



Effect of chloride dopant on the kinetics of the thermal decomposition of sodium oxalate

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ABSTRACT

The thermal decomposition kinetics of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) has been studied as a function of concentration of dopant, chloride, at five different temperatures in the range 783–803 K under isothermal conditions by thermogravimetry (TG). The TG data were subjected to both model free and model fitting methods of kinetic analysis. The results obtained from model fitting methods of kinetic analysis shows that no single kinetic model describes the whole α versus t curve with a single rate constant throughout the decomposition reaction. Separate kinetic analysis shows that Prout–Tompkins model best describes the acceleratory stage of the decomposition while the decay region is best fitted with the contracting cylinder model, and corresponding activation energy values were evaluated. The diffusion of Na^+ ions occupying normal lattice sites and interstitial sites was greatly affected by a change in the concentration of defects.

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1. Introduction

Thermal decomposition of metal oxalates has been the subject of many researches, both from a practical and theoretical viewpoint [1–3]. Duval [4] has summarized the thermogravimetric data for the drying and ignition temperature of a large number of metal oxalates. Galwey and Brown [5] has identified and discussed the studies on the thermal decomposition of silver oxalate. Dollimore [6] has made an excellent review on the thermal decomposition and stability of many oxalates. A review on the literature of the thermal behavior of inorganic oxalates reveals that except yttrium oxalate, all undergo thermal decomposition before melting and the decomposition kinetics are not complicated except in the case of a few. The decomposition invariably involves the C–C bond breaking and in many cases the C–C bond cleavage is the rate determining step [7]. Górski and Krašnická [7] proposed that the decomposition in oxalates begins with the heterolytic dissociation of C–C bond forming CO_2 and CO_2^{2-} . The cleavage may be heterolytic to produce CO_2 and CO_2^{2-} [7] or hemolytic to produce two CO_2^- anions [8]. In silver oxalate [9], the transfer of an electron from the $\text{C}_2\text{O}_4^{2-}$ to the cation is the first stage of the decomposition which leads to the rupture of

the C–C bond [10]. Chaiyo et al. [11] studied the thermal decomposition of $\text{Na}_2\text{C}_2\text{O}_4$ using non-isothermal TG–DTA, XRD, and SEM; performed the kinetic analysis of the non-isothermal decomposition data using the iso-conversional methods, proposed by Ozawa and KAS, and possible conversion functions have been estimated by the Liqing–Donghua method [12].

The objective of our investigations is to study the role of lattice defects on solid state decomposition kinetics of alkali metal oxalates with a view to controlling the reactivity of solids in general. As solid-state reactions often occur between crystal lattices or with molecules that must permeate into lattices where motion is restricted and may depend on lattice defects [13], the solids under investigation are subjected to pretreatments such as doping, pre-compression, and pre-heating, to modify the magnitude and nature of lattice defects. It has been reported that pre-treatments affect the rate and temperature of decomposition of oxalates [14–16]. The first two factors generally increase the rate and decrease the decomposition and dehydration temperatures. The effects of pretreatments on decomposition kinetics provide valuable information regarding the topochemistry of the solid and the kinetics and mechanism of the solid state reactions. In continuation of our work on metal oxalates [17–19], in the present paper we describe the effect of chloride dopants on the kinetics of thermal decomposition of sodium oxalate.

Doping of ionic solids with ions of different valences not only introduces impurity ions into the lattice but also changes the vacancy concentration so as to restore the electrical charge balance

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of the lattice. Thus doping $\text{Na}_2\text{C}_2\text{O}_4$ with Cl^- causes an increase in the concentration of cation vacancies. In ionic solids the following relationships holds good at a given temperature.

$$[+] [-] = \text{constant} \quad (1)$$

$$[+] [I^+] = \text{constant} \quad (2)$$

where $[+]$, $[-]$ and $[I^+]$ represent concentration of cation vacancy, anion vacancy and interstitial, respectively. Thus an increase in the concentration of cation vacancies will be accompanied by a decrease in the anion vacancies as per Eq. (1) and a decrease in the concentration of interstitials as per Eq. (2). This principle can be utilized for arriving probable mechanism of decomposition of solids doped with allivalent ions.

2. Experimental

2.1. Materials

All the chemicals used in the present study were of AnalaR grade samples of Merck. NaCl is used for doping chloride. Like earlier workers [20–25], the doped samples were prepared by the method of co-crystallization. Chloride doped samples of sodium oxalate were prepared as per the following procedure. 10 g of sodium oxalate was dissolved in 230 ml of distilled water at boiling temperature in a 500 ml beaker. 10 ml of a solution containing the desired quantity of Cl^- is added to the hot solution so as to achieve a total volume of 240 ml. The solution, containing desired concentration of the dopant, was then cooled slowly to room temperature. The beaker containing the solution was covered using a clean uniformly perforated paper and kept in an air oven at a temperature of 333 K over a period of 6–7 days to allow slow crystallization by evaporation. The resulting crystals were removed; air dried, powdered in an agate mortar, fixed the particle size in the range 106–125 μm and kept in a vacuum desiccator. The doped samples were prepared at five different concentrations, viz. 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} , and 1 mol%.

2.2. Thermogravimetric analysis

Thermogravimetric measurements in static air were carried out on a custom-made thermobalance fabricated in this laboratory [22,23], a modified one of that reported by Hooley [26]. A major problem [27] 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 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, atmosphere: static air and crucible: platinum. Thermal decomposition of sodium oxalate was found to be very slow below 783 K and very fast above 803 K. The decomposition was thus studied in the range 783–803 K. The loss in mass of sodium oxalate was measured as a function of time (t) at five different temperatures (T), viz., 783, 788, 793, 798 and 803 K.

2.3. Kinetic analysis

2.3.1. Model free (isoconversional) methods

Isoconversional methods have their origin in the single-step kinetic equation:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha)h$$

where E is the activation energy, A is the Arrhenius pre-exponential factor, $f(\alpha)$ is the reaction model or conversion function, R is the gas constant, T is the temperature, t is the time, and α is the extent of conversion. The fundamental assumption of isoconversional methods is that a single-step kinetic equation is applicable only to a single extent of conversion and to the temperature region related to this conversion. That is, isoconversional methods describe the kinetics of the process by simultaneously using multiple single step kinetic equations. The temperature dependence of the isoconversional rate can be used to evaluate the values of the activation energy, E_α without assuming/determining the reaction model. The isoconversional principle lays a foundation for a large number of isoconversional computational methods. They can generally be split in two categories: differential and integral [28].

The most common differential isoconversional method is that of Friedman [29], in which $\ln[(d\alpha/dt)_i]$ is plotted against $1/T_i$, measured at the same value of α_i , from α versus t curves at different isothermal reaction temperatures, T_i , and the activation energy values were evaluated from the slope of the plot. Under integral isoconversional method [10] the plot of $\ln t$ (t being the time required for reaching a given value of α at a constant temperature T) versus the corresponding reciprocal of the temperature ($1/T$) would lead to the activation energy for the given value of α .

2.3.2. Model fitting methods

Historically model-fitting methods were widely used because of their ability to directly determine the kinetic triplet. On the other hand, isoconversional methods do not compute a frequency factor nor determine reaction models which are needed for a complete kinetic analysis. In solid state kinetics, mechanistic interpretations usually involve identifying a reasonable reaction model [30] because information about individual reaction steps is often difficult to obtain. A model can describe a particular reaction type and translate that mathematically into a rate equation. Many models have been proposed in solid-state kinetics and these models have been developed based on certain mechanistic assumptions. Solid-state kinetic reactions can be mechanistically classified as nucleation, geometrical contraction, diffusion and reaction order models [10]. In the present work we have subjected kinetic analysis of TG data of all doped samples studied, by weighted linear least squares method, to all kinetic models presented in [10].

3. Results and discussion

The experimental mass loss data obtained from TG were transformed into α versus t data as reported earlier [25], in the range $\alpha = 0.05$ – 0.95 with an interval of 0.05, at all temperatures studied. Typical α versus t curve for the thermal decomposition of chloride doped, at different dopant concentrations, sodium oxalate at 793 K is shown in Fig. 1. Similar types of α versus t curve were obtained at all other temperature studied (not shown). The nature of the α versus t curves (sigmoid) remain unchanged on doping.

Kinetic analysis of the TG data of the chloride-doped sodium oxalate samples, in the range $\alpha = 0.05$ – 0.95 , were accomplished through the Friedman's [10,29] differential model free method, by plotting $\ln[(d\alpha/dt)_i]$ against $1/T_i$, and the activation energy values were evaluated from the slope of the plot. The values of E , standard

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