Effect of pre-treatments on isothermal decomposition kinetics of potassium metaperiodate

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ABSTRACT

The effect of pre-compression, pre-heating and particle size on the thermal decomposition kinetics of potassium metaperiodate (KIO_4) to potassium iodate (KIO_3) has been investigated by thermogravimetric analysis under isothermal conditions. Although the effect of pre-compression was negligible up to an applied pressure of 5×10^3 kg cm^{-2}, the rate increased drastically on a further increase in pressure. Results of pre-heating indicate that gross imperfections are not as easily annealed as point defects. Studies on the effect of particle size emphasize the need for fixing the particle size to enable a meaningful interpretation of the effects of pre-treatment on solid-state reactions. The rate law (Prout–Tompkins model) as well as the mechanism (electron-transfer) for the decomposition of KIO_4 remained unaffected by these pre-treatments. The α–t data of uncompressed and compressed samples of pure KIO_4 were also subjected to isoconversional studies for the determination of activation energy values.

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1. Introduction

Thermal decomposition of solids is an important field of solid-state chemistry with wide technical applications. Many recent studies on the thermal decomposition of inorganic solids have included measurements on samples that were subjected to various pre-treatments prior to heating, with a view to investigating the effects of pre-treatments on the thermal decomposition behaviour. For instance, pre-treatments can modify one or more properties of the material in an important way by creating imperfections and thereby increasing the number of nuclear forming sites in the solid. The kinetics of the thermal decomposition of inorganic materials could be markedly affected by certain pre-treatments, by the shortening of the induction period followed by an overall decrease in time needed to complete the reaction. The nature of influence of pre-treatments provides valuable information of the elementary steps and thereby on the mechanism and control of the solid-state reactions [1,2].

Thermogravimetric analysis has been used to obtain thermal stability parameters of solids [3–6]. The thermal decomposition data generated from TG can be analyzed and manipulated to obtain kinetic parameters such as activation energy (E) and pre-exponential factor (A) [7,8]. Solid-state kinetic data are of practical interest for the large and growing number of technologically

important processes. Kinetic studies predict how quickly a system approaches equilibrium and also help to understand the mechanism of the process [9]. A number of reviews are available in the literature on these processes [10–16]. Several authors have emphasized the practical and theoretical importance of information on the kinetics and mechanism of solid-state decompositions [17,18].

The methods of kinetic analysis can be classified based on experimental conditions selected and the mathematical analysis performed. Experimentally, either isothermal or nonisothermal methods are used. The isothermal methods are based on the initial assumption that a single conversion function and a single set of Arrhenius parameters, A and E, apply over the full range of the conversion. Kinetic analysis of isothermal results involves attempting to relate the experimentally observed α–t values with values predicted for a limited set of models (defined by $g(\alpha)$) [17,18] based on processes of nucleation and growth, diffusion or some simpler geometrical forms of progress of the reactant/product interface [19]. The linearity of plots of $g(\alpha)$ *vs* t is determined using standard statistical criteria, e.g., the correlation coefficient, r, to quantify a set of experimental points from the calculated regression line. The magnitude and direction of deviation of data from the least squares line and their variations with α can be useful [20] in identifying the most appropriate rate equation. If the form of the conversion function $g(\alpha)$ does not change with temperature, the values of k at a series of isothermal temperatures, T, can be used in conventional Arrhenius plot to calculate E and A [19].

Vyazovkin and Lesnikovitch [21] point out that the kinetic parameters calculated from isothermal data are not very depen-

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Table 1
Different reaction models used to describe the reaction kinetics.

Model no.	Reaction model	Function, $g(\alpha)$
1	Power law	$\alpha^{1/4}$
2	Power law	$\alpha^{1/3}$
3	Power law	$\alpha^{1/2}$
4	Exponential law	$\ln\alpha$
5	One-dimensional diffusion	α^2
6	Three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$
7	Mampel (first order)	$-\ln(1-\alpha)$
8	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$
9	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/3}$
10	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/2}$
11	Avrami-Erofeev	$[-\ln(1-\alpha)]^{2/3}$
12	Contracting sphere	$1-(1-\alpha)^{1/3}$
13	Contracting cylinder	$1-(1-\alpha)^{1/2}$
14	Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$

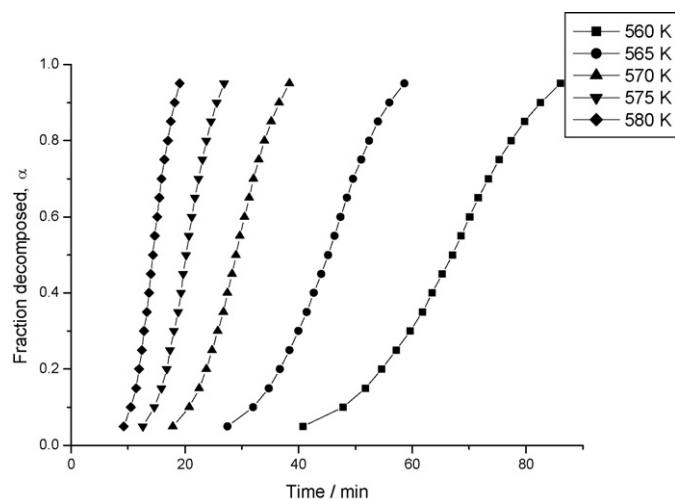**Fig. 1.** α–t curves for the decomposition of untreated KIO_4.

dent upon the kinetic models chosen, while the opposite is true for nonisothermal methods. Thus one could determine the Arrhenius parameters from isothermal measurements and the kinetic models from nonisothermal methods. Derivative methods may be more sensitive in determining the kinetic models [22], but the smoothing required may lead to distortions [23]. Vyazovkin and Lesnikovitch [24] have suggested that different aspects of the real process may
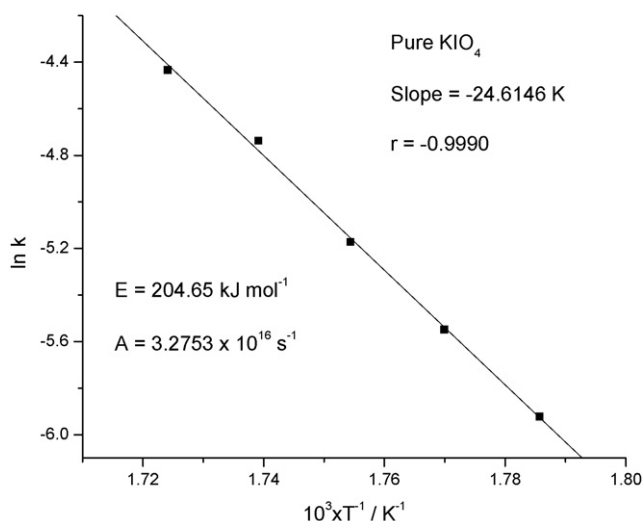

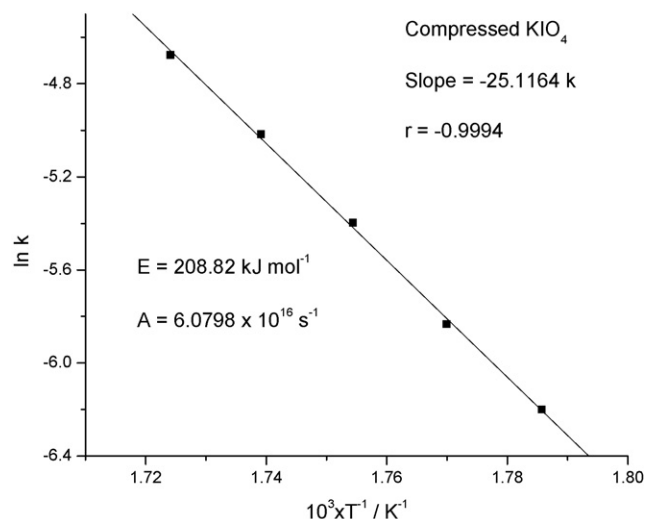**Fig. 2.** Arrhenius plot [$\ln k$ (k in s^{-1}) vs T^{-1}] for pure KIO_4.

Fig. 3. Arrhenius plot [$\ln k$ (k in s^{-1}) vs T^{-1}] for compressed (8×10^3 kg cm^{-2}) KIO_4.

be best described by a synthesis of individual features of ideal models from the existing set. It has been reported [7] that the popular model-fitting approach gives excellent fits for both isothermal and nonisothermal data for the thermal decomposition of HMX and ammonium dinitramide, but yields highly uncertain values for Arrhenius parameters when applied to nonisothermal data. Lua and Su [25] studied the kinetics involved in the thermal decomposition of Kapton® polyimide 100HN under nitrogen atmosphere by applying various fitting techniques to the isothermal thermogravimetric data. They examined the correlation of the reaction mechanism fitting, the analytical model fitting and the isoconversional method to these data in relation to the kinetic parameters and observed that the mechanisms for solid-state reactions fit the isothermal data very well but result in highly uncertain values for the kinetic parameters when applied to the nonisothermal data. They also observed that isoconversional methods can show the dependence if any, of apparent activation energy on the extent of conversion but do not provide information for the reaction order and the pre-exponential factor. Vyazovkin et al. [26] applied both model-fitting and model-free kinetic methods to derive kinetic characteristics of the isothermal decomposition process of solid ammonium nitrate and reported an activation energy value of 90 kJ mol^{-1} on application of the model-fitting method by the model of a contracting cylinder to the isothermal data. They also applied model-free isoconversional method to the isothermal data of the process and obtained an activation energy value of 90 kJ mol^{-1}, which is independent of the extent of conversion. It has been reported [27] that model-free isoconversional methods can be effectively applied to isothermal differential scanning calorimetry data on epoxy cures, yielding a dependence of the effective activation energy on the extent of cure. Thermoanalytical studies showed that KIO_4 decomposes in two steps [28,29]. At about 570 K, KIO_4 decomposes with heat evolution to potassium iodate (KIO_3) and oxygen. The decomposition of KIO_3 to KI takes place in the range 780–800 K. Our earlier investigations [30,31] showed that the isothermal decomposition of KIO_4 proceeds through two stages, an acceleratory stage ($\alpha = 0.05$–0.5) and a decay stage ($\alpha = 0.5$–0.95), the former following the Prout–Tompkins kinetics and the latter contracting area kinetics, at all temperatures studied. The influence of dopants (sulphate and barium) examined in these studies prompted us to propose that the probable rate-determining step in the thermal decomposition of KIO_4 is the transfer of an electron from the periodate anion to the potassium cation rather than the rupture of I–O bond or the diffusion of cations/anions.

Table 2
Values of correlation coefficient (r) calculated for various solid-state kinetic equations using weighted LSM for the decomposition of uncompressed and compressed ($8 \times 10^3\ kg\ cm^{-2}$) samples of pure KIO_4 at different temperatures.

Reaction model no	Pure sample of KIO_4					Compressed sample of KIO_4				
	Temperature (K)					Temperature (K)				
	560	565	570	575	580	560	565	570	575	580
1	0.9738	0.9726	0.9644	0.9597	0.9598	0.9611	0.9626	0.9596	0.9585	0.9665
2	0.9795	0.9785	0.9710	0.9668	0.9667	0.9680	0.9690	0.9660	0.9655	0.9729
3	0.9886	0.9880	0.9825	0.9722	0.9790	0.9801	0.9805	0.9978	0.9781	0.9839
4	0.9536	0.9523	0.9423	0.9369	0.9369	0.9389	0.9423	0.9396	0.9359	0.9451
5	0.7875	0.7966	0.8006	0.7959	0.8096	0.8150	0.8269	0.8376	0.8094	0.8060
6	0.6425	0.6507	0.6499	0.6439	0.6547	0.6663	0.6687	0.6726	0.6550	0.6568
7	0.9006	0.9064	09094	0.9052	0.9158	0.9167	0.9295	0.9392	0.9147	0.9116
8	0.9982	0.9988	0.9985	0.9988	0.9992	0.9995	0.9989	0.9980	0.9991	0.9994
9	0.9949	0.9960	0.9978	0.9975	0.9987	0.9987	0.9992	0.9993	0.9986	0.9978
10	0.9822	0.9845	0.9879	0.9878	0.9912	0.9907	0.9947	0.9970	0.9909	0.9882
11	0.9615	0.9653	0.9693	0.9682	0.9145	0.9738	0.9815	0.9866	0.9738	0.9700
12	0.9312	0.9363	0.9404	0.9378	0.9468	0.9469	0.9577	0.9656	0.9459	0.9420
13	0.9469	0.9514	0.9557	0.9538	0.9615	0.9615	0.9706	0.9771	0.9608	0.9569
14	0.9998	0.9999	0.9997	0.9999	0.9995	0.9998	0.9999	0.9999	0.9998	0.9999

The studies on the effect of metal oxide additives (viz., CuO, MnO_2 and TiO_2) on the thermal decomposition kinetics of KIO_4 (to KIO_3) in air by thermogravimetry under isothermal conditions

Table 3
Values of rate constant, k for the thermal decomposition of uncompressed and pre-compressed samples of KIO_4.

Pressure ($\times 10^3$/kg cm^{-2})	Temperature (K)	k ($\times 10^3$/s^{-1})
0 (uncompressed)	560	2.0294
	565	2.9309
	570	4.5308
	575	6.6256
	580	9.3259
2	570	4.5051
5	570	4.7184
8	560	2.6807
	565	3.8946
	570	5.6720
	575	8.7658
	580	11.8795
11	570	6.1833
14	570	7.6228

Table 4
Activation energy ($E\alpha$) and correlation coefficient (r) values obtained from isoconversional method for uncompressed and compressed ($8 \times 10^3\ kg\ cm^{-2}$) samples of pure KIO_4 at different conversions.

α	Uncompressed KIO_4		Compressed KIO_4	
	$E\alpha$ (kJ mol^{-1})	r	$E\alpha$ (kJ mol^{-1})	r
0.05	203.05	0.9987	202.57	0.9980
0.10	206.09	0.9990	202.63	0.9983
0.15	205.81	0.9990	202.99	0.9986
0.20	206.75	0.9992	202.67	0.9986
0.25	207.88	0.9991	203.32	0.9986
0.30	208.96	0.9992	203.22	0.9987
0.35	208.54	0.9993	203.55	0.9986
0.40	208.53	0.9992	203.60	0.9984
0.45	209.72	0.9992	203.63	0.9986
0.50	209.71	0.9991	203.64	0.9986
0.55	209.85	0.9992	203.85	0.9986
0.60	209.26	0.9992	203.48	0.9987
0.65	208.45	0.9993	203.70	0.9985
0.70	208.13	0.9993	203.16	0.9987
0.75	207.39	0.9993	203.24	0.9987
0.80	206.33	0.9992	203.30	0.9988
0.85	206.33	0.9994	203.73	0.9989
0.90	205.63	0.9994	203.13	0.9989
0.95	204.67	0.9995	203.64	0.9991

[32] revealed that irrespective of whether p- or n-type, the metal oxides show only a little or no influence on the rate of the decomposition except for the small decrease observed when the oxide concentration is as high as 10 wt%. This suggests that the electron work functions of these oxides might be smaller than that of KIO_4 so that they lack electron acceptor property with respect to KIO_4 and thus fail to favour electron-transfer processes. The rate laws for the decomposition of KIO_4 also remained unaffected by the additives. We have also studied the kinetics of isothermal decomposition of potassium metaperiodate, doped with phosphate and aluminium by thermogravimetry [33]. Here also the decomposition proceeds through two stages: an acceleratory stage up to $\alpha = 0.50$ and the decay stage beyond $\alpha = 0.50$, as found with divalent ion doped KIO_4 [30,31]. The TG data were found to be best described by the Prout–Tompkins equation. Separate kinetic analyses of the α–t data corresponding to the acceleratory region and decay region showed that the acceleratory stage gave the best fit with Prout–Tompkins equation itself whereas the decay stage fitted better to the contracting area equation. The rate of decomposition of phosphate doped KIO_4 increases approximately linearly with an increase in the dopant concentration. In the case of aluminium doped KIO_4, the rate passes through a maximum with increase in the dopant concentration. The α–t data of pure and doped (with phosphate and aluminium) KIO_4 [23] were also subjected to isoconversional studies for the determination of activation energy values. We observed that doping did not change the activation energy of the reaction. The results favour an electron-transfer mechanism for the isothermal decomposition of KIO_4, agreeing well with our earlier observations [30–32].

In continuation of our investigations on the thermal behaviour of periodates of alkali metals, in this paper we report the effect of pre-compression, pre-heating and particle size on the isothermal decomposition kinetics of potassium metaperiodate,

$$2KIO_4 \rightarrow 2KIO_3 + O_2.$$

2. Experimental

All the chemicals used were of AnalaR grade reagents of *E* Merck. Pure and doped sample of KIO_4 were prepared by the method described earlier [30]. *Pre-compression* of KIO_4 samples was carried out on a hydraulic pelleting press. About 200 mg of the sample in the powder form (particle size: 90–106 μm) was taken in a stainless steel disc and then compressed to the required pressure up to a time of about one minute. The pellet was taken out and lightly
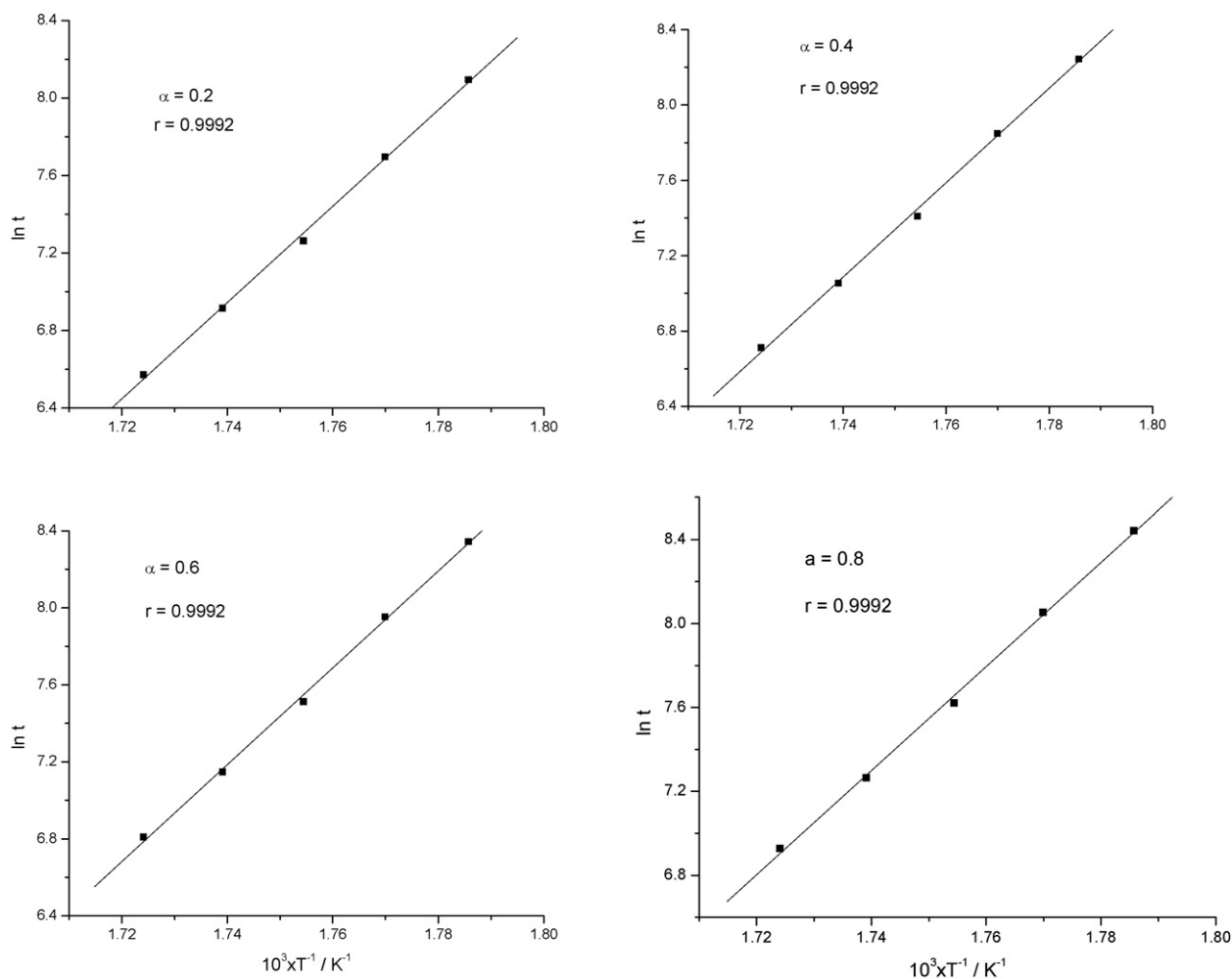
Fig. 4. Typical isoconversional plots [$\ln t$ (t in s) vs T^{-1}] for the thermal decomposition of pure KIO_4 at different conversions.

ground in an agate mortar and the particle size was again fixed in the range 90–106 μm. Samples pressed to 2×10^3, 5×10^3, 8×10^3, 11×10^3 and 14×10^3 kg cm^{-2} of pressures, were used to study the effect of pre-compression. Thermogravimetric analysis of the pre-compressed samples was always carried out on the same day of the pre-treatment in order to avoid the possible ageing effect.

Pre-heating of KIO_4 samples (particle size: 90–106 μm) was effected by storing them in an air oven at a temperature of 400 K. Two samples each of sulphate doped (1×10^{-4} and 1×10^{-3} mol %), barium doped (1×10^{-4} and 1×10^{-2} mol %) and pre-compressed (5×10^3 and 11×10^3 kg cm^{-2}) and untreated KIO_4 were subjected to pre-heating at 400 K for 24 and 48 h and then subsequently decomposed at 570 K with a view to unveiling the effect of pre-heating on decomposition rate. The pre-heated samples were sieved to regulate the particle size before subjecting to decomposition in order to ensure that the observed effect is not complicated by the possible change in the particle size as a result of sintering.

To study the effect of *particle size*, pure KIO_4 samples were sieved into five different particle size ranges, viz., 63–75, 75–90, 90–106, 106–125 and 125–150 μm.

Thermogravimetric measurements in static air were carried out on a custom-made thermobalance fabricated in this laboratory [30], an upgraded version of Hooley [34]. A major problem [35] of the isothermal experiment is that a sample requires some time to reach the experimental temperature. During this period of nonisothermal heating, the sample undergoes some transformations that are likely to affect the succeeding kinetics. The situation

is especially aggravated by the fact that under isothermal conditions, a typical solid-state process has its maximum reaction rate at the beginning of the transformation. So we fabricated a thermobalance particularly for isothermal studies, in which loading of the sample is possible at any time after the furnace has attained the desired reaction temperature. The operational characteristics of the thermobalance are, balance sensitivity: $\pm 1 \times 10^{-5}$ g, temperature accuracy: ± 0.5 K, sample mass: 5×10^{-2} g, particle size: 90–106 μm and crucible: platinum. Comparative runs were always made using samples of same age and particle size. The fraction of solid decomposed (α) was measured as a function of time (t) at five temperatures (T), viz., 560, 565, 570, 575 and 580 K for pure and one pre-compressed (8×10^3 kg cm^{-2}) samples of KIO_4 and at 570 K for all others.

The activation energy and pre-exponential factor for the thermal decomposition of uncompressed as well as compressed (8×10^3 kg cm^{-2}) samples of KIO_4 were calculated from Arrhenius plot for the Prout–Tompkins model, which was found to give the highest statistical correlation.

3. Results

The α–t curves (in the range $\alpha = 0.05$–0.95) for the decomposition of pure KIO_4 at different temperatures are shown in Fig. 1. Similar curves were obtained for all pre-treated samples of KIO_4 (not shown). Pre-treatments did not change the basic shape (sigmoid) of the α–t plots and the decomposition proceeded through
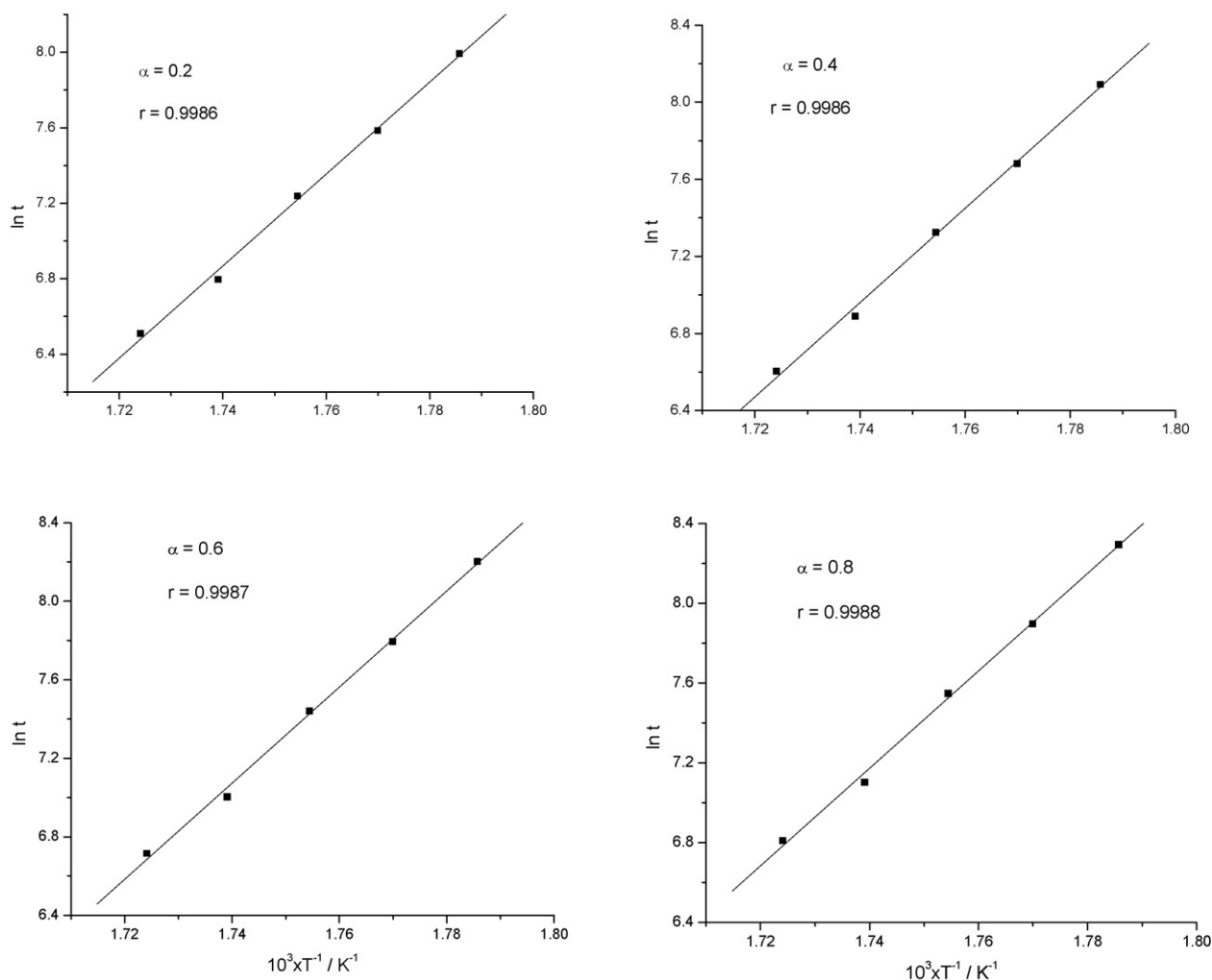
Fig. 5. Typical isoconversional plots [ln t (t in s) vs T^{-1}] for the thermal decomposition of compressed (8×10^3 kg cm^{-2}) KIO$_4$ at different conversions.

the same way as that of untreated KIO$_4$. The α–t data were fitted to various solid-state kinetic equations available in the literature (Table 1) using the method of weighted least squares as described earlier [30]. In all cases the Prout–Tompkins equation [36], $\ln[\alpha/(1-\alpha)] = kt$, which is the simplest case of an autocatalytic reaction, gave the best fits at all the temperatures studied as in the case of pure KIO$_4$. Values of correlation coefficient (r) for the different solid-state kinetic equations in Table 1 were calculated using weighted LSM for the decomposition of uncompressed and compressed (8×10^3 kg cm^{-2}) samples of KIO$_4$ at different temperatures and are given in Table 2. Perusal of Table 2 shows that Prout–Tompkins model gives maximum correlation in all cases.

The values of rate constant (k) for the decomposition of uncompressed and pre-compressed samples of pure KIO$_4$ at different temperatures, determined from the Prout–Tompkins fits are given in Table 3. The rate is enhanced by pre-compression. Activation energy and pre-exponential factor for the thermal decomposition of uncompressed and pre-compressed (8×10^3 kg cm^{-2}) samples of KIO$_4$ were determined from Arrhenius plots shown in Figs. 2 and 3. It has been found that the activation energy remained unaffected by pre-compression. The α–t data, in the range $\alpha = 0.05$–0.95, of uncompressed and compressed (8×10^3 kg cm^{-2}) samples of pure KIO$_4$ were also subjected to isoconversional studies for the determination of apparent activation energy as a function of α. A plot of ln t (t being the time required for reaching a given value of α at a constant temperature T) vs the corresponding reciprocal of the

temperature ($1/T$) would lead to the activation energy ($E\alpha$) for the given value of α. The results are given in Table 4. Typical isoconversional plots for the thermal decomposition of pure and compressed (8×10^3 kg cm^{-2}) samples of KIO$_4$ are given in Figs. 4 and 5, respectively.

The rate constants at 570 K for all the pre-heated (for 24 h) samples, along with the values for untreated samples, are given in Table 3. Pre-heating generally decreases the rate of decomposition, the magnitude of the effect being dependent on the nature of the pre-treatment prior to pre-heating. No further effect is seen beyond a pre-heating time of 24 h, which indicates that the effect of pre-heating is complete in this solid by 24 h.

The effect of particle size on the thermal decomposition of KIO$_4$ is shown in Table 6 and Fig. 6. The rate is strongly dependent on particle size; it passes through a maximum as the particle size decreases.

4. Discussion

Philips and Taylor [37] studied the kinetics of thermal decomposition of KIO$_4$ in vacuum by EGA, reported an E value of 191 kJ mol^{-1} and proposed that the rupture of I–O bond determines the rate of the decomposition. Our earlier investigations [30–33] showed that the isothermal decomposition of KIO$_4$ follows Prout–Tompkins kinetics at all temperatures studied with an E value of 206 $\pm$3 kJ mol^{-1}, with transfer of an electron from
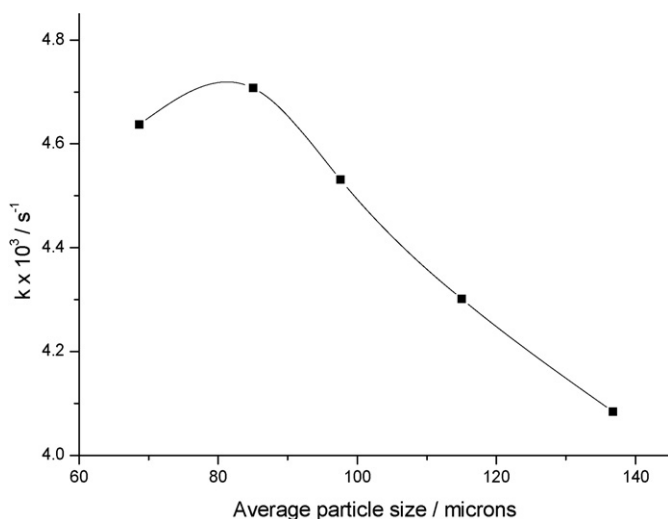
Fig. 6. Dependence of rate of decomposition of KIO_4 (at 570 K) on particle size.

the periodate anion to the potassium cation as the most probable rate-determining step.

Very few studies were reported in the literature on the thermal decomposition of pre-treated KIO_4. Solymosi [38] found that the prior mixing of KIO_4 with KIO_3 caused practically no change in the course of the reaction. In both cases the decomposition was found to be auto catalytic, and the rate maximum appeared at about 50% conversion, independent of the temperature.

4.1. Effect of Pre-compression

The effect of pre-compression was negligible up to an applied pressure of 5×10^3 kg cm^{-2}, but the rate increased drastically on a further increase in pressure (Table 3). For instance, the rate at 570 K increased by ca. 68% when KIO_4 was subjected to a pelleting pressure of 14×10^3 kg cm^{-2}. The rate law and activation energy, however, remained unchanged by pre-compression. Similar results were obtained by several workers for the thermal decomposition of ammonium perchlorate [1,2,39,40]. Kannan and Ganga Devi [41] reported that the rate of decomposition increased with increase in the applied pressure in the case of $KMnO_4$ and NH_4ClO_4, but the rate dramatically decreased in the case of $KBrO_3$. Lang and Vya-zovkin [42] has studied the thermal decomposition of ammonium perchlorate samples in the form of 2 mm monocrystals, 265- and 3-μm powders, and pellets pressed at 4 and 7 tons by DSC, TGA and HP-DSC. They observed that the sublimation and decomposition of NH_4ClO_4 were highly dependent on sample preparation and applied pressure.

The basic defects generated by compressing a solid are gross imperfections like dislocations. When compressed, crystals undergo plastic deformation as a result of slip (shearing motion)

leading to the production of dislocations. Disorientation of crystallites resulting in the generation of grain boundaries can also occur during compression; small angle grain boundaries consist of a series of edge dislocations and twist grain boundaries constitute a series of screw dislocations. Several authors [2,40,43,44] have shown by X-ray and IR studies that pre-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 pelleting pressure.

Nucleation occurs preferentially at dislocations and grain boundaries because (i) 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. Thus evidently an increase in the dislocation density will increase the concentration of reactive sites where nuclei can grow leading to an enhancement of the rate of decomposition, as we have observed here. This is in agreement with the earlier finding from this laboratory [41] that the shrinking of solid on compression will not affect the diffusion of electrons through the lattice unlike the diffusion of ions.

The invariance of activation energy of the decomposition by pre-compression (Figs. 2 and 3) implies that pre-compression does not affect the decomposition mechanism. Isoconversional analysis (Table 4) reveals that the activation energy values for pre-compressed (8×10^3 kg cm^{-2}) samples of KIO_4 (in the range $\alpha = 0.05$–0.95) lie in the range 202–204 kJ mol^{-1} and they show only a small deviation ($\pm 0.6\%$) over the whole range of conversion. Similar is the case with uncompressed KIO_4 too. Further, these values agree very well with those obtained from conventional method (Figs. 2 and 3) emphasizing that the mechanism is essentially the same throughout the decomposition process in both compressed and pre-compressed samples.

4.2. Effect of pre-heating

The effect of thermal annealing on thermoluminescence yield in quartz has been investigated by several authors [45–47] and observed that the defect structure of quartz is sensitive to heat treatments. It has also been observed [48] that the heat treatment could affect the individual charge traps in quartz.

Pre-heating at 400 K results only in a slight decrease in the decomposition rate of untreated and pre-compressed KIO_4, whereas it results in a significant decrease in the case of doped samples (Table 5). In fact on pre-heating, the rates of all doped samples decrease and approach the rate of pure pre-heated sample, thus nullifying the doping effect. For instance, the rate is enhanced approximately by 11% by 10^{-4} mol% SO_4^{2-} and by 27% by 10^{-4} mol% Ba^{2+}. These enhancements are reduced almost to zero on pre-heating for 24 h. On the other hand, the decrease in the rate of pre-compressed samples on pre-heating is only about 3%, which is comparable to the 2% decrease found with the pure untreated sample. Thus, the 36% enhancement in rate caused by a pelleting pressure of 11×10^3 kg cm^{-2} is reduced only by about 3% on pre-heating for 24 h.

Table 5
Values of rate constant, k, for the thermal decomposition (at 570 K) of annealed (at 400 K for 24 h) and unannealed samples of KIO_4 and decrease/increase (%) in k upon pre-treatments.

Description of sample	$k (\times 10^3/s^{-1})$		% increase in k by doping/pre-compression	% decrease in k by annealing
	Annealed	Unannealed		
Untreated	4.4303	4.5308	0	2
Doped, 10^{-4} mol% SO_4^{2-}	4.4288	5.0292	11	17
Doped, 10^{-2} mol% SO_4^{2-}	4.4183	5.3804	19	18
Doped, 10^{-4} mol% Ba^{2+}	4.4470	5.7710	27	23
Doped, 10^{-2} mol% Ba^{2+}	4.4368	4.6431	2	4
Pre-compressed, 5×10^3 kg cm^{-2}	4.6230	4.7184	4	3
Pre-compressed, 11×10^3 kg cm^{-2}	6.0017	6.1833	36	3

Table 6
The effect of particle size on the rate of decomposition of KIO_4 at 570 K.

Range of particle size (μm)	Average particle size (μm)	$k\ (\times 10^3/s^{-1})$
63–75	68.65	4.6371
75–90	85.04	4.7079
90–106	97.56	4.5308
106–125	114.98	4.3014
125–150	136.74	4.0843

The present results indicate that heat treatment anneals the imperfections generated by doping but not that produced by precompression. In other words, pre-heating leads to combinations among vacancies, interstitials and impurity ions leading to the annealing of point defects and lowering of the concentration of active sites.

The invariance in the reactivity of the pre-compressed samples on pre-heating would mean that gross imperfections such as dislocations and grain boundaries are not easily annealed unlike point defects, by the heat treatment programme employed here. Furthermore, the fact that the heat treatment causes only a slight decrease in the reactivity of pure untreated sample would imply that the concentration of point defects in this sample is very low.

4.3. Effect of particle size

The results presented in Table 6 show that the rate constant increases with decrease in the particle size (i.e., with an increase in the surface area) until a certain critical size (75–90 μm) is reached. This behaviour is shown in Fig. 6 where the rate of reaction is plotted against the average particle size. (The average particle size of the grains was calculated according to the Andersen method [49].) A similar effect has been reported in the thermal decomposition of NaN_3 [50] and in the thermal decomposition [51] and sublimation [44] of ammonium perchlorate. It has been shown by several authors [50–55] that particle size is an important factor in the kinetics of the thermal decomposition of solids. Huang et al. [56] have studied the effect of particle size on combustion of aluminium particle dust in air and observed that the particle burning time is size dependent.

It is well known that the gross imperfections are present more on the surface than in the bulk [44]. When the particle size is decreased, the surface area increases which in turn results in an increase in the concentration of gross imperfections. The larger the concentration of gross imperfections, the greater the number of nuclei formed [51] leading to an enhancement in the rate of decomposition. The thermal decomposition of solids in which the rate increases and shows a maximum by decreasing the particle size [51] has been explained on the basis of Mampel's theory [57]. Mampel's theory is concerned with nucleation and growth in systems consisting of microcrystals in the form of spheres, and theoretically Mampel has shown that the isothermal decomposition rate of a solid should pass through a maximum because, as the particle size is decreased (i.e. when the surface area is increased) the number of surface defects, which can act as potential nucleus forming sites, increases leading to an enhanced nucleation and growth, or in other words, a sensitization in the rate of decomposition. When the particle size becomes very small, the number of nucleus forming surface defects is so high that there will not be sufficient time for the surface to become completely nucleated before marked penetration occurs. Further as the nuclei exceed certain concentrations, an overlap of the growing nuclei takes place much earlier resulting in desensitization.

5. Conclusions

The importance of dislocations and grain boundaries and their ability to promote the decomposition by functioning as electron accepting centers are brought out by pre-compression studies. The magnitude of the influence of dislocations/grain boundaries on the decomposition is found to be much more than that of point defects. This is probably because; by virtue of their open structure dislocations/grain boundaries facilitate the nucleation and branching of nuclei (Prout–Tompkins model) more easily than point defects.

Pre-heating generally decreases the rate of decomposition, the magnitude of the effect being dependent on the nature of the pre-treatment (doping, compression, etc.) the solid has already undergone. Pre-heating nullifies the effect of doping whereas it does not affect the influence of pre-compression at all. This important observation clearly points out the difference in the nature of defects produced by doping and pre-compression. This also implies that gross imperfections, such as dislocations and grain boundaries, are not easily annealed unlike point defects.

The importance of surface in solid-state reactions is illustrated in the study of the decomposition reaction as a function of particle size. The rate increases as the particle size decreases. But, when the particle size is too small, the "germ nuclei", although numerous in number, fail to develop in to "growth nuclei" before marked penetration occurs and therefore the growth terminates leading to a decrease in rate. The results emphasize the need for fixing the particle size to enable a meaningful interpretation of the effects of pre-treatments on solid-state reactions.

Solid-state reactions are generally complex since they are very sensitive to the history of the solid. A number of factors associated with mechanical and chemical treatments are found to influence the reactivity of solids. This work demonstrates how strongly such treatments influence the reactivity of KIO_4 providing information to the solid-state reactivity database. Knowledge of the way in which different pre-treatments affect the rate of reaction, allows drawing important conclusions regarding the mechanisms involved.

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