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THERMAL DECOMPOSITION IN AIR OF HYDRATED VANADYL SULPHATE

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ABSTRACT

The decomposition of hydrated $VOSO_4$ in air was studied. Water was found to evolve in three stages and the dissociation of the anhydrous salt to occur as a fourth step. The kinetics of this latter reaction were studied using both non-isothermal and isothermal techniques. The activation energy was calculated and the reaction mechanism elucidated.

INTRODUCTION

Very little has been published to date about the decomposition of oxysulphates in general and vanadyl sulphate in particular. Selbin [1] studied the structure of the vanadium salt $VOSO_4$, but his results were mainly concerned with the dissociation of the salt in solution. On the other hand, the anhydrous salt dissociates according to the reaction [2]

$$2VOSO_4 = V_2O_5 + SO_2 + SO_3$$

Moreover, Dearnaley and Kerridge [3] found that the anhydrous salt begins to dissociate at 450 °C. These authors presented a TG curve for anhydrous $VOSO_4$ decomposition, but did not attempt to analyse their data.

The hydrated salt was reported by Cotton [4] to have the formula $VOSO_4 \cdot 5H_2O$, but he only interpreted the presence of four of the water molecules.

In the present work, the mechanism of dissociation of the hydrated salt was studied using both non-isothermal and isothermal kinetics.

EXPERIMENTAL

The hydrated salt was supplied by B.D.H. The formula indicated by the supplier was $VOSO_4 \cdot H_2O$, but this number of water molecules was later

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found not to match the weight-loss results. The samples were first ground to pass a 100-mesh screen and then dried overnight at 120 °C. The humidity content was found to be 4% and this was taken into account in subsequent calculations of weight loss.

The non-isothermal study was accomplished using a MOM type derivatograph (Budapest) in which the sample was heated at a constant rate of 10 °C $\min^{-1}$ in an alumina crucible against alumina as reference material.

The isothermal kinetics were followed by equilibrium heating in a thermobalance fitted with an on–off control device. The temperature was recorded using a Rh/Pt (10% Pt) thermocouple. The maximum error in temperature recording was found to be ±5 °C.

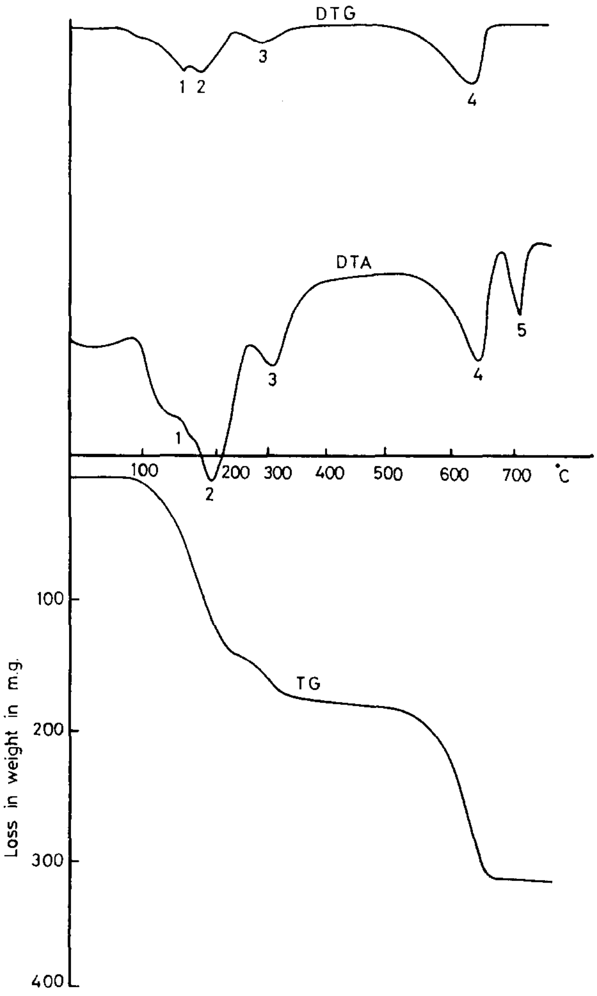

Fig. 1. Thermal analysis curves of hydrated $VOSO_4$.

RESULTS AND DISCUSSION

Non-isothermal results

The results obtained on heating a 500-mg sample in the derivatograph are shown in Fig. 1. The combined TG, DTA and DTG curves show five peaks on the DTA and four on the DTG curves. Weight-loss calculations showed that there are about four molecules of water per molecule of $VOSO_4$. The water molecules are eliminated in three stages: one molecule is eliminated between 140 and 170 °C (peak 1), two molecules between 170 and 220 °C (peak 2) and one molecule between 250 and 320 °C (peak 3). The anhydrous salt remains stable up to about 540 °C when it dissociates to give V_2O_5, SO_2 and SO_3, as expected (peak 4). Finally, a fifth peak was observed on the DTA curve without loss in weight; this corresponds to the melting of V_2O_5.

The decomposition of the anhydrous salt was studied kinetically using the method proposed by Sabry et al. [5]. This consists of selecting equal values of $\mathrm{d}w/\mathrm{d}t$ on the DTG peak and obtaining the corresponding values of W_1, W_2, T_1 and T_2 (Fig. 2). (The definitions of the symbols are given below.) The parameter

$$\lambda = \frac{E}{n} = \frac{R \ln W_1/W_2}{(1/T_1) - (1/T_2)}$$

was calculated for four different values of $\mathrm{d}w/\mathrm{d}t$. The values obtained were fairly constant with an average value of $\lambda = 154$ kJ mol^{-1} V_2O_5. The slope of a plot of $\ln \mathrm{d}w/\mathrm{d}t$ versus $(\ln w) - \lambda/RT$ (Fig. 3) is then the apparent order of reaction n at that particular rate of heating (10 °C min^{-1}). For an activation energy of $E \simeq 226$ kJ mol^{-1} (54.1 kcal mol^{-1}) the value of n is 1.47.

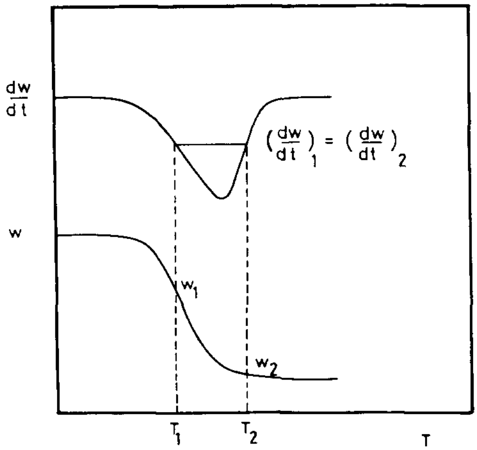

Fig. 2. DTG and TG parameters.

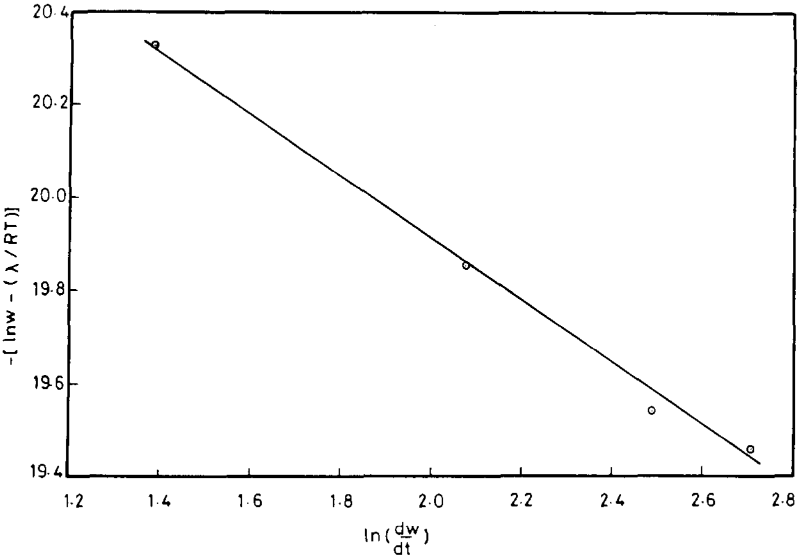

Fig. 3. Plot of $-[\ln w - (\lambda/RT)]$ versus $\ln(\mathrm{d}w/\mathrm{d}t)$.

Isothermal results

To elucidate the decomposition mechanism of the anhydrous salt, equilibrium heating of a sample was performed until the weight remained constant at selected temperatures. It was found that the reaction proceeds isothermally at 450 °C at an extremely low rate. Then, a sample of 2 g was heated in the thermobalance at 400 °C until all the water had been evolved, as checked by a weight-loss calculation. The sample was then transferred rapidly to another thermobalance maintained at 500 °C, and the weight loss was then recorded as a function of time. Another run was executed at 550 °C. The conversion–time relationship at 550 °C is shown in Fig. 4. The time required for the completion of the reaction was about 460 min. The plot of $1-(1-X)^{1/3}$ versus time is shown in Fig. 5. A straight line was obtained with a slope of $1/\tau = 0.002\,19$, corresponding to a reaction time of 455 min, which is in excellent agreement with the experimental value. This indicates that the decomposition proceeds by a boundary reaction mechanism. The kinetic equation proposed is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{3}{\tau}(1-X)^{2/3} = 0.006\,57(1-X)^{2/3}(\mathrm{min}^{-1})$$

The rate constant is therefore $K_1 = 0.00657$ at 550 °C (823 K).

Similar calculations were performed at 500 °C (773 K) to obtain $K_2 = 0.001\,07\ \mathrm{min}^{-1}$ ($\tau = 2780$ min). The activation energy can be calculated using the equation

$$\ln\frac{K_2}{K_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

which gives $E \simeq 192\ \mathrm{kJ\ mol^{-1}}$ (46 kcal $\mathrm{mol^{-1}}$).

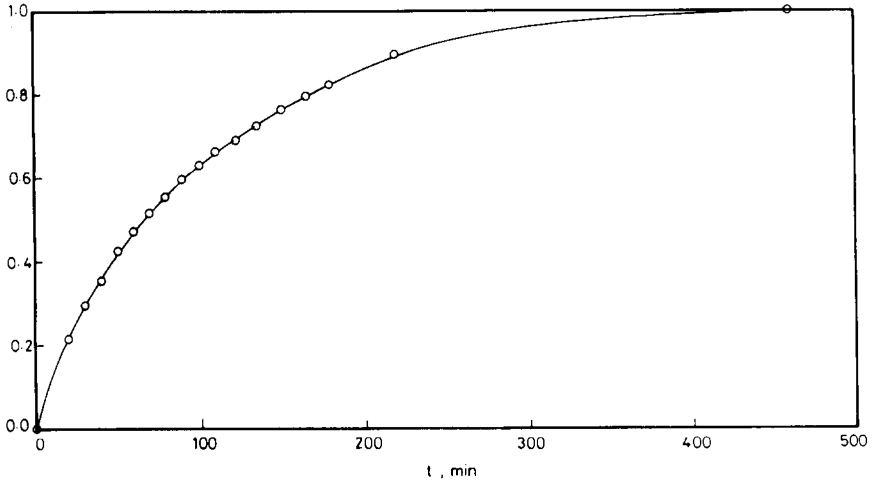

Fig. 4. Plot of fractional conversion versus time (t).

It is worth noting that the reaction kinetics can also be described by a first-order homogeneous reaction of the type $dx/dt = K(1 - X)$ or $\ln(1 - X) = -Kt$. The plot of $\ln(1 - X)$ versus time at 550 °C (823 K) is shown in Fig. 6. The value of K derived from this plot is 0.00974 min^{-1}. A reaction time of 460 min (the experimental time of complete reaction) corresponds to a conversion of 98.7%. At 500 °C (773 K), the calculated value of K, according to that mechanism, is 0.0017 min^{-1}. The activation energy calculated accordingly is 184 kJ mol^{-1} (44 kcal mol^{-1}), which coincides with the

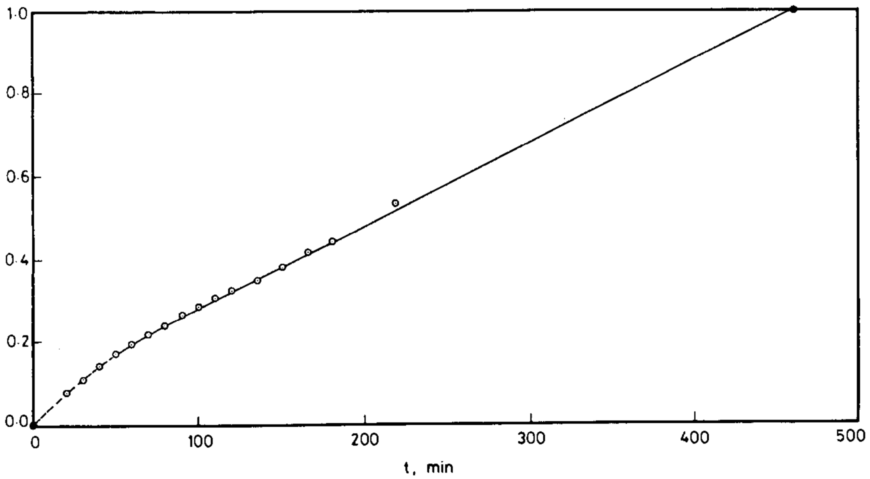

Fig. 5. Plot of $1-(1-X)^{1/3}$ versus time (t).

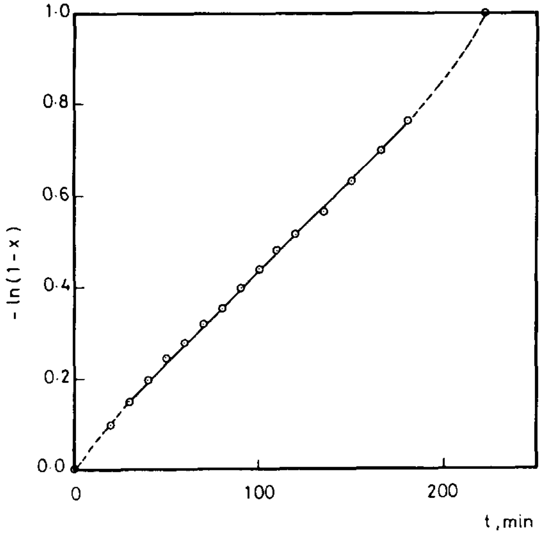

Fig. 6. Plot of $-\ln(1-X)$ versus time (t).

value obtained on assuming a boundary reaction to control the decomposition of $VOSO_4$.

CONCLUSION

The decomposition of hydrated $VOSO_4$ occurs in four stages: three involving the evolution of water and the other being the decomposition to V_2O_5, SO_2 and SO_3. Non-isothermal kinetic analysis gave a value of $E \simeq 226$ kJ mol^{-1} for the decomposition of the anhydrous salt. Isothermal analysis showed that this step can be interpreted either by assuming a boundary reaction mechanism or by assuming homogeneous first-order kinetics. The calculated activation energies obtained for both interpretations were very similar (192 and 184 kJ mol^{-1}, respectively).

LIST OF SYMBOLS

W	Weight (mg)
T	Temperature (°K)
t	Time (min)
$\frac{dw}{dt}$	DTG reading (mg min^{-1})
n	Apparent order of reaction
E	Activation energy (J mol^{-1})
R	General gas constant (J mol^{-1} K^{-1})
X	Conversion
τ	Time required to complete the reaction (min)
K	Rate constant (min^{-1})

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