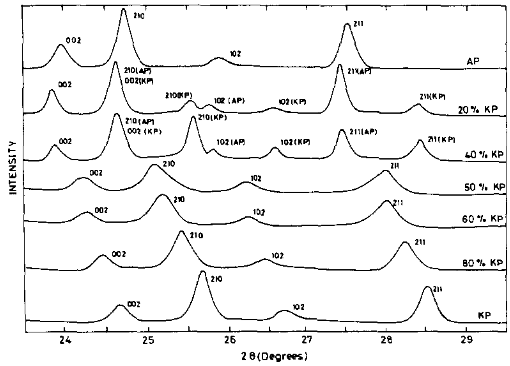

FIG. 1. X-Ray diffractograms of pelletized *AP*, K*P*, and *AP*-K*P* mixtures.

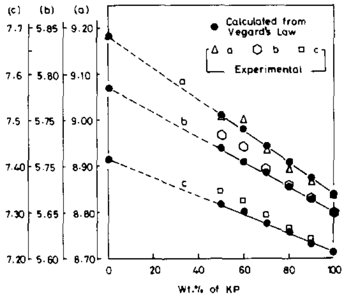

FIG. 2. Variation of lattice parameters in *AP*-K*P* solid solutions on pelletization.

This is indicative of the formation of a series of homogeneous solid solutions from 50% K*P* upward. Also noticeable is the fact that the widths of the reflections increase due to the strains developed in forming homogeneous solid solutions. Lattice parameters of *AP*-K*P* solid solutions obtained from X-ray diffractograms, and those calculated from Vegard's Law are presented in Fig. 2. The agreement between experimental and calculated values is good in the range of solid solution formation. *AP* and K*P*, together crystallize into an orthorhombic structure because of their similarities in crystal structures (orthorhombic), valencies (NH_4^+(+1); K^+ (+1)) and ionic sizes (NH_4^+, 1.48 Å; K^+, 1.33 Å).

The reflections of 40% K*P* occurred at relatively higher 2θ values in relation to 10, 20, and 30% K*P*, but much lower 2θ values compared to pure K*P*. It is evident from the nature of the peaks that stresses and stacking faults are increasing in *AP* and K*P* crystals. The increase could be due to the friction between *AP* and K*P* particles. The 40% K*P* pellet does not form a homogeneous solid solution but the formation of a heterogeneous solid solution cannot be ruled out.

Surface examination of *AP*-K*P* pellets under SEM revealed that the surface structures of pellets containing 50% or more of K*P* (up to 90%) were entirely different from that of *AP*, 10% K*P*, 30% K*P*, and K*P*. Figure 3 gives the SEM micrographs of *AP*, 50% K*P*, 70% K*P*, and K*P*. The micrographs of 50 and 70% K*P* indicate an incipient melting near the grain boundaries facilitating interdiffusion of *AP* and K*P*. Thus it is evident that solid solution formation has started near the grain boundaries and, at places, has extended even to the surface. These pictures indicate the presence of two phases in the pellet; however, the X-ray diffractograms of 50, 60, 70, 80 and 90% K*P* do not show any evidence of a two-phase mixture. It is difficult to give any valid reason for the presence of a physical mixture (on compaction) at low K*P* contents (up to 40% of K*P*) in the absence of an equilibrium diagram of *AP* and K*P*.

An analysis of the DTA curves (Fig. 4) of *AP*, K*P*, and *AP*–K*P* pellets indicates that the *AP*–K*P* pellets show a single phase transition from orthorhombic to cubic at a temperature characteristic of the composition of the pellet. On the other hand, DTA runs of a mixture of *AP* and K*P* powders (in the required proportions) give two peaks, one corresponding to each ingredient. Also the exotherms of *AP* are sensitized markedly, moreso in the case of the 60 and 90% K*P* samples. Another interesting feature of *AP*–K*P* pellets is that the temperatures of melting and subsequent decomposition of K*P* decrease. As the *AP* content in the pellet decreases, the temperatures of melting and subsequent decomposition increase toward that of pure K*P*. This effect is seen even in the DTA's of mixtures of *AP* and K*P* powders. Thus it can be concluded that

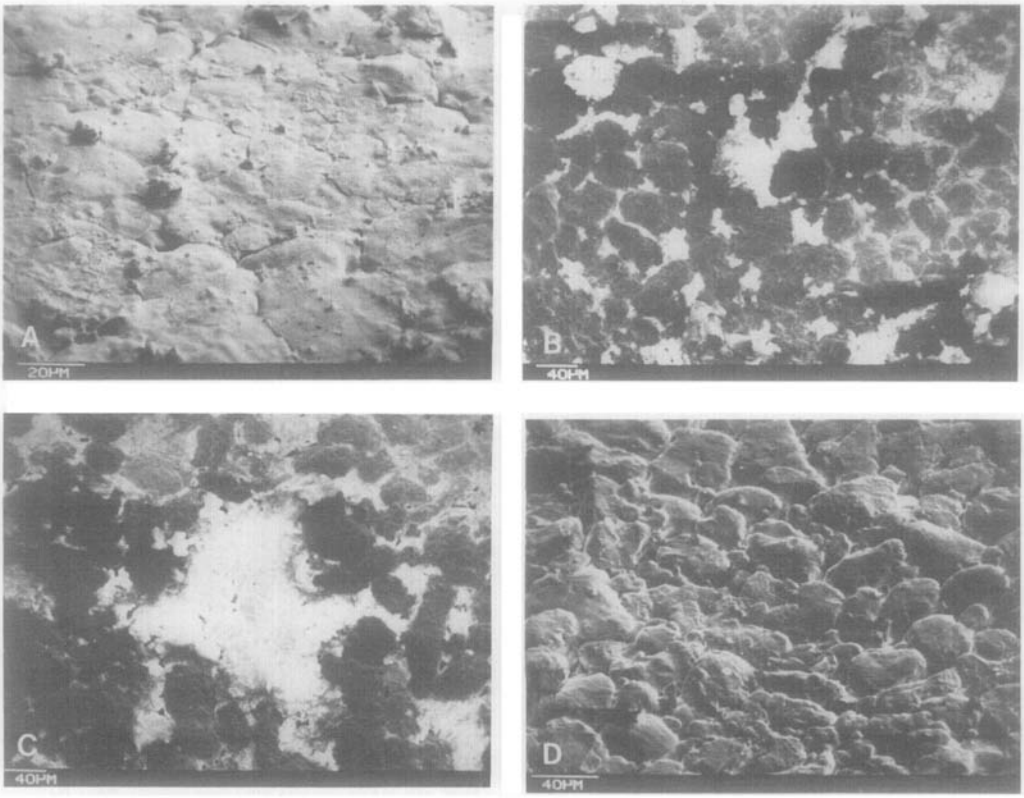

FIG. 3. SEM photographs of (A) *AP*, (B) 50% K*P*, (C) 70% K*P*, and (D) K*P* pellets.

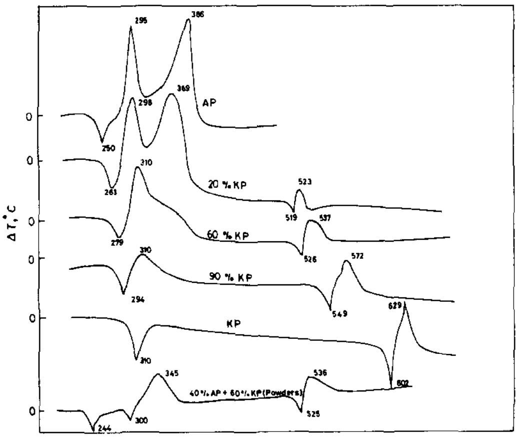

FIG. 4. DTA curves of pelletized *AP*, *KP*, and *AP*–*KP* mixtures.

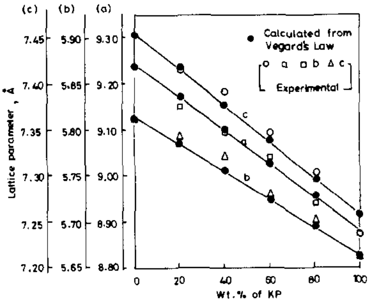

FIG. 6. Variation of lattice parameters in *AP*–*KP* solid solutions with cocrystallization.

the decomposition products of *AP* sensitize the thermal decomposition of *KP*.

In short, application of pressure to a mixture of *AP* and *KP* has resulted in the formation of solid solutions of *AP*–*KP* having characteristic X-ray patterns, SEM micrographs, and DTA peaks. During compression, solids slide together and at locally restricted points (grain boundaries) the temperature rises to an extremely high value. It is known that at the points of contact the temperature could increase to the melting point of a substance but never rise above it (*6*). Therefore, compression at 1500 kg/cm^2 for 5 min causes melting of *KP* at interfaces, as is observed in SEM micrographs. Since the lifetime of these temperatures is of the order of microseconds (*6*), melting of the whole pellet is not possible (Note: *AP* does not melt). These localized high temperatures facilitate interdiffusion, which results in the formation of a homogeneous solid solution. Decomposition of *AP* at interfaces cannot be ruled out at these locally high temperatures. In the case of low *KP* contents (a) the applied pressure and dwell time may not be sufficient for bringing about mutual dissolution, (b) the limited *AP*/*KP* interface region may restrict the formation of solid solutions, or (c) a critical concentration of *KP* is needed.

While formation of solid solutions on application of pressure is restricted to only a few compositions, it can be brought about

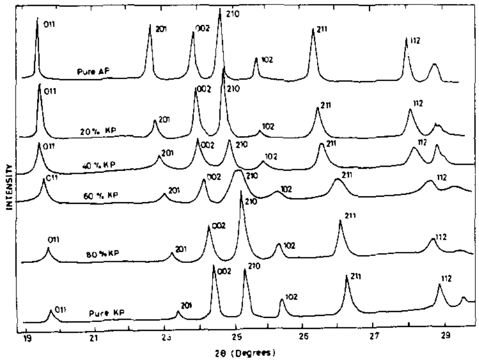

FIG. 5. X-Ray diffractograms of crystallized *AP*, *KP*, and cocrystallized *AP*–*KP* mixtures.

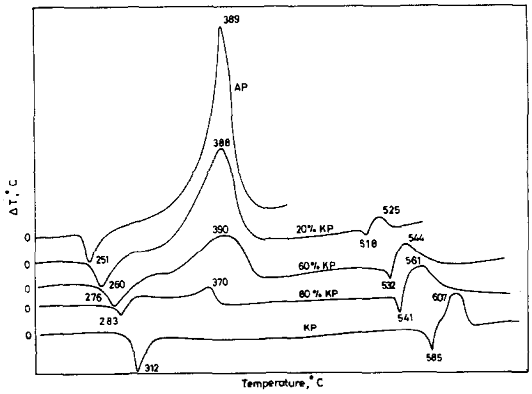

FIG. 7. DTA curves of crystallized *AP*, *KP*, and cocrystallized *AP*–*KP* mixtures.

in a convenient manner by cocrystallizing *AP* and K*P*, as described in the Experimental section. Cocrystallization in this manner forms a series of homogeneous solid solutions, as indicated in Fig. 5. That solid solutions are indeed formed can be deduced from the variation of lattice parameters. The variation is linear, obeying Vegard's Law (Fig. 6). A point to be noted is that cocrystallization in the usual manner does not yield solid solutions, whereas cocrystallization taking the solution to dryness has resulted in a series of homogeneous solid solutions. This is because of the fast evaporation of water.

Lattice parameters of *AP* and K*P*, indicated in Fig. 6, agree well with the values reported in X-ray powder diffraction files (*7*). Comparison of Figs. 2 and 6 indicate that lattice parameters of pelletized *AP*, K*P*, and *AP*-K*P* differ considerably from those of cocrystallized samples. This is due to the strains and dislocations developed on compaction of *AP*, *AP*-K*P*, and K*P* powders. These strains have energies characteristic of dislocations and a stress field exists around each dislocation. These dislocations and stress fields enhance the thermal decomposition of *AP*, as indicated in Fig. 4.

In the absence of intentionally created dislocations, thermal decomposition of *AP* does not alter even with the addition of K*P*. In the DTA curves of cocrystallized *AP*-K*P* powders (Fig. 7) the peak temperatures of *AP* are unaltered (except for 80% K*P*, in which a smaller amount of *AP* is present) from pure *AP* value, all the curves showing only one exotherm.

A study was also conducted on the combustion characteristics of solid solutions of *AP*-K*P* obtained by pelletization. The results presented in Fig. 8 clearly indicate that as the K*P* content in the *AP*-K*P* pellet increases, the burning rate also increases until the *AP* concentration reaches 30%. At this stage the burning rate decreases. On further increase of K*P* concentration, one notices a partial burning of the pellet, and finally the burning ceases. It is interesting to note that the *AP*-K*P* composition which ceases to burn is also the one which brings about the single-phase solid solution. However, this could be just a sheer coincidence because the oxidizer to fuel ratio increases drastically in that composition range. The increase in the burning rate of *AP*-K*P* composite up to 30% K*P* content is in tune with the results of Lengelle *et al.* (*4*), who used 90% *AP* coprecipitated with 10% K*P* (instead of pure *AP*) and reported an increase in the propellant burning rate, which has, in addition to *AP* and K*P*, a polymeric binder carboxyterminated polybutadiene.

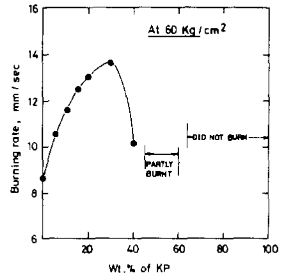

FIG. 8. Variation of burning rate with K*P* content.

Acknowledgment

This work has been supported by a grant from the Indian Space Research Organization (ISRO), which provides financial support to one of the authors (D. Seetharamacharyulu). This assistance is gratefully acknowledged.

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