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Effect of precompression on the thermal stability of solids

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Abstract

Thermal decompositions of precompressed and uncompressed samples of $KBrO_3$, $KMnO_4$ and NH_4ClO_4 have been studied by thermogravimetry under isothermal conditions in static air. The rate of decomposition increased with increase in the applied pressure in the case of the last two solids, but the rate dramatically decreased in the case of $KBrO_3$. The results indicate that precompression generally sensitizes electron transfer reaction as a result of an increase in the dislocation density, whereas it desensitizes diffusion-controlled reactions as a result of the densification of solid matrix. The method of precompression is suggested as a quick and simple tool for testing whether a decomposition reaction is diffusion controlled or not. © 1997 Elsevier Science B.V.

Keywords: Thermal stability; Precompression; Densification; Electron transfer; Diffusion

1. Introduction

Information on the effects of pretreatments like doping, precompression, preheating, irradiation etc. on the kinetics of decomposition of solids provides a deep insight not only into the topochemistry but also into the mechanism (rate-controlling step) of solid-state reactions. With this view, effect of precompression on the thermal stability of $KBrO_3$, $KMnO_4$ and NH_4ClO_4 has been studied in this investigation.

2. Experimental

2.1. Materials

AR grade samples of the above solids were used in this study.

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2.2. Method

Precompressed samples were prepared by the following procedure. About 2 g of the powdered solid (with fixed particle size – $KBrO_3$: 106–150 μm, $KMnO_4$: 90–106 μm, NH_4ClO_4: 90–106 μm) was taken in a 13 mm steel die and compressed to a known pressure (P) in a hydraulic press (Specac Kent, England) and kept at this pressure for one minute. The pellet formed was removed, broken gently and the particle size was again controlled to the original value before subjecting to decomposition. The pelleting pressure applied lied in the range 0 to 14×10^7 N m^{-2}.

The precompressed and uncompressed samples of $KBrO_3$, $KMnO_4$ and NH_4ClO_4 were decomposed under isothermal conditions in static air at 668, 513 and 473 K, respectively in a manually operated thermogravimetry unit similar to the one used by Hooley [1]. The fraction of the solid decomposed (α) was measured as a function of time (t). The sample size used for each analysis was 50 mg. The compressed samples were decomposed soon after the compression procedure was completed in order to avoid any possible removal of the compression effect by ageing.

3. Results

Typical α vs. t curves of the decompositions are shown in Fig. 1. The α–t data were fitted to the various solid-state kinetic equations by the method of weighted least squares as described elsewhere [2] and the best rate laws describing these decompositions were determined. We found that no single kinetic equation described satisfactorily the whole range of decomposition (α=0 to 1) with a single rate constant. Either the same rate law with different rate constants for the initial (α=0 to 0.5) and final (α=0.5 to 1) regions of the decomposition (as in the case of $KBrO_3$ and NH_4ClO_4) or different rate laws themselves for these two regions (as for $KMnO_4$) existed, though the rate law(s) obeyed by a given solid is not affected by precompression. This type of experience is not uncommon in the study of solid-state reactions as can be seen from the literature [3–5]. Generally, the initial region of the reaction is associated with the formation and growth of nuclei and the final region with the decay of the growing nuclei as a result of their overlap. Thus it is not unlikely that these two regions follow different kinetics as we see here. The rate laws governing the initial region of the decompositions considered in this investigation are given in Table 1. The values of rate constants (k), which are taken as a measure of reactivity, are presented in Table 2 as a function of pelleting pressure.

Precompression sensitized the decompositions of $KMnO_4$ and NH_4ClO_4, whereas it dramatically desensitized the decomposition of $KBrO_3$ revealing the operation of a very complex phenomenon. For instance, the rate increased by ca. 118 and 418% respectively when $KMnO_4$ and NH_4ClO_4 samples

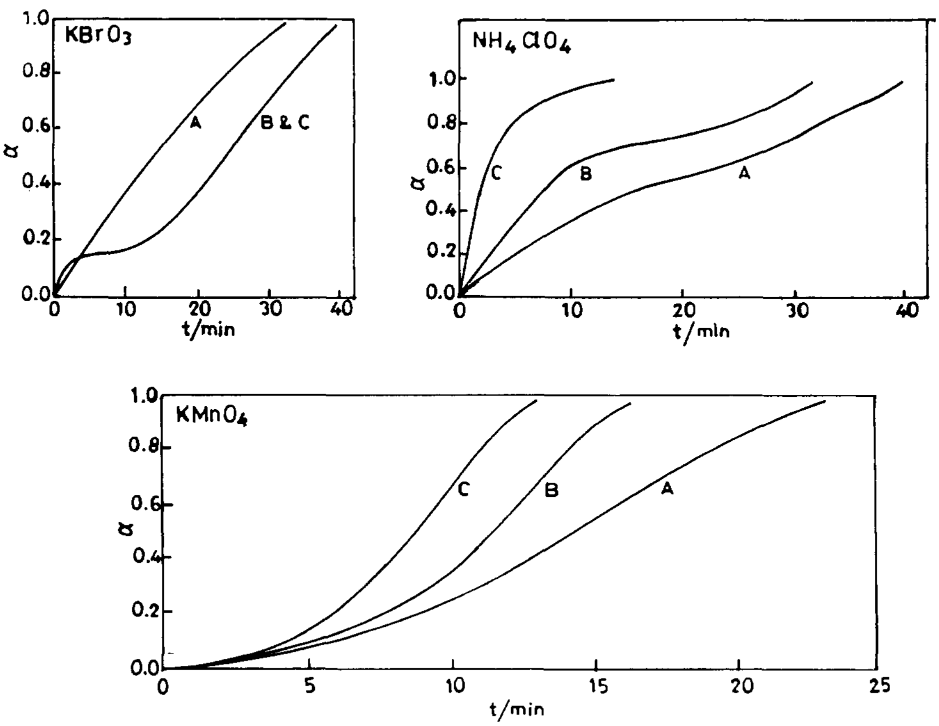

Fig. 1. Typical α–t plots of the thermal decomposition of A – uncompressed, B – precompressed (P=2×10^7 N m^{-2}) and C – precompressed (P=14×10^7 N m^{-2}) samples of $KBrO_3$ (at 668 K), $KMnO_4$ (at 513 K) and NH_4ClO_4 (at 473 K).

Table 1
Rate laws obeyed by the initial stage of the thermal decomposition of uncompressed and precompressed samples of $KBrO_3$, $KMnO_4$ and NH_4ClO_4

Sample	Decomposition temperature (K)	Rate law	Valid range of α
$KBrO_3$ (uncompressed and precompressed)	668	Contracting square law: $1-(1-\alpha)^{1/2}=kt$	0.15–0.50
$KMnO_4$ (uncompressed and precompressed)	513	Prout–Tompkins law: $\ln[\alpha/(1-\alpha)]=kt$	0.05–0.50
NH_4ClO_4 (uncompressed and precompressed)	473	First order law: $-\ln(1-\alpha)=kt$	0.05–0.50

Table 2
Rate constants (k) for the thermal decompositions of $KBrO_3$, $KMnO_4$ and NH_4ClO_4 at 668, 513 and 473 K, respectively as a function of precompression pressure (P)

10^{-7} P (N m^{-2})	10^3 k (s^{-1})		
	$KBrO_3$ at 668 K	$KMnO_4$ at 513 K	NH_4ClO_4 at 473 K
0 (uncompressed)	0.3318	3.751	0.693
2	0.1859	5.831	1.368
4	–	–	1.597
5	0.1898	6.880	–
6	–	–	2.738
8	0.1920	7.436	3.593
10	–	–	4.107
11	0.1913	7.906	–
12	–	–	4.107
14	0.1864	8.183	4.107

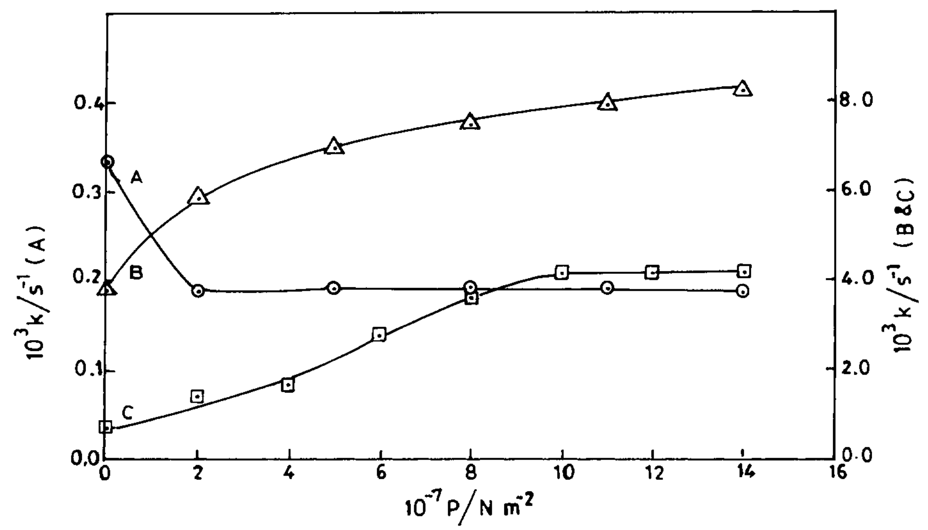

Fig. 2. Dependence of the rate constant (k) for the thermal decomposition of A – $KBrO_3$ (at 668 K), B – $KMnO_4$ (at 513 K) and C – NH_4ClO_4 (at 473 K) on precompression pressure (P).

were precompressed to 8×10^7 N m^{-2}. On the other hand, the rate decreased by ca. 42% in the case of $KBrO_3$ sample precompressed to the same pressure. The sensitizing effect reached a saturation in the vicinity of a pelleting pressure of 8×10^7 N m^{-2} in the case of $KMnO_4$ and NH_4ClO_4. Similarly, the desensitizing effect observed with $KBrO_3$ also reached a saturation, but at a much lower pelleting pressure, viz. 2×10^7 N m^{-2}. Fig. 2 illuminates the phenomenon.

4. Discussion

Not many studies of the present kind have been reported in the literature making a direct comparison of our results difficult. Thermal decomposition [6–8] as well as sublimation [9] of NH_4ClO_4 has been reported to be sensitized by precompression. This was attributed to the generation of grain boundaries and dislocations as a result of precompression.

When compressed, crystals undergo plastic deformation as a result of slip (shearing motion) leading to the production of dislocations by the operation of dislocation sources such as Frank–Reed source. Misorientation of crystallites resulting in the generation of low-angle grain boundaries also occurs during compression. Low-angle grain boundaries of the 'tilt' type consist of a series of edge dislocations and of the 'twist' type constitute a series of screw dislocations. X-ray diffraction and IR studies [8–10] have shown that compression results in an increase in the concentration of gross imperfections like dislocations in the crystal lattice and that the dislocation density increases with an increase in the applied pressure.

The region containing the 'extra half plane' associated with an edge dislocation is in a state of compression whereas the region opposite to it, i.e. below or above the half plane, is in a state of tension. Consequently, vacancies flow and tend to be around the compression side and interstitials in the tension side to help relieve the strain. The atoms (ions) along the dislocation line are vulnerable to the attack of vacancies and/or interstitials developing 'jogs' along the dislocation line. Jogs are also created whenever two dislocations intersect. Jogs are seats of high reactivity. Nucleation occurs preferentially at these potential sites because (i) the extra free energy required for the formation of a nucleus is low at these sites and (ii) they help relieve stresses involved in the transformation. Evidently, therefore, an increase in the dislocation density will increase the concentration of reactive sites where nuclei can grow leading to an enhancement in the rate of reaction, and this generally explains the observed behaviour of precompressed samples of $KMnO_4$ and NH_4ClO_4 (see Fig. 2). But, obviously, plastic deformation causing an increase in the dislocation density is not the only phenomenon taking place during compression as indicated by the decrease in the rate of decomposition of precompressed $KBrO_3$.

Compression is known to affect sintering and densification of powdered materials. A powder normally consists of a large number of randomly oriented individual grains (crystallites) which touch one another at every small sections of their surfaces leaving a lot of free space called intergranular pores. On compression, the average distance between the surfaces of the adjacent grains, i.e. the intergranular porosity, is markedly reduced leading to densification of the solid on the whole in addition to the plastic deformation caused within the grains. Kukolev [11] observed that under pressure magnesia sinters to a high density even at very low temperatures. Murray et al. [11] obtained a high dense sinter by hot pressing the oxides of Be, Mg, Ca, Al, Th and U under a pressure of up to 0.140×10^7 N m^{-2} at temperatures of up to 2273 K. They have shown that the densification rate during sintering at 0.070×10^7 N m^{-2} is 105–178 times greater than the rate at atmospheric pressure (0.010×10^7 N m^{-2}). Klyucherov et al. [11] demonstrated that there is about 82% increase in the density of magnesia–alumina spinel by increasing the pelleting pressure from 0.6×10^7 to 6×10^7 N m^{-2}. Pozin et al. [11] observed that the rate of reaction between $CuSO_4$ and PbO drastically reduced with rise in the pressure applied to the solid mixture. This is obviously due to the densification of the solid matrix and the consequent increase in the resistance to the diffusion of the reactant species through the solid. The results of Pozin et al. [11] indicate that densification plays important role in diffusion-controlled solid-state reactions.

As already mentioned, the same rate law holds good for both precompressed and uncompressed samples of the solids used in this study (see Table 1). Activation energy determination (not included in this paper) also showed that precompression did not affect the activation energy of the decompositions. These facts indicate that the basic mechanism of the decompositions is not altered by precompression.

It has been shown that the rate-determining step in the decomposition of $KMnO_4$ [12,13] and NH_4ClO_4 [14–17] is an electron transfer process. On the other hand, the recent studies carried out in this laboratory [18] strongly favour a diffusion-controlled mechanism for the decomposition of $KBrO_3$. Thus, $KBrO_3$ is basically different from the other two solids that in its thermal stability is determined by the diffusion of ionic species (K^+ and BrO_3^-) through the solid matrix, and this is likely to be the reason for the dramatic behaviour of this solid on precompression.

Both plastic deformation (causing an increase in dislocation density) and densification (causing a reduction in intergranular porosity) occur on compressing a powdered body. Intergranular pores are intercommunicative with one another and with the surface of the material and hence facilitate the diffusion of ionic species towards potential sites present in the solid matrix where they undergo reaction. But such movement of ions will be obstructed significantly in a densified solid matrix leading to a desensitization of diffusion-controlled reactions, as we observed with the decomposition of $KBrO_3$ where diffusion of ions plays vital role in determining the rate. On the other hand, unlike the movement of an ion, the movement of an electron from one ion to another would not be significantly affected by densification of the solid matrix, by virtue of the extremely small size of the electron compared with that of the ion. Therefore, on precompression an electron transfer reaction would not be desensitized by the densification effect but would only be sensitized by the dislocation effect. This accounts for the faster decomposition of precompressed samples of $KMnO_4$ and NH_4ClO_4. It is also possible that densification itself is likely to promote, rather than obstructing it, the electron transfer reaction at least to some extent, because compression allows interpretation of orbitals of the neighbouring ions in the solid matrix making such transfers easy.

5. Conclusion

The decomposition of a solid takes place either via a bond breaking mechanism or via a mechanism involving charge transfer as a result of the movement of electrons, protons or cations and/or anions [19]. Except the movement of the ions (i.e. diffusion), all the other processes are likely to be unaffected by densification of the solid matrix and consequently precompression will enhance such processes by dislocation effect. However, densification is crucial for ionic diffusion and can lead to remarkable decrease in the rate of diffusion-controlled reactions, as we see in this study. It thus appears that the method of precompression can serve as a valuable tool for testing, in a simple manner, whether the decomposition kinetics of a solid is limited by diffusion.

References

[1] J.G. Hooley, Can. J. Chem., 35 (1957) 374.
[2] M.P. Kannan and K. Muraleedharan, Thermochim. Acta, 158 (1990) 259.
[3] B.R. Phillips and D. Taylor, J. Chem. Soc., (1963) 5583.
[4] M.M. Markovitz and D.A. Boryta, J. Phys. Chem., 65 (1961) 1419.
[5] F. Solymosi and Gy. Braun, Acta Chim. Sci. Hung., 52 (1967) 1.
[6] P.W.M. Jacobs, P.W. Levy and P.J. Herley, Proc. Roy. Soc. A., 318 (1970) 197.
[7] P.W.M. Jacobs, P.W. Levy and P.J. Herley, J. Chem. Soc. (A), (1971) 434.
[8] V.R. Pai Vernekar and K. Rajeshwar, J. Phys. Chem. Solids, 37 (1976) 63.
[9] V.R. Pai Verneker, K. Kishore and M.P. Kannan, J. Appl. Chem. Biotechnol., 27 (1977) 309.
[10] V.R. Pai Verneker and M.N. Radhakrishnan Nair, Combust. Flame, 25 (1975) 301.
[11] P.P. Budnikov and A.M. Ginstling in Kennethshaw (Ed.), Principles of solid state chemistry, Reactions in solids, Maclarens and Sons Ltd., London (1968) pp. 244–245.
[12] V.V. Boldyrev, J. Phys. Chem. Solids, 30 (1969) 1215.
[13] M.P. Kannan and T. Ganga Devi, unpublished work.
[14] L.L. Bircumshaw and B.H. Newman, Proc. Roy. Soc., A227 (1955) 228.
[15] J.N. Maycock and V.R. Pai Verneker, Proc. Roy. Soc., A307 (1968) 303.
[16] M.P. Kannan, J. Thermal Anal., 32 (1987) 1219.
[17] T. Ganga Devi, M.P. Kannan and B. Hema, Thermochimica Acta, 285 (1996) 269.
[18] M.P. Kannan and T. Ganga Devi, unpublished work.
[19] V.V. Boldyrev, M. Bulens and B. Delmon, The control of the reactivity of solids, Elsevier, Amsterdam (1979) p. 21.