Thermal decomposition of potassium metaperiodate doped with trivalent ions

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ABSTRACT

The kinetics of isothermal decomposition of potassium metaperiodate (KIO_4), doped with phosphate and aluminium has been studied by thermogravimetry (TG). We introduced a custom-made thermobalance that is able to record weight decrease with time under pure isothermal conditions. The decomposition proceeds mainly through two stages: an acceleratory stages up to $\alpha = 0.50$ and the decay stage beyond. The decomposition data for aluminium and phosphate doped KIO_4 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 KIO_4 were also subjected to isoconversional studies for the determination of activation energy values. 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.

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1. Introduction

The thermal decomposition study of solids is one of the most common and widely used techniques to obtain insight into the elementary steps of solid-state reactions. Information on the kinetics and mechanism of solid decomposition is of both practical and theoretical importance [1,2]. Reactivity of solids is greatly modified by pre-treatments such as doping, pre-compression, pre-heating, etc. The nature of influence of the pre-treatments provides valuable information on the elementary steps of solid-state reactions and thereby on the mechanism and control of solid-state reactions [3,4]. Kinetic study is one of the important applications of thermal analysis. Solid-state kinetic data are of practical interest for the large and growing number of technologically important processes. A number of reviews are available in the literature on these processes [5–12].

Several methods have been applied for kinetic studies of solid-state reactions. The methods of kinetic analysis can be classified based on experimental conditions selected and the mathematical analysis performed. Experimentally, either isothermal or non-isothermal 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. A major problem encountered in the kinetic anal-

yses of isothermal decomposition is the effect of pre-heating, on the sample [13]. This problem has been solved to a large extent by fabricating a thermobalance, particularly for studying isothermal kinetics of solid-state reactions [14]. We have reported the effects of pre-treatments on the thermal reactivity of several high-energy solids such as halates and perhalates [14–21] that throw light on the mechanism of their decomposition and also of other solid-state reactions in general and more data of this kind are desirable.

Thermoanalytical studies showed that KIO_4 decomposes in two steps [23,24]. 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 of 780–800 K. In the thermal decomposition of KIO_4 it has not been proved possible to identify the hexavalent iodine compound, K_2IO_4, analogous to the compounds, M_2IO_4, formed in the decomposition of lithium and sodium periodates. Our earlier investigations [14,17] 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. These results 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

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 potassium iodate (KIO_3) in air by thermogravimetry under isother-

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mal conditions [21] 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. Studies on the effect of pre-compression, annealing and particle size on the isothermal decomposition kinetics of KIO_4 to KIO_3 have been investigated by thermogravimetry [22]. 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 annealing indicate that gross imperfections are not easily annealed like 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. We observed that the rate law for the isothermal decomposition of KIO_4 remained unaffected by pre-treatments.

In continuation of our investigations on the thermal behaviour of periodates of alkali metals [14,17,20–22], in this paper we report the effect of the anion dopant phosphate and the cation dopant aluminium on the isothermal decomposition kinetics of KIO_4 in the temperature range of 560–580 K.

2. Experimental

All the chemicals used were of AnalaR grade from E Merck. Doped samples of KIO_4, at four concentrations, viz., 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mol% were prepared by the method described earlier [14,17]. K_3PO_4 and $AlCl_3 \cdot 6H_2O$ were used for doping PO_4^{3-} and Al^{3+}, respectively. The thermogravimetric (TG) measurements in static air were carried out on a custom-made thermobalance, fabricated in this laboratory [14], an upgraded version of Hooley [25].

A major problem [13] of the isothermal experiment is that a sample requires some time to reach the experimental temperature. During this period of non-isothermal 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 attaining 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 different temperatures (T), viz., 560, 565, 570, 575 and 580 K.

3. Results and discussion

The α–t curves for the decomposition of pure KIO_4 and the results of its thermal decomposition kinetics were reported earlier [14,17]. Similar curves were obtained for all doped samples of KIO_4 at all temperatures. The α–t curves for the decomposition of phosphate and aluminium doped KIO_4 at 570 K are respectively shown in Figs. 1 and 2. The decomposition proceeds mainly through two stages: (i) an acceleratory stage (α, 0.05–0.50) and (ii) the decay stage (α, 0.5–0.95).
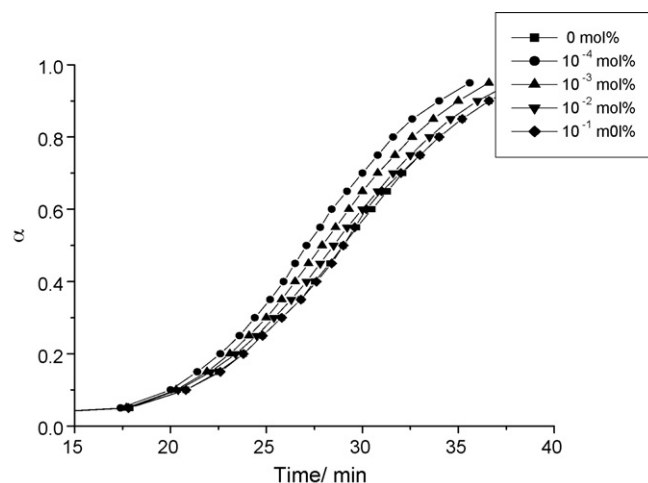

Fig. 1. α–t curves for the decomposition of pure and Al^{3+} doped KIO_4 at 570 K.
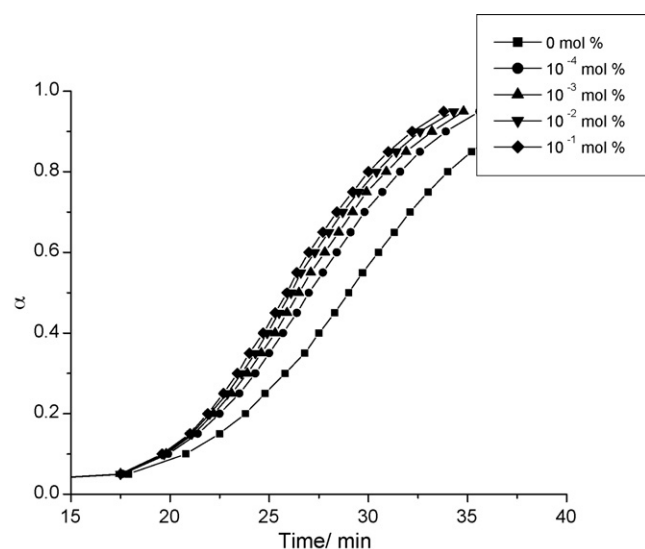

Fig. 2. α–t curves for the decomposition of pure and PO_4^{3-} doped KIO_4 at 570 K.

The α–t data in the range of $\alpha = 0.05$–0.95 (range I) were fitted to various solid-state kinetic equations given in Table 1, using the method of weighted least squares as described earlier [17]. The Prout–Tompkins equation [26], $\ln[\alpha/(1-\alpha)] = kt$, which is the simplest case of an autocatalytic reaction, gave the best fits for the whole range of data at all the temperature studied. Separate kinetic

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

Sl. 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	Power law	$\alpha^{3/2}$
5	One-dimensional diffusion	α^2
6	Mampel (first order)	$-\ln(1-\alpha)$
7	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$
11	Contracting sphere	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	$1-(1-\alpha)^{1/2}$
13	Second order	$(1-\alpha)^{-1}-1$
14	Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$