QUANTITATIVE THERMOANALYTICAL STUDIES OF THE KINETICS AND MECHANISMS OF THE THERMAL DECOMPOSITION OF INORGANIC SOLIDS

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ABSTRACT

A selection of papers from the Proceedings of the 8th ICTA Conference is discussed in terms of the quantitative contributions they have made to the understanding of the mechanisms of thermal decomposition of simple inorganic solids. The reliability of kinetic parameters and the absence in many studies of the use of complementary techniques to provide evidence supporting proposed mechanisms, are found to be matters of concern.

INTRODUCTION

Thermal analysis has been used in numerous studies to examine the sequence of reactions occurring during the thermal decomposition of inorganic solids [1]. Such studies may stop at various levels of sophistication: (i) after determining the stoichiometry of the reactions involved; (ii) after obtaining kinetic parameters for some or all of the reactions in (i); or (iii) after attempting to provide a detailed reaction mechanism based on the stoichiometry in (i), including interpretation [2] of the kinetic parameters from (ii) in terms of chemical and physical processes, and the gathering of as much complementary evidence as possible [3]. Many of the papers presented at the 8th ICTA Conference fall into group (i) and, for the purposes of this review, only those falling into groups (ii) and (iii) are considered further. The reactions of coordination compounds, which is a rich field of kinetic and mechanistic information, has also been excluded, with attention thus being directed only at "simple" inorganic compounds (including metal carboxylates [3]), and, in particular, those compounds which have achieved the status of "model compounds" for the illustration of kinetic behaviour and for comparison of instruments and techniques (e.g., calcium carbonate, calcium oxalate dihydrate, potassium permanganate, etc.).

In most of the studies considered, kinetic parameters have been derived using one or more of the many methods of non-isothermal kinetic analysis

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[4,5] and less frequently from isothermal measurements. The correspondence of kinetic parameters determined by the two different approaches was discussed by Louis and Garcia Cardovilla [6] and the whole topic of kinetic analysis was discussed in depth in one of the workshops.

DISCUSSION

The structural factors which are of importance in the thermal decomposition of solids are discussed by Stoch [7] and a classification is suggested according to whether decomposition is a surface process with no solid product (A-1), or with a solid product layer formed in an irreversible reaction (B-1), or with reversible formation of the solid product layer (B-2). Alternatively, decomposition may involve the formation of product nuclei throughout the bulk of the crystal in a topotactic relationship with the reactant (C-1) or in a pseudomorphic or recrystallized form (C-2).

Much of the fundamental work on decomposition mechanisms has arisen from studies on the dehydration of hydrates which may fall into any of the above classes, except A-1. Okhotnikov and Lyakhov [8] have measured the rate of advance of the reaction interface in different crystallographic directions for two sets of hydrates: those with non-equivalent water molecules (type I) and those with equivalent water molecules (type II). Dehydration of the type 1 hydrates was found, on SEM examination of crystal cross-sections, to be structurally more complex than for type II, although activation energies lay in the range 75–90 kJ mol^{-1} for all the hydrates studied except $K_4Fe(CN)_6 \cdot 3H_2O$, where the value was 54 kJ mol^{-1}.

Braun et al. [9] have examined the multi-stage dehydration of $BeSO_4 \cdot 4H_2O$. The stages are $-2H_2O$ (95°C), $-1H_2O$ (178°C), $-0.8H_2O$ (236°C), followed by decomposition of $BeSO_4$ to BeO at 706°C. Apparent orders of reaction and activation energies were calculated for each stage, using the Coats and Redfern, Freeman and Carroll and Boy and Bohme methods. The three dehydration steps had E_a values of 150, 119 and 211 kJ mol^{-1}, respectively. E_a for the decomposition was 187–252 kJ mol^{-1} depending upon the atmosphere.

Alloun and Nair [10], also using the Coats and Redfern analysis on their TG results, found activation energies of 65–85 kJ mol^{-1} for the dehydration of nickel oxalate dihydrate and 210–300 kJ mol^{-1} for the subsequent decomposition in nitrogen to nickel metal. The spread of values arose from variations with sample mass and with heating rate.

The dehydration of calcium oxalate monohydrate, one of the "model compounds", was used by Varhegyi et al. [11] to test their proposed method of kinetic analysis. The kinetics of dehydration are known to depend strongly on experimental conditions and E_a values of 64–104 kJ mol^{-1} were obtained under various conditions, in reasonable agreement with other

kinetic treatments, e.g., in another test of a kinetic treatment, Malyshev et al. [12] found a value of 84 kJ mol^{-1}.

Tanaka [13] has examined the effect of deuteration on the E_a and ΔH values for a wide range of dehydration processes, including that of calcium oxalate monohydrate. The isotope effects were generally small and within experimental error. The activation energies for dehydration of the series of hydrates and deuterates considered ranged from 70 to 125 kJ mol^{-1}. The values for $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$ were 90 ± 5 and 93 ± 6 kJ mol^{-1}, respectively. Much larger isotope effects had been reported previously and were attributed by Tanaka to lack of control of experimental conditions. In a further paper, Tanaka and Kawabata [14] reported on the dehydration of single crystals of oxalic acid dihydrate, in nitrogen, under both isothermal and dynamic temperature conditions. Analysis of the isothermal results was in terms of the Avrami–Erofeev model (An) with $n = 2.4$, or the phase-boundary model (Rn) with $n = 1.3$, giving E_a values of 85 ± 12 and 86 ± 13 kJ mol^{-1}, respectively. Dynamic runs, treated by the Coats and Redfern method, gave comparable E_a values for the R1 and R2 models (81 and 96 kJ mol^{-1}) but the values for the A2 and A3 models were very low (54 and 34 kJ mol^{-1}). Microscopic examination of the partially dehydrated crystals suggested that the value of $n = 1.3$ for the Rn model arose from combined operation of the R1 and R2 mechanisms. Some nucleation was also observed and Tanaka suggested that further combination with the An model may occur and that application of a single model throughout the whole course of a decomposition is unlikely. Mixed models are even more likely to be found to operate under non-isothermal conditions.

Dollimore et al. [15] have studied the dehydration of strontium oxalate monohydrate and of the polyhydrate ($\sim 2.5H_2O$), as well as the decomposition of the oxalate in nitrogen to form $SrCO_3$ and CO. Structural aspects of the dehydrations are discussed, but no kinetic parameters are reported. The early stages ($\alpha < 0.2$) of isothermal decomposition of the oxalate fitted a first-order rate equation and had an activation energy of 317 ± 3 kJ mol^{-1}. For $0.2 < \alpha < 0.6$ an An model was applied and E_a was 305 ± 3 kJ mol^{-1}. Analysis of non-isothermal results gave comparable E_a values only at low values of α and it is suggested that at higher values secondary reactions involving oxidation of CO become more important.

Prodan [16] has discussed the more complex dehydration processes in phosphate systems and Linkešová and Langfelderová [17] the structural aspects of removal of water from selenate complexes.

It is very clear from the reports above that kinetic parameters for dehydration are very sensitive to experimental conditions and very carefully controlled experimentation is necessary if the influence of any chemical factor, such as the structural environment of the H_2O molecule, is to be determined from measurements of activation energies alone. Similar reserva-

tions apply to other reversible processes, for example, for the much studied decomposition of calcium carbonate, Maciejewski and Baldyga [18] have stressed again the importance of allowing for the effect of the CO_2 pressure. The effects are reported as being greater than those predicted from simple adsorption models. Modification of these models led to the prediction of a linear dependence of the activation energy on P_{CO_2}. These predictions were in good agreement with experimental values, which ranged from 210 kJ mol^{-1} at very low pressures, to 460 kJ mol^{-1} at $P_{CO_2} = 6$ kPa.

The decompositions of magnesite, $MgCO_3$, and brucite, $Mg(OH)_2$, in various atmospheres of air, water vapour and CO_2, were studied by Hrabě and Svetík [19]. Activation energies were determined from TG curves using the An model and the method of Craido and Morales. For magnesite, the E_a value in air of 152 kJ mol^{-1} increased to 236 kJ mol^{-1} in water vapour and to 450 kJ mol^{-1} in pure CO_2. Even higher values (up to 505 kJ mol^{-1}) were obtained in mixtures of water vapour and CO_2. For brucite, E_a was 107 kJ mol^{-1} in air, 185 kJ mol^{-1} in water vapour and 221 kJ mol^{-1} in CO_2. Intermediate values were obtained in mixed atmospheres. The specific surface areas of the products also varied with the atmosphere during decomposition, indicating the importance of the atmosphere in promoting recrystallization processes. Kinetic analysis of TG measurements [20] on basic zinc carbonate gave an activation energy for decomposition of 59 kJ mol^{-1}. This value varied slightly with heating rate, sample mass, sample disposition and the kinetic model used. The results were used to define conditions for the optimum production of high-surface-area ZnO.

An isothermal study [21] of the decomposition of copper chromate

$$CuCrO_4 \rightarrow CuO + CuCr_2O_4 + 1.5O_2$$
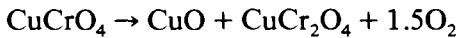
in air and N_2, using TG supplemented by X-ray diffraction measurements, gave α–time curves which were fitted ($0.2 < \alpha < 0.9$) by the A2 model. Activation energies were 248 ± 8 kJ mol^{-1} in static air and 229 ± 8 kJ mol^{-1} in flowing N_2. α–time curves derived from intensities of characteristic X-ray reflections were fitted by the first-order rate equation and gave an activation energy of 262 ± 4 kJ mol^{-1} for the reaction in air.

The decomposition of copper hypophosphite, $Cu(H_2PO_2)_2$, mixed 1:1 with quartz sand, under isothermal conditions in the range 45–60°C has a marked induction period [22]. This induction period was attributed to the formation of H_3PO_2. Introduction of H_3PO_2 into the compound during crystallization decreased the induction period in proportion to the acid concentration. The rate of further decomposition is controlled by the rate of acid removal from the reaction interface. Activation energies, determined from the variations of the induction period and of the maximum rate with temperature, were 111 ± 6 and 100 ± 5 kJ mol^{-1}, respectively.

Another compound with "model" status is potassium permanganate. The

Prout–Tompkins kinetic equation:

$$\ln(\alpha/(1 - \alpha)) = kt + c$$

was originally applied to describe the decomposition of $KMnO_4$ in vacuum. Brown et al. [23] have used isothermal DSC to test the applicability of the model. Results show that when product oxygen is continuously removed, the decomposition is more complex than expected, with several exothermic and endothermic contributions overlapping one another. Activation energies, estimated from the isothermal DSC curves, ranged from 123 to 158 kJ mol^{-1} in N_2 and from 160 to 191 kJ mol^{-1} in O_2. Crushing the samples lowered these values. SEM photographs showed cracking and generation of fresh surfaces consistent with an overall autocatalytic process.

CONCLUSIONS

The studies quoted above were selected on the basis of their more quantitative application of thermal analysis techniques to kinetic problems. Much of the effort put into these studies has been directed at deriving apparent activation energies, but two main problems restrict the interpretation of these values in reaction mechanisms:

(1) the procedures for non-isothermal kinetic analysis are still an area of controversy, and

(2) the E_a values obtained are very sensitive to experimental conditions and definition and control of these conditions still need much attention.

Many studies still lack adequate supporting observations from complementary studies [2,3], in spite of the ever accumulating evidence that the decomposition mechanisms of even the formally most simple compounds cannot be described adequately in simple terms. The suggestion and evidence of Tanaka and Kawabata [14] that mixed models may need to be considered in such descriptions is valuable.

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