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THE THERMAL DECOMPOSITION OF OXALATES*
PART 14. DEHYDRATION OF MAGNESIUM OXALATE DIHYDRATE

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ABSTRACT

The isothermal dehydration of magnesium oxalate dihydrate has been studied under various pressures of water vapour by use of a thermogravimetric balance. The rate of dehydration was found to be dependent upon the water vapour pressure.

The reaction rate at temperatures below 124°C decreases sharply with an increase in water vapour pressure up to 0.5 mm Hg. With further increase in pressure an increase in rate is observed; this rises to a maximum and then falls again as the pressure is increased. The limitation of this phenomena to a limited temperature range is shown in the case of magnesium oxalate dihydrate. Above 124°C the initial fall in rate is not observed, the rate rises with increasing pressure from vacuum to a maximum and then falls. X-ray diffraction studies indicated that the anhydrous product prepared in the second region where a decrease of rate of dehydration occurred was crystalline but the sample dehydrated under vacuum or in the first region produced an amorphous anhydrous salt. A compensation effect is demonstrated with plots of the activation energy against the logarithm of the pre-exponential term in the Arrhenius equation.

INTRODUCTION

The unusual variation in the dehydration rate constant with the partial pressure of water vapour has been reported by several workers[2-4] but has not been reported for magnesium oxalate. In the reported cases at low pressures of water vapour, the dehydration rate constant decreased with increasing water vapour until a critical pressure was reached. The rate constant then increased sharply and in the higher pressure range, the behaviour in the presence of water vapour was normal. In the first region the product has been shown to be amorphous, in the second region the product was crystalline.

The transition from an amorphous to a crystalline form of dehydrated salt has been reported by Dell and Wheeler[5] using DTA and X-ray diffraction techniques. A

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detailed examination of their work reveals that although the general concept is correct, some of their quoted examples are inaccurately interpreted. It has also been shown that the existence of this phenomena in the dehydration of calcium oxalate monohydrate might be a factor in the analytical interpretation of the products of decomposition[6]. On one hand the decomposition might lead to a metastable amorphous phase, whilst on the other it might lead to a crystalline stable phase. In a recent paper on the subject, Watelle-Marion[7] suggests that the metastable state is set up when the initial conditions are far from the position of equilibrium.

EXPERIMENTAL

A Control Instruments Limited, E.S.1. thermogravimetric balance was used to study the isothermal dehydration of magnesium oxalate dihydrate. This balance could detect changes in weight to an accuracy of 10^{-5} g which were displayed on a potentiometric recorder. Magnesium oxalate dihydrate, Hopkin & Williams, Fine Chemical Grade of 160–200 mesh was outgassed for 4 h below 10^{-4} mm Hg prior to the experiment. The formula of the initial material was shown by analysis to be $Mg(C_2O_4) \cdot 2H_2O$ and as used, to contain no detectable moisture. In each case a 10-mg sample was used. The temperature of the sample was recorded during the dehydration using a thermocouple positioned just above the sample. It was shown in blank experiments that in the temperature range investigated here, isothermal conditions could be achieved in less than 1 min from the commencement of the heating.

The water-vapour pressure of the system was maintained constant by using thermostated sulphuric acid solutions of known concentrations[8] and measured on a thermostated oil manometer. X-ray diffraction analysis was carried out by use of a Van Arkel camera with a Cu-K_α target.

RESULTS

Studies using the thermogravimetric balance

The weight loss during the isothermal dehydration of magnesium oxalate dihydrate was monitored until complete. The dehydration was studied under vapour pressures of 0, 0.124, 1.03, 3.97 and 8.45 mm Hg. Figure 1 shows weight-loss data for the complete dehydration at a water-vapour pressure of 3.97 mm Hg at temperatures between 123 and 136°C. The data recorded at the other pressures was similar and isokinetic. The complete dehydration corresponded to within 1.0% of the theoretical weight loss of 24.6%. An examination of the kinetics of these curves by the use of reduced time plots as advocated by Sharp et al.[9] showed the dehydration to follow fairly closely first order kinetics.

However, an inspection of all the isothermal curves showed that up to about 15–18% they were linear. A rate constant (k) could be obtained for this initial linear region and plots of log k against $1/T$ constructed, (where T is the temperature of the

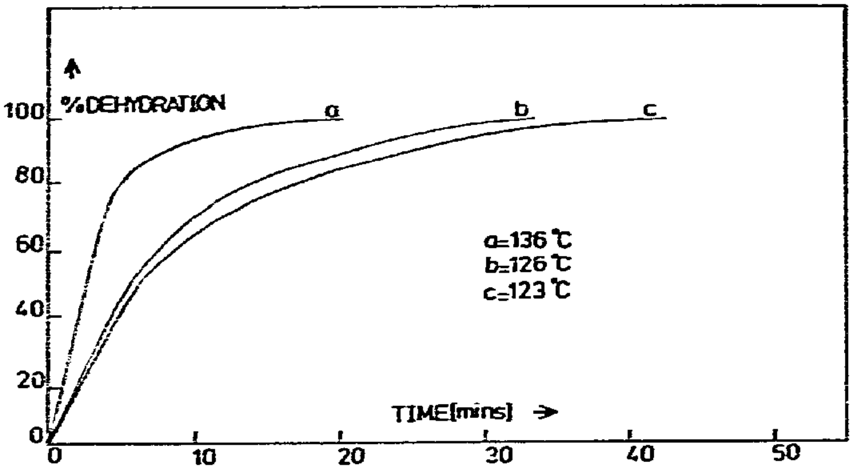
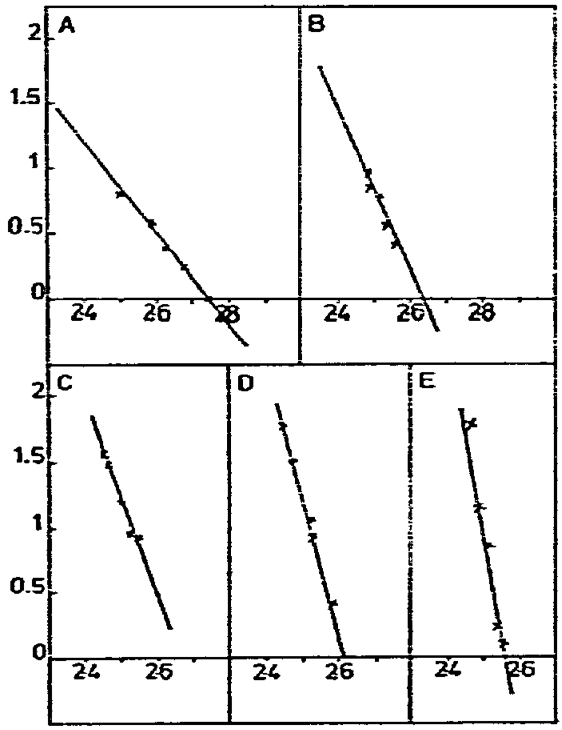


Fig. 1. Weight loss data for the dehydration of magnesium oxalate dihydrate at a water-vapour pressure of 3.97 mm Hg at temperatures of: a = 136°C; b = 126°C; c = 123°C. Abscissae, time (min); ordinate, percentage dehydration.



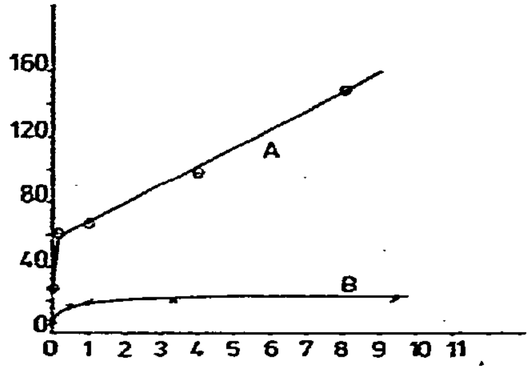


Fig. 2. Dehydration at various pressures of water vapour. log k vs. $1/T$: a = vacuum; b = 0.124 mm Hg; c = 1.103 mm Hg; d = 3.97 mm Hg; e = 8.45 mmg Hg. Abscissae, $T^{-1} \times 10^3$; ordinate, log K.

Fig. 3. The energy of activation E_a (kJ mol^{-1}) as a function of water vapour pressure (mm Hg) for magnesium oxalate dihydrate and calcium oxalate monohydrate. (1 mm Hg = 0.1333 kN m^{-2}.) A = magnesium oxalate dihydrate; B = calcium oxalate monohydrate. Abscissae, water-vapour pressure in mm Hg. Ordinate, E_a, activation energy in kJ mol^{-1}.

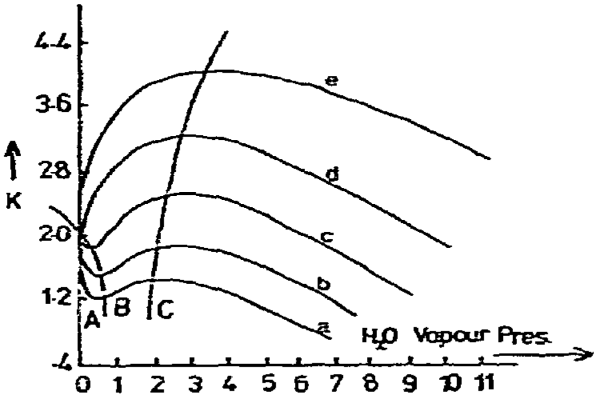


Fig. 4. The variation of reaction rate with water vapour pressure at temperatures of: a = 114°C; b = 118°C; c = 122°C; d = 126°C; e = 130°C. Abscissae, water-vapour pressure in mm Hg. Ordinate, specific reaction rate k.

isothermal run in degrees Kelvin), and these are shown in Fig. 2. The variation of the Arrhenius activation energy formally calculated in this manner is presented in Fig. 3. The important observation here is the change observed with the variation in pressure. A comparison can be made of these data with the corresponding data for the change in activation energy for the dehydration of calcium oxalate monohydrate[6] which is also plotted on the same figure.

The linear plots of $\log_{10} k$ against $1/T$ (Fig. 2) make it possible to read off values of k at specific values of T and so allow plotting of k against vapour pressure at specific temperatures. Plots of k against the pressure of water vapour at temperatures of 114, 118, 122, 126 and 130°C are given in Fig. 4.

X-ray diffraction data

Powder diffraction photographs were taken of samples prepared in vacuum and under water vapour in excess of 1 mm Hg pressure. The dehydrations were carried out in the X-ray tubes so the sample prepared in vacuum could be sealed and so have no contact with the water vapour present in the atmosphere. The X-ray diffraction photographs indicated that the sample prepared under water vapour was crystalline whilst the sample prepared in vacuum was amorphous to X-rays.

DISCUSSION

The variation of the rate of dehydration of magnesium oxalate dihydrate as a function of water-vapour pressure described in this study has also been found by workers investigating the dehydration of other salt systems[2-4]. In all cases, the phenomena has been attributed to the difference in form of the dehydrated product. That formed in vacuum is amorphous and that formed in water vapour above a certain stated pressure is crystalline. The results for magnesium oxalate dihydrate dehydration show exactly the expected trends below 124°C. In Fig. 4 three regions can be observed: A, B and C.

In A the rate falls from an extremely fast rate at vacuum to a slower rate as the water vapour pressure is increased, then in region B as the water vapour pressure is further increased the rate increases to a maximum, and then falls in region C where the water-vapour pressure is increased still further. The region B is a region in which some of the anhydrous material is found in a crystalline form and some in an amorphous form. Region A corresponds to amorphous product and region C to a crystalline product.

In this study, we have shown that there is a temperature limitation to the phenomenon, and above 124°C it can be seen that, for the dehydration of magnesium oxalate dihydrate region A, no longer exists. Since region B still exists, it seems likely that, at this higher temperature, there is effectively a pressure of water vapour at the surface even in vacuum since the water is evolved more quickly and diffusion from the sample will be a finite process. This is probably why the "Smith-Topley" effect has not commonly been noted in "rising-temperature" experiments.

The Smith-Topley effect has in the past been explained in terms which tend to concentrate in the appearance of the amorphous phase. However, if the effect illustrated in Fig. 4 is examined carefully, it is seen to consist of two separate systems each behaving perfectly normally with respect to the effect of water vapour; e.g., System A (in Fig. 4)

hydrated salt → amorphous anhydrous salt + water vapour

System C (in Fig. 4)

hydrated salt → crystalline anhydrous salt + water vapour

The speculation must therefore be why the amorphous phase appears under conditions of high vacuum and low water-vapour pressure whilst the crystalline phase appears at higher pressures of water vapour. Here the explanations of Volmer and Seydell[10] and of Topley[11] are very helpful. The conditions under which water vapour is driven off in the first system cause the reaction interface to be distorted and irregular and in particular the appearance of micro-cracks help in this distortion. The nett effect is to produce an irregular amorphous product because such conditions impede the formation of perfect crystallites forming a barrier to the diffusion processes necessary for the formation of perfect crystals. However, the appearance of a critical amount of water vapour would cause the diffusion process to be enhanced (many sintering studies show the acceleratory effect of water vapour) and the combined effect of the back reaction and re-deposition of material in cracks from the water produced by dehydration could cause cracks, especially the micro-cracks to be annealed out of the system so that in the second system the product is crystalline.

It is worthwhile examining the pre-exponential term to the Arrhenius equation, when a plot of this term against the activation energy should provide an example of the compensation effect.

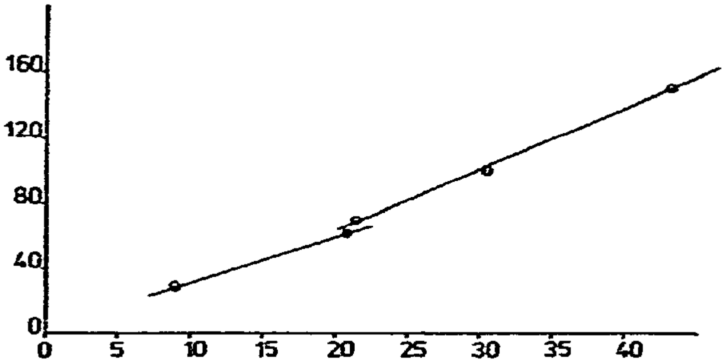


Fig. 5. Plot of $\log_e A$ vs. E_a (kJ mol^{-1}). Abscissae, $\log_e A$; ordinate, E_a.

From the Arrhenius equation we have:

$$\log_e A = \log_e K + \frac{E_a}{RT}$$

hence from plots of $\log_e K$ vs. $1/T$ (Fig. 2) the intercept on the $\log_e K$ axis is equal to $\log_e A$. The values of A varied from 10^3 to 10^{20} in going from vacuum to 8 mm Hg water-vapour pressure. This indicates a surface reaction[12].

A plot of $\log_e A$ vs. E_a (Fig. 5) showed two linear portions, the change in slope occurring between $E_a = 60$ and $E_a = 65$ kJ mol^{-1} which is found, from the plot of E_a vs. water vapour pressure (Fig. 3), to correspond to a water-vapour pressure of 0.1 to 1.0 mm Hg. This pressure is approximately the limiting pressure for the amorphous product. Thus each region in the system showing the Smith-Topley phenomena produces a compensation effect whereby a change in the activation energy is reflected by a compensating change in the pre-exponential term. The effect has been discussed by Laidler[13] for homogeneous reactions. The energy of activation and the pre-exponential terms in the Arrhenius equation may be identified with the heat of reaction and the entropy change associated with the formation of the activated complex, i.e.,

$$K = \frac{RT}{Nh} e^{-\Delta G^{\neq}/RT}$$

where K is the specific reaction rate; R is the gasco nstant; N is Avogadro's number; h is Planck's constant; T is the temperature in degrees absolute; and $\Delta G^{\neq}$ is the Gibbs free energy for the formation of the activated complex (kJ mol^{-1}).

but $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$

where $\Delta H^{\neq}$ is the heat of reaction for the formation of the activated complex; and $\Delta S^{\neq}$ is the entropy change associated with the formation of the activated complex.

$\Delta H^{\neq}$ is equated with E_a, while A is given by

$$A = \frac{RT}{Nh} e^{\Delta S^{\neq}/R}$$

or

$$\log A = \log \frac{RT}{Nh} + \frac{\Delta S^{\neq}}{R}$$

and

$$T\Delta S^{\neq} = RT\ln A - \ln \frac{RT}{h}$$

Setting T at 400 K gives $T\Delta S^{\neq} = 5.545 \log_{10} A - 71.65$ and $\Delta G^{\neq} = \Delta H^{\neq} + 71.65 - 5.545 \log_{10} A$.

The linear relationships shown between $\log_e A$ and E_a (Fig. 5) are due eventually to linear relationships between $T\Delta S^{\neq}$ and $\Delta H^{\neq}$ for both the "amorphous product" system at vacuum and at low water-vapour pressures and the "crystalline product" system at higher pressures of water vapour.

The compensation effect is an experimental observation. It has been applied to homogeneous reactions but is now increasingly applied to heterogeneous reactions. This could mean that for it to apply in these latter circumstances certain of the conditions apertaining to homogeneous reactions might still apply in these studies on heterogeneous dehydrations.

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