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Effect of prior Mechanical and Thermal Treatment on the Thermal Decomposition of Orthorhombic Ammonium Perchlorate

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The effect of prior mechanical and thermal treatment on the isothermal decomposition of ammonium perchlorate has been studied in the temperature range 215–235°C. Prior compression or heating of the material is seen to result in a lengthening of the induction period and a decrease in the decomposition rate. The final extent of the decomposition also decreases from the usual 30% to ~20% for the materials subjected to prior treatment. A significant correlation is observed between the effects of prior treatment on the thermal reactivity and the broadening observed in the X-ray diffraction patterns and the infrared spectra of the materials subjected to prior compression and heating.

1. Introduction

In recent years, a lot of attention has been focused on the role of crystal imperfections in the thermal decomposition of metastable solids (*1–8*). Thus, changes in the thermal reactivity of solids induced by preirradiation, grinding, or, in general, any mechanical treatment have been explained in terms of gross imperfections like dislocations. That dislocations result from mechanical treatment or cold-working is a well-documented fact. However, in decomposable materials there are very few instances where intentionally created imperfections have been characterized well. In ammonium perchlorate (AP), Raevskii et al. (*9*) showed that dislocations are associated with growth defects and points of mechanical damage. They also found that the dislocation density is extremely sensitive, even to slight mechanical disturbance. Direct observations of dislocations in AP have been made by Jacobs et al. (*10*) and by Thomas et al. (*11*). However, no systematic attempt has been made to study the effect of imperfections created by prior treatment of the material on its subsequent decomposition kinetics.

The objectives of the present work are to investigate the effects of prior mechanical and thermal treatment on (1) the X-ray diffraction and the infrared (ir) absorption of AP, (*2*) the kinetics of the thermal decomposition of orthorhombic AP, and (3) to seek a correlation, if any, between the observed effects of prior treatment on the X-ray diffractograms and the ir spectra and the thermal reactivity of orthorhombic AP.

2. Experimental

AP (analytical grade) supplied by Fluka, Switzerland, was used as received in all the experiments. The material was crushed in a mortar (circular motion of the pestle was always avoided) and sieved to the particle size range 149–177 μm. Precompression of the materials was effected as follows: About 200 mg of the powdered material was taken in a stainless-steel die and then compressed in a hydraulic pellet press. The applied pressure was read on a calibrated gauge. The pellet was dismantled and lightly ground and sieved to the same particles size as the uncompressed material. All experiments on precompressed

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AP were thus carried out in the powdered form. Since it has been shown that ageing has an effect on the thermal reactivity of AP (*12*, *13*), care was taken to see that all experiments were carried out on the same day as the pretreatment. The material was weighed before and after the pelleting process to check whether any mechanodecomposition (*14*) had taken place. There was no weight loss corresponding to decomposition during the pelleting process.

Thermogravimetric analysis (TGA) was carried out on a conventional McBain–Baer-type quartz spring balance (*15*). Samples were heated in a tubular quartz furnace whose temperature was maintained to ± 1°C of the required temperature. A convenient sample size for decomposition studies was found to be 50 mg

The ir spectra were taken in Nujol mull on a Carl Zeiss UR 10 spectrophotometer.

X-ray diffraction patterns were taken on a Phillips diffractometer with specimen spinner and pulse-height discriminator. The patterns were recorded with a copper tube run at 50 kV and 20 mA using a nickel filter and 1° divergence, scatter, and 0.006-in. receiver slits. The diffraction peak profiles were obtained by step-scanning and taking the number of counts for 40 sec. The peaks thus obtained represented the intensity as a function of the diffracrion angle (in 2θ). For studies on line-broadening, the observed line breadths (B_0) were corrected for $K\alpha$ doublet separation by means of the equation:

$$\Delta = 0.285 \tan \theta_{\mathrm{av}} \qquad (1)$$

derived by Rosauer and Handy (*16*) for copper Kα radiation. The ratio Δ/B_0 was calculated and a graphical correction applied. The instrumental broadening (b) was determined at various angles using pure BeO as the reference standard. The pure diffraction breadths (β) were obtained from the corrected peak breadths (B) and the instrumental broadening by the graphical method outlined by Alexander (*17*).

Preheating was carried out by maintaining the material in an air-oven at the required temperature. The samples were always stored in powder form over phosphorus pentoxid at room temperature.

3. Results

3.1. *Effect of prior Mechanical and Thermal Treatment on the X-Ray Diffraction and ir Absorption of AP*

Figure 1 shows typical X-ray diffraction peak profiles of AP and AP precompressed at 200 kg/cm^2. The observed linewidths at half-maximum intensity B_0, the line widths corrected for $K\alpha$ doublet separation B and the pure diffraction linewidths β obtained after correcting for instrumental broadening for the different peaks are summarized in Table I. It can be seen that the 101, 002, 211, and 202 peaks are broadened as a result of precompression. The peak positions, however, are not altered significantly. A broadening of the diffraction peaks is again evident in the case of the pre-heated material.

Figure 2 shows the ir spectra of AP and AP subjected to different pelleting pressures. It is evident that there is a pronounced broadening of the absorption peaks in the case of the precompressed samples. Furthermore, the extent of broadening of the absorption peaks (or the half-width change with respect to uncompressed AP) seems to show a regular increase with an increase in the applied pelleting pressure (shown in Fig. 3). A broadening

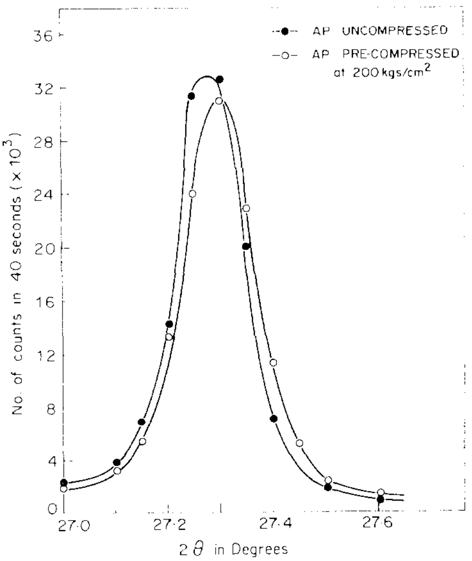

FIG. 1. Typical X-ray diffraction peak profiles of AP and AP precompressed at 200 kg/cm^2.

TABLE I

EFFECT OF PRIOR COMPRESSION ON THE X-RAY DIFFRACTION PEAK PROFILES OF AMMONIUM PERCHLORATE (AP)

		Peak widths					
		AP			AP precompresed at 200 kg/cm^2		
d (Å)	$h\,k\,l$	B_o	B	β	B_o	B	β
5.764	1 0 1	0.120	0.108	0.050	0.140	0.129	0.077
4.580	0 1 1	0.190	0.177	0.131	0.200	0.188	0.143
3.912	2 0 1	0.150	0.128	0.072	0.150	0.128	0.072
3.719	0 0 2	0.160	0.139	0.083	0.190	0.171	0.123
3.610	2 1 0	0.120	0.088	0.025	0.120	0.088	0.025
3.250	2 1 1	0.140	0.108	0.048	0.160	0.131	0.076
2.961	1 1 2	0.150	0.113	0.052	0.160	0.125	0.068
2.898	2 0 2	0.190	0.160	0.106	0.240	0.214	0.167

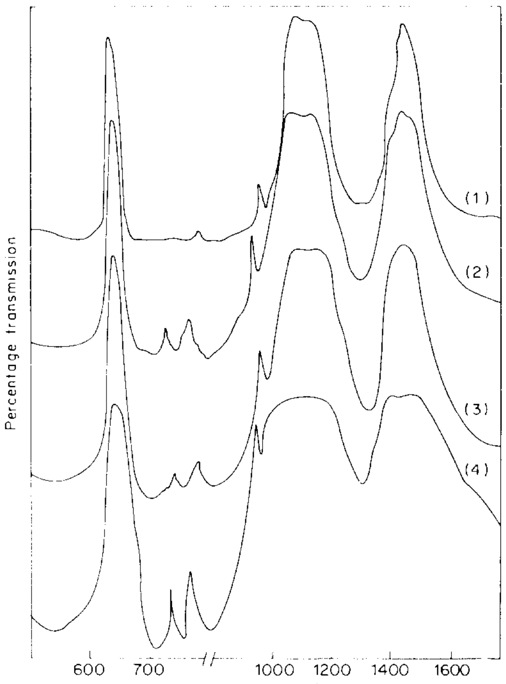

FIG. 2. Infrared spectra of AP and of AP precompressed at different pelleting pressures: (1) Uncompressed material. (2) AP precompressed at 100 kg/cm^2. (3) AP precompressed at 200 kg/cm^2. (4) AP precompressed at 350 kg/cm^2.

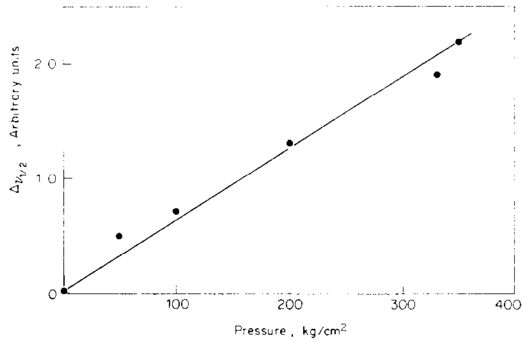

FIG. 3. Variation of the half-width change of the ν_3 absorption band (1111 cm^{-1}) with the pelleting pressure.

of a similar nature, though the extent of broadening is much less, is observed in the ir spectrum of AP preheated at 110°C for 24 hr.

3.2. *Effect of Precompression and Preheating on the Kinetics of Thermal Decomposition*

Figure 4 shows the results of the isothermal decomposition at 235°C of AP and AP precompressed at different pelleting pressures. The data on the precompressed samples reveal that (1) the induction period (arbitrarily taken as the time for 2% decomposition) has increased, the decomposition rate (taken as the

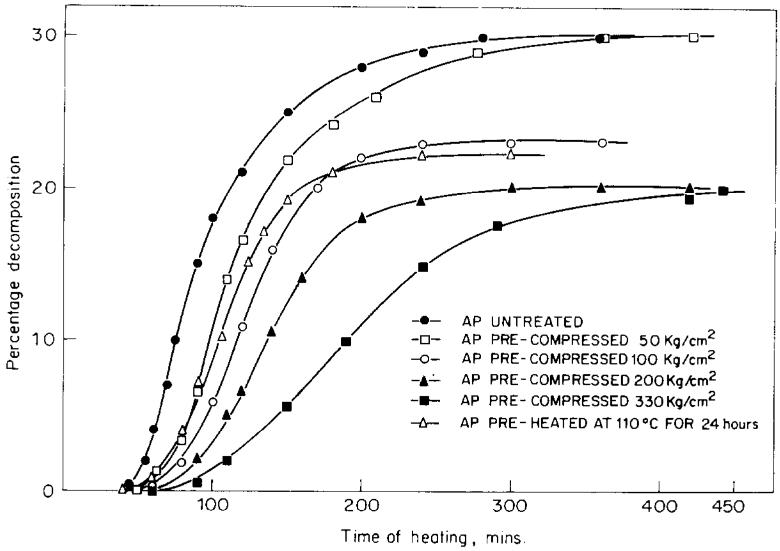

FIG. 4. Isothermal decomposition (235°C) in air of AP, AP precompressed at different pelleting pressures and of AP preheated at 110°C for 24 h.

slope of the linear portion of the α–t curves) has decreased and, more significantly, the final extent of decomposition has decreased from the usual 30% in the case of untreated AP to 20% for AP precompressed at 330 kg/cm^2. The variation of the three parameters, namely, induction period, decomposition rate, and final extent, of the decomposition with the pelleting pressure is shown in Fig. 5.

The α–t curves were fitted to various kinetic equations. The Avarami–Erofeyev equation (*18*)

$$-\ln(1-\alpha)^{1/n} = kt \qquad (2)$$

with $n = 4$ was found to give the best fit in the range $\alpha = 0.01$ to $\alpha = 0.7$. The calculated rate constants for AP precompressed at various pelleting pressures and for AP preheated at 110°C are listed in Table II. These rate constants can be seen to vary with the applied pressure. Also presented in Table II are the rate constants at various temperatures for AP and AP precompressed at 200 kg/cm^2. The activation energies determined from the temperature dependence of the rate-constants were 30 ± 2 kcal/mole for both uncompressed and precompressed samples. The effect of

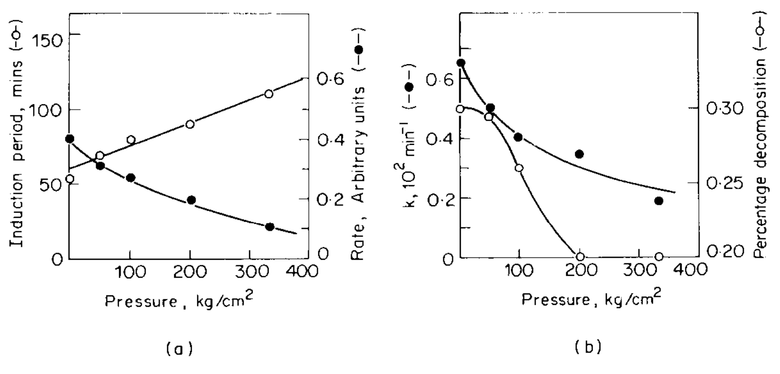

FIG. 5. Variation of the induction period, decomposition rate, rate constant and the final extent of the decomposition at 235°C with the pelleting pressure.

TABLE II

KINETIC DATA ON AP AND ON AP SUBJECTED TO PRIOR COMPRESSION AND HEATING

Temperature (°C)	Rate constants (10^2 min^{-1})	
	AP 0[a]	AP 200
215	0.15	0.10
228	0.35	0.25
235	0.65	0.35

	AP 0	AP 50	AP 100	AP 200	AP 330	AP 110[b]
235	0.65	0.50	0.40	0.35	0.19	0.45

[a] The number indicates the pressure, in kilograms per square centimeter, at which the sample was precompressed.

[b] AP preheated at 110°C for 24 hr.

preheating AP at 110°C for 24 hr on its subsequent isothermal decomposition at 235°C is similar to that observed on precompressed AP.

3.3. Correlation of the Thermal Reactivity of Pretreated AP and the Observed Effects on ir Absorption

The broadening in the ir bands observed on subjecting AP to precompression and preheating is a combined effect of all sorts of imperfections created by the pretreatment. The change in the thermal reactivity of the pretreated materials does not necessarily involve all the imperfections. Surprisingly enough, an analysis of the data reveals the possibility of a correlation between the change in the thermal reactivity (as determined by the change in the rate constants) and the broadening of the ir bands (determined by the change

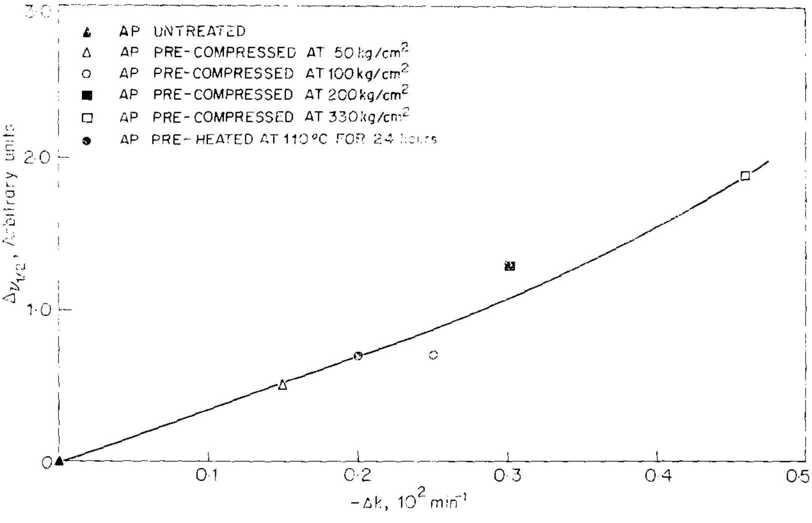

FIG. 6. Correlation of the ir peak half-width change ($\Delta\nu_{1/2}$) with the change in the rate constant for the isothermal decomposition at 235°C ($-\Delta$k) for the precompressed and the preheated samples.

in half-width with respect to untreated AP). This is shown in Fig. 6. The correlation is remarkably good. It is particularly significant that the points for the preheated material fall on the same curve as those for the precompressed samples.

4. Discussion

The present investigation has used the broadening of the X-ray diffraction peaks and the ir absorption bands as an indication of the creation of gross imperfections like dislocations in AP as a result of prior mechanical or thermal treatment. This is not unreasonable considering that dislocations give rise to a broadening of the X-ray diffraction peaks (*19*). The broadening observed in the present investigation is similar to that observed by Bogardus and Roy (*20*) on grinding and pelleting $BaTiO_3$. Broadening of the ir bands has been observed by Baker (*21*) on pressing pellets under pressure. This has been attributed to the fact that the material is recrystallizing from a disordered or a strained state to an ordered state. This together with the direct observations of Jacobs et al. (*10*) that straining an AP crystal by compression produces nuclei which are strongly aligned on the *m* and *c* faces makes us believe that the broadening observed in the X-ray diffraction peaks and the ir spectra is a direct consequence of an increase in the dislocation density resulting from the pretreatment.

The data presented in Figs. 1 to 6 clearly indicate that both precompression and preheating lead to the formation of gross imperfections in AP. Further, the extent of disorder in the materials bears a direct relationship to the pelleting pressure. Significantly enough, the desensitization of the thermal decomposition as a result of the pre-treatment also bears a simple relationship to the applied pressure (Figs. 3 and 5), and therefore, to the extent of disorder (Fig. 6). It is noteworthy that this relationship holds good irrespective of whether the effect is brought about by preheating or precompression. The effects of precompression are observed only when the pressure is applied isostatically. Precompression of the sample under hydrostatic conditions (in the presence of a pressure-transmitting medium) does not result in any of the observed effects. This seems to show that only anisotropic stresses brought about by uniaxial compression play a significant role.

Osada and Kakinouchi (*22*) have reported that AP freshly recrystallized from an acid solution or from water shows a number of defects and the rate of thermal decomposition of the freshly recrystallized material is lower than that of the "normal" material. Our observations on pretreated AP also show that although the dislocation density increases, the decomposition is desensitized. The identity of the activation energies for the thermal decomposition of untreated and pretreated AP precludes the possibility of any change in the mechanism as a result of the pretreatment.

The reasoning based on the topochemistry of AP decomposition seems to give an insight into the phenomenon. Raevskii and Manelis (*23*) have shown that decomposition centres in orthorhombic AP consist of a large number of spherical nuclei, each center being formed by the aggregation of several nuclei within the immediate neighborhood of the nuclei. If dislocations hinder the aggregation of the nuclei, then this would result in a decrease in the decomposition rate. Jacobs et al. (*10*) have shown that straining an AP crystal by compression produces nuclei which are strongly aligned on the *m* and *c* faces. This sort of alignment can hinder the aggregation process and further decrease the number of growth nuclei at low temperatures. This would not only lead to a desensitization of the thermal decomposition but also to a reduction in the final extent of the decomposition.

It must be pointed out that the observed effects of precompression and preheating disappear on heating the sample to 250°C and cooling it back to room temperature. The broadening observed in the ir spectra of the pretreated materials also disappears on subjecting them to thermal cycling. Thermal cycling, in all probability, results in an annealing of the imperfections.

In conclusion therefore, the thermal decomposition kinetics of orthorhombic AP is markedly dependent on the thermal and mechanical history of the material. Precompression and preheating of AP result in a pronounced broadening of the X-ray diffraction peaks and the ir absorption bands. These broadening effects show a significant correlation with the observed effects of prior mechanical and thermal treatment on the decomposition kinetics.

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