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THE CATALYTIC EFFECT OF IRON(III) OXIDE, α-Fe_2O_3, UPON THE THERMAL DECOMPOSITION OF ANTIMONY(III) OXYCHLORIDE, SbOCl.

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ABSTRACT

The thermal decomposition of antimony(III) oxychloride, SbOCl, has been studied by DSC complimented by TG,XRD and classical analytical methods. The system was seen to satisfy the conditions of the Kissinger equation (ref.1) a modification of which (ref.2) was employed to calculate the Arrhenius parameters for the decomposition leading to $Sb_4O_5Cl_2$. The presence of α-Fe_2O_3 in admixture, was found to lower the decomposition temperature. Application of an equation based upon the Kissinger model demonstrated the catalytic role of α-Fe_2O_3. Lowering of the decomposition temperature was accompanied by a decrease in the calculated Arrhenius activation energy.

INTRODUCTION

In conjunction with chlorinated organic materials, antimony(III) oxide, Sb_2O_3, has been found to have a pronounced flame retardancy action; the "in situ" formation of SbOCl being implicated as an intermediate in the production of the thermally and hydrolytically unstable flame retardant species, antimony (III) chloride, $SbCl_3$ (ref.3). The presence of iron(III) oxide, Fe_2O_3, has been reported to enhance the flame retardancy properties of Sb_2O_3 (ref.4), but no quantitative data were available in the literature. In this work an investigation has been made into the effect of the presence, in admixture, of α-Fe_2O_3 upon the kinetics of the decomposition reaction. From the work of Murray and White (ref.5) Kissinger developed a method based upon non-isothermal DTA for the determination of the Arrhenius activation energy. Since 1956 the method has been discussed extensively in the literature, and is still widely employed (ref.6). The principal objection to the method is that it was based upon a false premise, namely that the DTA peak characterized the temperature corresponding to the instant of maximum reaction rate,

$$\text{at the peak: } \frac{d}{dt}\frac{dx}{dt} = 0 \qquad (1)$$

where x is the fraction of material decomposed at time t. For the system studied, the nature of the thermal event was such that all points on the curve

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fell within a 1K interval. Thus, due to the sharpness of the decomposition, the basic assumption of the Kissinger model was satisfied. The work of Augis and Bennett (ref.2) was recognised to be an improvement upon the original Kissinger model, since it took into account the starting temperature of the sample.

EXPERIMENTAL METHODS

Techniques

DSC was carried out using the Du Pont R90 Thermal Analyzer in conjunction with the 910 Differential Scanning Calorimeter. A sample mass of 3 mg. was used throughout.

Preparations

$SbOCl$ was prepared by a standard method based upon the controlled hydrolysis of $SbCl_3$ (ref.7). α-Fe_2O_3 was prepared by the thermal decomposition of α-$FeOOH$, itself prepared according to a standard method (ref.8).

RESULTS AND DISCUSSION

DSC of $SbOCl$ in air and argon, revealed a single sharp endothermic event at 530 K. XRD,TG and classical analysis indicated that the decomposition product was $Sb_4O_5Cl_2$. Addition of α-Fe_2O_3 was found to lower the decomposition temperature. Attempts to quantify this effect in terms of the molefraction of α-Fe_2O_3 present in admixture, were unsuccessful; decomposition temperatures of some samples were lowered by up to 50 K, whilst other samples containing similar concentrations of α-Fe_2O_3, showed little or no effect. The observed lack of correlation was not due to non-reproducibility of decomposition temperature for a given sample. The results suggested that the phenomenon was attributable to a surface property, rather than a bulk property of the added α-Fe_2O_3.

The following relationship was derived by Murray and White (ref.5)

$$Z = \frac{dT}{dt}(E^{\ddagger})/\exp(-E^{\ddagger}/RT_d)RT_d^2 \qquad (2)$$

where Z = Arrhenius pre-exponential factor, $E^{\ddagger}$ = Arrhenius activation energy and T_d = decomposition temperature. From equation (2) the following relationship can be derived

$$-E^{\ddagger}/R = d \quad \ln \frac{dT}{dt}/T_d^2 \quad /d \ \frac{1}{T_d} \qquad (3)$$

By monitoring the effect of heating rate, $\frac{dT}{dt}$, upon the decomposition temperature, T_d, Kissinger (ref.1) calculated $E^{\ddagger}$ for kaolinite minerals, using DTA. Using a modified version of equation (3) (see equation 8) (ref.2), the value of $E^{\ddagger}$

for the catalysed and uncatalysed thermal decomposition of SbOCl was calculated. The value of Z was subsequently calculated from equation (2). Insertion of $E^{\ddagger}$ and Z into the Arrhenius equation gave the value of k, the rate constant.

Using equation (4), derived by application of statistical mechanics to activated complex theory (ref.9), and equation (5), we obtain an expression for $\Delta S^{\ddagger}$ (equation 6).

$$k = (k_B\ T/h)\ \exp\ (-\Delta G^{\ddagger}/RT) \qquad (4)$$

$$\Delta H^{\ddagger} = E^{\ddagger} - RT \qquad (5)$$

$$\Delta S^{\ddagger} = R\ell nZ - R\ell n\ (k_B\ T/h) - R \qquad (6)$$

where k = reaction rate constant, k_B = Boltzmann constant, h = Plank's constant, $\Delta G^{\ddagger}$ = Gibbs function of activation, $\Delta H^{\ddagger}$ = entropy of activation.

In this work, the calculated Arrhenius activation energy was lowered by approximately 50% by the incorporation of 5.58% mol α-Fe_2O_3 in admixture. However, the accompanying decrease in $\Delta G^{\ddagger}$ was only approximately 10%, the following explanation is given:

It was noted that decreasing $E^{\ddagger}$ caused a more than proportional decrease in $\Delta S^{\ddagger}$. $E^{\ddagger}$ and Z are related exponentially and a decrease in $E^{\ddagger}$ leads to a dramatic decrease in the value of Z. Z is related to the entropy component, $\Delta S^{\ddagger}$, of $\Delta G^{\ddagger}$, hence the above observation relating a decrease in $\Delta S^{\ddagger}$ to a decrease in $E^{\ddagger}$. Furthermore, at high temperatures, entropy effects become significant, $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, and the resulting decrease in the $\Delta S^{\ddagger}$ component of $\Delta G^{\ddagger}$ can partially offset the decrease in $\Delta H^{\ddagger}$ accompanying a decrease in $E^{\ddagger}$.

It has been shown that equation (3) was based upon an incorrect neglect of the temperature dependence of the rate constant, k (ref.10). By taking this into account, Augis and Bennett (ref.2) derived the equation:

$$\frac{-E^{\ddagger}}{R} = d \quad \ell n\,\frac{dT}{dt}\,/(Td-To) \quad /d(1/T_d) \qquad (7)$$

Where To is the starting temperature of the experiment. In this work it has been demonstrated that graphical solution of equation (7), for $E^{\ddagger}$, (see Fig.1) led to a very similar result to that obtained from equation (3).

The catalytic role played by α-Fe_2O_3 in the lowering of the decomposition temperature of SbOCl was confirmed by the observed decrease in the calculated Arrhenius activation energy (see Table 1).

TABLE 1

Activation energies for catalysed and uncatalysed decompositions.

% molefraction α-Fe_2O_3	Tz (K)	calculated Arrhenius activation energy /(k J mol^{-1})	
		Kissinger	Augis-Bennett
-	531	371	370
1.75	510	280	278
5.58	476	174	171

Tz = extrapolated (least squares) zero heating-rate decomposition temperature.

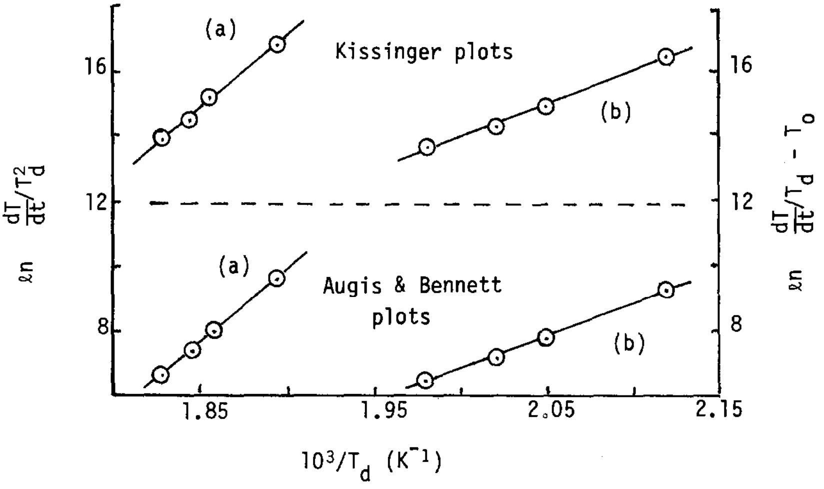

Fig. 1. Kissinger, and Augis and Bennett plots for: (a) uncatalysed and (b) catalysed decomposition of SbOCl.

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