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A KINETIC STUDY OF WATER EVOLUTION FROM A MOLTEN HYDRATED SALT

The dehydration of meso lithium potassium tartrate dihydrate

A. K. Galwey, G. M. Laverty, V. B. Okhotnikov and J. O'Neill*

SCHOOL OF CHEMISTRY, THE QUEEN'S UNIVERSITY OF BELFAST, BELFAST BT9 5AG, NORTHERN IRELAND
*INSTITUTE OF SOLID STATE CHEMISTRY, NOVOSIBIRSK 630091, USSR

Meso lithium potassium tartrate dihydrate melted before dehydration and a kinetic study of this reaction has been completed. This system is of interest in establishing the kinetic characteristics of a homogeneous rate process in the absence of added solvent. Results are of interest in considering the mechanisms of solid or condensed state reactions where melting is a possibility.

The evolution of the initial $1.2H_2O$ from the single crystal dihydrate reactants was zero order, the rate then became deceleratory and the first order expression was obeyed to $1.6H_2O$. The activation energy of the process was high, 230±10 kJ mol^{-1} (350–380 K). Evolution of the remaining water occurred by a slower first-order process to give the anhydrous salt. The dehydration of crushed powder reactant was initially relatively more rapid but was deceleratory throughout, obeying the first order equation. It is concluded that salt dehydration is controlled by the rate of surface release of water that is comparatively mobile within the reactant melt.

Keywords: kinetics, meso lithium potassium tartrate dihydrate, molten hydrated salt

Introduction

In formulating the mechanism of a reaction proceeding in a condensed phase, a central consideration is whether or not the chemical change occurs in a melt. Bond redistribution steps occurring in fused materials may be expected to be controlled by parameters similar to those operating in other homogeneous reactions though the absence of a solvent means that reactant concentrations and the frequencies of reactant collisional encounters are unusually high. Under such conditions, however, the parameters recognized as influencing, and sometimes regarded as promoting, reactivities of solids are absent: these include strain at reaction interfaces, catalytic interactions

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within the reactant/product contact zone and topotactic processes. To characterize fully the sequence of chemical steps through which reactants are converted into products, and their controls, therefore, it is essential to establish the nature of the environment within which such changes proceed, including characterization of the phases participating, solid or liquid. Moreover, reactions in a melt are believed [1] to proceed relatively more rapidly than those in a solid because the stabilizing forces of a crystalline structure are absent and there is greater stereochemical freedom to adopt a transition state configuration.

Positive recognition of local or temporary melting, during what appears to be a solid state decomposition reaction, can be very difficult. These difficulties were most effectively demonstrated during a study of the thermal decomposition of copper(II) malonate [2]. Electron microscopic textural examinations of the crystal interiors of partially reacted crystals revealed the development of froth structures, ascribed to gas formation within a fluid reaction medium following the production of copper(II) acetate intermediate. The individualities and approximate shapes of the original reactant crystals were, however, maintained during this decomposition by the generation of an unreactive superficial layer which included bubble-like protuberences. Careful thermoanalytical studies failed to give any evidence of the early onset of comprehensive melting, consistent with its progressive occurrence throughout the reaction: see, however [3].

Other reactions previously accepted as proceeding in the solid state, for which there is now strong evidence for the participation of a liquid intermediate, include the following. The thermal decomposition of ammonium perchlorate [4], involving the intervention of NO_2ClO_4, the pyrolysis of ammonium dichromate [5], where CrO_3 was identified as the intermediate and the reaction of chlorine with potassium bromide [6] in which the large, brown-coloured nuclei contain liquid bromine. The significant feature of these processes is the intervention of a fluid or melt, although the sigmoid-shaped fractional reaction (α)-time curves for the isothermal reaction are more usually ascribed to, and sometimes uncritically accepted as sufficient evidence of, a nucleation and growth process. However, it must be remembered that the kinetic characteristics of reactions in solvent-free condensed phases and processes involving local and/or temporary melting have not been extensively characterized. It is with a system of this type that the present paper is concerned.

Recent comparative studies of the thermal dehydrations of lithium potassium tartrate hydrates [7] led to the conclusion that these salts represent a particularly favourable set of compounds, of identical compositions, in which the influence of structure on reactivity can be investigated. The dehydrations of *d* $LiKC_4H_4O_6 \cdot H_2O$, *dl* $LiKC_4H_4O_6 \cdot H_2O$ and meso $LiKC_4H_4O_6 \cdot 2H_2O$ have been studied and the kinetic characteristics shown to be different. The present paper describes the water evolution process from meso $LiKC_4H_4O_6 \cdot 2H_2O$ in which reaction involves melting.

Experimental

The kinetics of isothermal dehydration of meso $LiKC_4H_4O_6 \cdot 2H_2O$ was investigated from measurements of evolved water vapour pressure in a constant volume glass vacuum apparatus. After initial evacuation, the reactant sample (50 mg) was introduced into the constant temperature reaction zone (±0.5 K) and the extent of reaction determined from the pressure rise measured at selected time intervals using a MKS 222B absolute pressure gauge in the range 0–10 Torr (measured ±0.001 Torr). Time, pressure, temperature values at suitable time intervals were recorded and stored in the memory of a computer for later kinetic analysis including the presentation of results in graphical form. The apparatus has been described in detail [2].

Reactant

The salt used was studied previously [7], elemental analysis of the prepared reactant (20.75%C and 3.48%H) corresponded closely with theoretical expectation (20.87%C and 3.50%H) for $LiKC_4H_4O_6 \cdot 2H_2O$. Kinetic studies were concerned with individual single crystals obtained by slow evaporation of saturated aqueous solution and powder samples from freshly crushed crystals.

Results

Stoichiometry

The gaseous reaction product evolved during the present kinetic studies 350–380 K was identified as water only. All the gas released was condensed at 178 K, confirming the absence of CO_2 evolution, the principal product of anion breakdown.

Measurement of the gas pressure evolved in the known apparatus volume and determinations of reactant weight losses confirmed the evolution of 1.9±0.1 H_2O/mole of salt reacted, representing completed dehydration:

$$\text{meso } LiKC_4H_4O_6 \cdot 2H_2O \rightarrow \text{meso } LiKC_4H_4O_6 + 2H_2O$$

It has been shown already [7] that the anhydrous solid product is crystalline.

Reaction proceeded to completion in two stages, the first more rapid process was completed at 1.6±0.15H_2O and the evolution of the remainder, 0.3H_2O, was significantly slower.

Electron microscopy

Examination of dehydrated crystals in the scanning electron microscope gave direct evidence of reactant melting. After dehydration, crystal surfaces were rounded and smooth, characteristic of morphological control by surface free energy rather than the flat faces and sharp edges that result from crystallographic forces. The salt also wetted glass fibres (used to retain the reactant in the reaction tube) and these became embedded in the reactant mass. Surface textures also included star-shaped scar features that are interpreted as sites of former bubble formation and collapse following release of a puff of steam.

Kinetics of dehydration

Single crystals

Typical fractional reaction (α)-time plots for the main dehydration reaction (evolution of *ca.* 1.6H_2O) of meso LiK tartrate dihydrate are shown in Fig. 1. An initial short acceleratory process was completed rapidly at low α (=*ca.* 0.05) and is identified with the onset of melting. Thereafter the reaction proceeded at constant rate, zero order kinetics, between $0.05 < \alpha < 0.75$, representing the evolution of *ca.* 1.2H_2O. Reaction rates above 365 K were constant but at lower temperatures there was some evidence of irregularities, these can be seen from the 362 K plot on Fig. 1. The calculated activation energy for these zero order rate constants was 230±10 kJ mol^{-1} (350–380 K), a relatively high value.

Above $\alpha = 0.75$ the reaction became deceleratory and obeyed the first order equation, again the activation energy was 210±20 kJ mol^{-1} (350–380 K), comparable with that for the zero order stage. After completion of this rate process, water evolution continued at a slower rate, finally completing dehydration of the dihydrate.

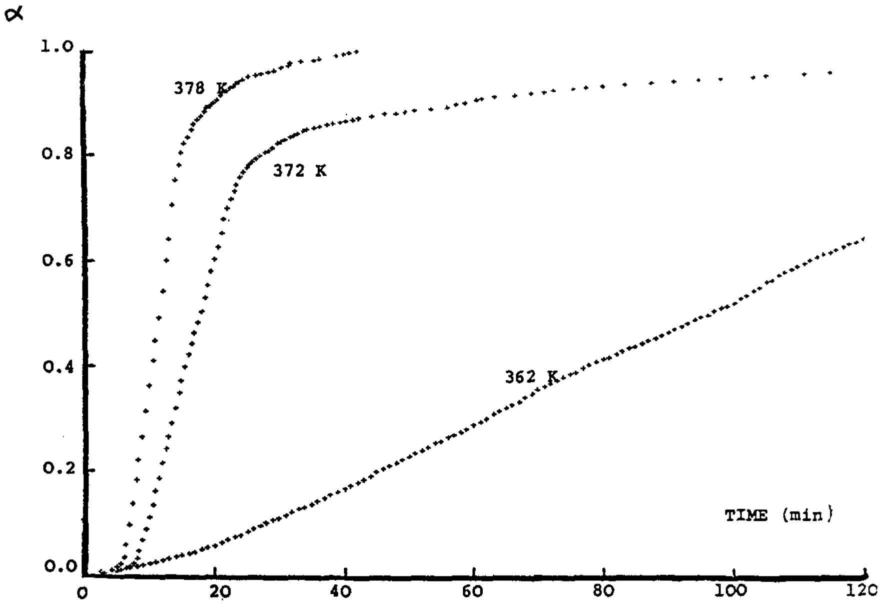

Fig. 1 Fractional reaction (α)-time plots for the isothermal dehydration of crystals of meso lithium potassium tartrate dihydrate at three reaction temperatures 362, 372, and 378 K. The reaction is approximately zero order when $\alpha<0.7$ and becomes deceleratory in the final stages

Powder

Dehydrations of freshl crushed powder samples were deceleratory throughout. A typical α-time plot is compared with the reaction of a single crystal at the same temperature, 362 K, in Fig. 2. This reaction showed very satisfactory obedience to the first order equation. Again reaction was completed after release of $1.6H_2O$ and the remainder of the water from the dihydrate was evolved more slowly.

Discussion

The microscopic evidence positively identified the reactant as melting before or during reaction, together with indications of water release through the generation of subsurface bubbles that subsequently burst. This representation is entirely consistent with the predominantly zero order kinetic behaviour observed for single crystal reactants if it is assumed that dehydration process is controlled by the overall evaporation rate at the

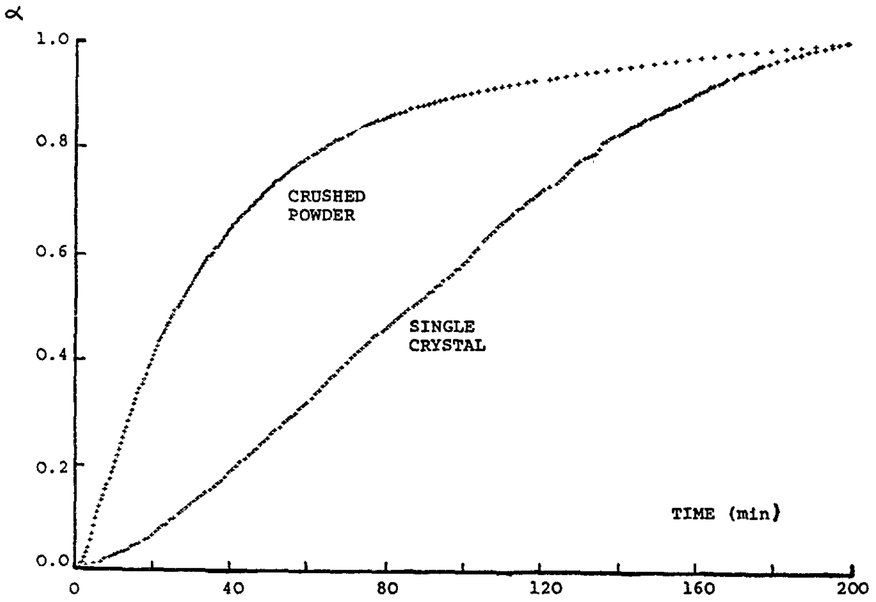

Fig. 2 α-time plots for the isothermal dehydration at 362 K of meso lithium potassium tartrate dihydrate samples in the form of a single crystal and freshly crushed powder

outer boundary and bubble cavity surfaces. It is concluded that the high activation energy arises as a composite term probably including contributions from

(i) the energy required to release the water molecule from the highly hydrogen-bonded environment within the salt, in which the anion includes hydroxyl and carboxyl groups, and from cation coordination,

(ii) evaporation/desorption from the hydrophilic salt surface and

(iii) temperature dependent changes in the ease of water migration within the viscous melt.

Reaction of the powder differed in being deceleratory throughout. The relatively more rapid initial rate (x3, Fig. 2) does not adequately reflect the large increase in surface area caused by crushing (x1000?). This apparent inconsistency may, however, be reconciled if it is assumed that heating results in extensive interparticular sintering of the crystallites comprising the assemblage with consequent marked reduction in area. Such aggregation is expected to involve temporary retention of interparticulate pores filled with water vapour. These bubbles of gas (steam) will develop by coalesence and burst at reactant mass surfaces after movement in the viscous fluid leading to the progressive diminution in reaction rate, see Fig. 2, expressed by the first order equation.

We conclude, therefore, that the reaction is controlled by the rate of surface loss of water that is relatively mobile within the reactant phase. In powder, the effective surface area participating in water loss progressively diminished during sintering and bubble collapse. The rate diminished in the final stages as the water concentration within the melt was reduced (α>0.75).

No conclusions concerning the final slow dehydration (after loss of $1.6H_2O$) were obtained. We note that the final (anhydrous) product of this dehydration is crystalline [7] and suggest the possibility that a final proportion of the water (ca. $0.3H_2O$) may be strongly retained during the reorganization of the residual product into a crystalline structure.

Comparison with other stereoisomers

dl $LiKC_4H_4O_6 \cdot H_2O$

The racemic salt melted before a dehydration that was studied [8] in a temperature interval (420–460 K) somewhat higher than that of the relatively more reactive meso salt (350–380 K). Dehydration of the *dl* salt was initiated by a short deceleratory process leading into a zero order reaction that was extensive for single crystal reactants. Again the final stage was deceleratory and the first order equation was obeyed. Thus the kinetic characteristics of the dehydrations of the *dl* monohydrate and the meso dihydrate were closely similar though the latter was appreciably more reactive: both salts melted.

d $LiKC_4H_4O_6 \cdot H_2O$

This reactant did not melt during dehydration. An initial deceleratory reaction [9] is identified as the diffusion controlled loss of water from a surface layer 10 μm thickness, this was completed at α =0.04 in single crystal reactants and at α =ca. 0.5 in crushed powder. The subsequent reaction, completing water loss from the salt, was a nucleation and growth process [10].

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Zusammenfassung — Meso-Lithiumkaliumtartrat-Dihydrat schmilzt noch vor der Dehydratation, eine kinetische Untersuchung dieser Reaktion wurde vollzogen. Dieses System ist interessant für die Abschätzung kinetischer Parameter von Prozessen mit gleichbleibender Geschwindigkeit ohne Gegenwart zugesetzter Lösungsmittel. Die Ergebnisse sind von Interesse bei Überlegungen zu Mechanismen von Feststoffreaktionen oder Reaktionen im kondensierten Zustand, bei denen Schmelzen als Möglichkeit auftritt.

Die Freisetzung der ersten 1.2 H_2O aus den Einkristall-Dihydratreaktanden ist eine Reaktion nullter Ordnung, anschließend wird die Geschwindigkeit verlangsamt und unterliegt bis 1.6 H_2O einem Ausdruck erster Ordnung. Der Vorgang weist eine hohe Aktivierungsenergie auf: 23010 kJ/mol (bei 350-380 K). Die Freisetzung des restlichen Wassers erfolgt in einer langsameren Reaktion erster Ordnung, man erhält das wasserfreie Salz. Die Dehydratation von zerkleinerten pulverisierten Reaktanden verlief anfangs relativ schneller, verlangsamt dann jedoch ganz und gar und unterliegt einer ersten Reaktionsordnung. Es wird geschlußfolgert, daß die Dehydratation des Salzes durch die Freisetzungsgeschwindigkeit des Wassers an der Oberfläche kontrolliert wird, wobei das Wasser innerhalb der Reaktionsschmelze relativ beweglich ist.