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THERMAL DECOMPOSITION OF HYDROLYSIS PRODUCTS OF $Fe(OH)SO_4$

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ABSTRACT

Hydrolysis products of $Fe(OH)SO_4$ obtained at 15 °C and concentrations of 5 and 15 g l^{-1} of $Fe(OH)SO_4$ were examined by thermal decomposition and X-ray diffraction studies. The products were found to be mixtures of β-FeOOH, $Fe_2O_3 \cdot 2SO_3 \cdot nH_2O$ and $\frac{1}{2}(3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O)$. The basic sulphates lose water of crystallisation and sulphur trioxide on heating. The SO_3 is lost in two stages. The enthalpy changes for water loss were found to be 158 kJ mol^{-1} for product 1 and 176 kJ mol^{-1} for product 2. The corresponding enthalpy changes for loss of SO_3 were 177 and 221 kJ mol^{-1}. The entire thermal decomposition process for both the products takes place in a single mechanism of Avrami's A_3, which assumes random nucleation. The linear regression kinetic equations, together with energies of activation for various types of decomposition, are also given.

INTRODUCTION

Hydrolysis of iron(II) and iron(III) salts has been the subject of intense study during the last several decades. The earlier studies were carried out in relevance to soil conditioning. However, recent studies are being carried out to find industrial applications (catalysts, pigments, magnetic materials, etc.) for the products of hydrolysis. In this connection, it has been felt that a study of the hydrolysis of $Fe(OH)SO_4$ should be very interesting, as this salt can much more easily be hydrolysed than the normal iron salts. The study involves the examination of the products for their chemical composition, phases present and their thermal decomposition behaviour.

EXPERIMENTAL

Apparatus

The carry out thermal decomposition studies, a Derivatograph Model OD-102 supplied by M/S Metrimpex, Hungary, was used. The experiments

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were carried out from ambient temperature to 1000 °C employing a standard heating rate of 10 °C min^{-1} in static air.

Materials

The materials used in this investigation were obtained by the hydrolysis of $Fe(OH)SO_4$. This basic salt was obtained from analytical reagent grade iron(II) sulphate heptahydrate as described earlier [1]. The process of hydrolysis was described elsewhere [2].

Methods

Thermal decomposition studies

About 300–400 mg of the sample was loaded into the platinum sample crucible supplied by the company by gently tapping three times. Inert alumina was loaded into the reference crucible in the same manner.

Compositional studies

A known weight of the material was dissolved in hydrochloric acid. The iron content was determined by the standard dichromate method [3] after reducing iron(III) with stannous chloride. The sulphate content was obtained by the standard barium sulphate method [4]. To find the amount of water present (in the solid dried at 110 °C), a known amount of the material was heated at 250–300 °C to constant weight. From the loss of weight the water content was calculated.

Calculation of kinetic parameters

The kinetics of thermal decomposition were evaluated using the nine kinetic models reported in the literature [5]. To fit the thermal decomposition data into various models, a Lotus spreadsheet macro program was used for obtaining R^2 values as well as linear kinetic equations. The program depends on the linearity of model equations as represented by

$$Y = a + bX \tag{1}$$

where b is the slope and a and b are calculated using the following equations:

$$b = \frac{\Sigma XY - n\overline{X}\overline{Y}}{\Sigma X^2 - n\overline{X}^2} \tag{2}$$

where n is the number of readings, $\overline{X}$ and $\overline{Y}$ are average values of X and Y, and

$$a = \overline{Y} - b\overline{X} \tag{3}$$

The regression value R^2 is given by the equation

$$R^2 = \frac{\left[\Sigma XY - n\overline{X}\overline{Y}\right]^2}{\left[\Sigma X^2 - n\overline{X}^2\right]\left[\Sigma Y^2 - n\overline{Y}^2\right]} \tag{4}$$

In applying this procedure, the regression line having a value of R^2 nearest to unity is selected. If two or more lines have the same R^2 value, then the line having the minimum slope is selected.

Heats of reaction

The heats of various decomposition reactions were calculated from the DTA areas. For this purpose the area under the endothermic melting DTA peak of analytical reagent grade $NaNO_3$ was taken as standard. The value for heat of melting was taken as 3760 cal g^{-1} mol^{-1}.

X-ray analysis

The hydrolysis products were examined by using a Philips X-ray diffractometer. To obtain d values from 2θ values, a computer program was used. Based on these d values and their intensities, various phases present in the hydrolysis products were identified.

RESULTS AND DISCUSSION

The hydrolysis products obtained at six different temperatures (15, 20, 27.5, 40, 60 and 80 °C) and three different concentrations (5, 10 and 15 g l^{-1}) were examined for their chemical composition, phases and thermal decomposition. In this communication we present our results for the hydrol-

TABLE 1

X-ray diffraction data for the compound obtained at temperature 15 °C, concentration 5 g l^{-1} (important d lines). System: $Fe(OH)SO_4 + H_2O$. Molecular formula: $Fe_2O_3 \cdot 1.147SO_3 \cdot 2.353H_2O$

d (intensity) experimental	*d* (intensity) literature		
	$Fe_2O_3 \cdot 2SO_3 \cdot nH_2O$ [a]	$\frac{1}{2}(3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O)$ [b]	β-FeOOH [c]
5.11 (54)	5.05 (20)	5.11 (95)	–
3.57 (38)	3.56 (60)	–	–
3.26 (100)	3.25 (100)	–	3.31 (100)
3.21 (76)	3.20 (80)	–	–
3.14 (65)	–	3.13 (95)	–
3.10 (62)	–	3.09 (100)	–
1.99 (41)	1.99 (20)	1.99 (40)	1.94 (60)
1.59 (32)	1.62 (40)	–	1.64 (100)

X-ray card index numbers: [a] 21-928 (1980); [b] 18-653 (1974); [c] 13-157 (1972).

TABLE 2

X-ray diffraction data for the compound obtained at temperature 15 °C, concentration 15 g l^{-1} (important *d* lines). System: $Fe(OH)SO_4 + H_2O$. Molecular formula: $Fe_2O_3 \cdot 1.272SO_3 \cdot 2.303H_2O$

d (intensity) experimental	*d* (intensity) literature		
	$Fe_2O_3 \cdot 2SO_3 \cdot nH_2O$ [a]	$\frac{1}{2}(3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O)$ [a]	β-FeOOH [a]
5.95 (18)	–	5.97 (18)	–
5.10 (73)	5.05 (20)	5.11 (95)	–
3.56 (35)	3.56 (60)	3.55 (12)	–
3.25 (100)	3.25 (100)	–	3.31 (100)
3.21 (75)	3.20 (80)	–	–
3.13 (89)	–	3.13 (95)	–
3.08 (94)	–	3.09 (100)	–
1.99 (47)	1.99 (20)	1.99 (40)	1.94 (60)
1.63 (24)	1.63 (40)	–	1.64 (100)

[a] X-ray card index numbers as in Table 1.

ysis products obtained at 15 °C for two concentrations (5 and 15 g l^{-1}). The chemical compositions and X-ray diffraction data (for the strongest lines) are presented in Tables 1 and 2. The thermal decomposition data are presented in Table 3. The thermal analysis curves of these compounds are given in Figs. 1 and 2.

The products of hydrolysis at 15 °C at concentrations of 5 and 15 g l^{-1} of $Fe(OH)SO_4$ are mixtures of oxy-hydroxide and basic sulphates. The molecular formula changes from concentration to concentration. However, the basic sulphates and oxy-hydroxide are the same. The data given in Tables 1

TABLE 3

Thermal decomposition data for the basic sulphates

Step	Reaction	Temp. range (°C)	DTA peak (°C)	Wt. loss (%)	
				Isothermal	Dynamic
Product 1, $Fe_2O_3 \cdot 1.147SO_3 \cdot 2.353H_2O$ (5 g l^{-1})					
1	Loss of water	50–450	205 (endo)	14.42	15.54
2	Crystal change	525–565	550 (exo)	–	–
3	Loss of SO_3	550–810	565 745 (endo)	31.24	31.32
Product 2, $Fe_2O_3 \cdot 1.272SO_3 \cdot 2.303H_2O$ (15 g l^{-1})					
1	Loss of water	50–490	225 320 (endo) 385	13.68	13.68
2	Crystal change	490–545	525 (exo)	–	–
3	Loss of SO_3	525–800	565 755 (endo)	33.59	33.58

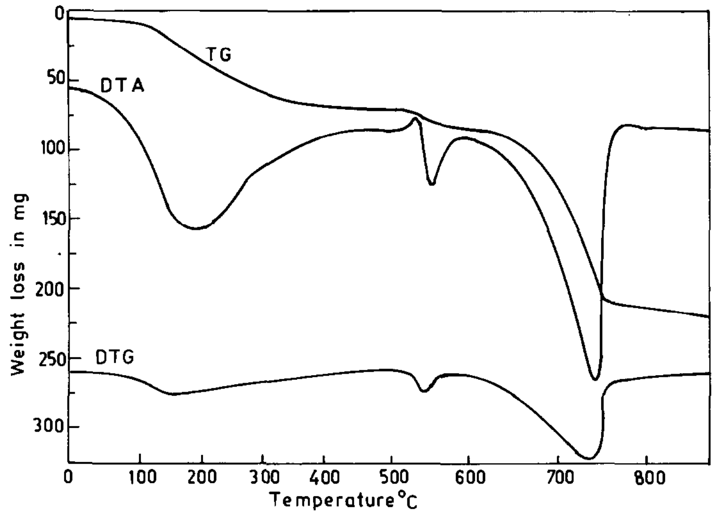

Fig. 1. Thermal decomposition of the hydrolysis product of Fe(OH)SO_4; concentration, 5 g l^{-1}; temperature, 15 °C.

and 2 show that the product contains two basic sulphates: $Fe_2O_3 \cdot 2SO_3 \cdot nH_2O$ and $\frac{1}{2}(3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O)$. The oxy-hydroxide is a β-modification. The thermal analysis results of Table 3 show that there are three prominent regions of weight loss, together with a crystalline transformation. As the products are mixtures of basic sulphates, the weight loss due to loss of SO_3 is given together for the two reactions involving decomposition of basic

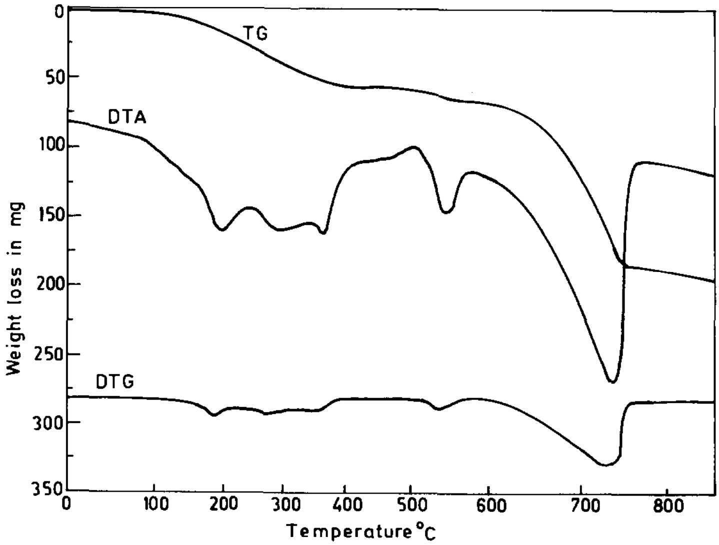

Fig. 2. Thermal decomposition of the hydrolysis product of Fe(OH)SO_4; concentration, 15 g l^{-1}; temperature, 15 °C.

sulphates. The water loss occurs in the region 50–450 ° C. The endothermic DTA peak at 205 ° C for product 1 and the endothermic peaks at 225, 320 and 385 ° C for product 2 are indicative of water loss. Sulphur trioxide is evolved in two regions, as indicated by the endothermic DTA peaks at 565 and 745 ° C for product 1 and at 565 and 755 ° C for product 2. The isothermal and dynamic weight losses for both water loss and SO_3 loss agree well. The crystal transformation from β-Fe_2O_3 to α-Fe_2O_3 takes place in the region 525–565 ° C with an exothermic DTA peak at 550 ° C for product 1. The corresponding change for product 2 occurs in the region 490–545 ° C with an exothermic DTA peak at 525 ° C. The above-mentioned reactions are represented by the following equations.

Product 1 (5 g l^{-1})

$$Fe_2O_3 \cdot 1.147SO_3 \cdot 2.353H_2O \xrightarrow{50\text{–}450\,^\circ C} Fe_2O_3 \cdot 1.147SO_3 + 2.353H_2O \tag{5}$$

$$Fe_2O_3 \cdot 1.147SO_3 \xrightarrow{550\text{–}810\,^\circ C} Fe_2O_3 + 1.147SO_3 \tag{6}$$

$$\beta\text{-}Fe_2O_3 \xrightarrow{525\text{–}565\,^\circ C} \alpha\text{-}Fe_2O_3 \tag{7}$$

Product 2 (15 g l^{-1})

$$Fe_2O_3 \cdot 1.272SO_3 \cdot 2.303H_2O \xrightarrow{50\text{–}490\,^\circ C} Fe_2O_3 \cdot 1.272SO_3 + 2.303H_2O \tag{8}$$

$$Fe_2O_3 \cdot 1.272SO_3 \xrightarrow{525\text{–}800\,^\circ C} Fe_2O_3 + 1.272SO_3 \tag{9}$$

$$\beta\text{-}Fe_2O_3 \xrightarrow{490\text{–}545\,^\circ C} \alpha\text{-}Fe_2O_3 \tag{10}$$

In reactions (7) and (10) it is assumed that β-FeOOH forms β-Fe_2O_3 on loss of water.

The heats of reaction for various steps in the thermal decomposition of the basic sulphates are given in Table 4. The enthalpy change for loss of water appears to be reasonably high, indicating that water in the compounds is firmly attached. The enthalpy change for the loss of SO_3 is rather low when compared to the enthalpy changes for lower basic sulphates of iron,

TABLE 4

Heats of thermal decomposition

Step	Reaction	ΔH (kJ mol^{-1})
Product 1, $Fe_2O_3 \cdot 1.147SO_3 \cdot 2.353H_2O$ (5 g l^{-1})		
1	Loss of water	158.3
2	Loss of SO_3	176.7
Product 2, $Fe_2O_3 \cdot 1.272SO_3 \cdot 2.303H_2O$ (15 g l^{-1})		
1	Loss of water	176.3
2	Loss of SO_3	220.7

TABLE 5

Kinetics of thermal decomposition of basic sulphates

Step	Reaction	Equation for straight line	E (kJ mol^{-1})	Kinetic model
Product 1, $Fe_2O_3 \cdot 1.147SO_3 \cdot 2.353H_2O$				
1	Loss of water	$\log(g\alpha) = (-0.4463/T) \times 10^3 + 0.8672$	8.6	$[-\ln(1-\alpha)]^{1/3}$
2	Loss of SO_3 (I)	$\log(g\alpha) = (-10.2338/T) \times 10^3 + 12.4569$	197.0	$[-\ln(1-\alpha)]^{1/3}$
3	Loss of SO_3 (II)	$\log(g\alpha) = (-4.6337/T) \times 10^3 + 4.6323$	89.2	$[-\ln(1-\alpha)]^{1/3}$
Product 2, $Fe_2O_3 \cdot 1.272SO_3 \cdot 2.303H_2O$ (15 g l^{-1})				
1	Loss of water	$\log(g\alpha) = (-0.8390/T) \times 10^3 + 0.7935$	16.2	$[-\ln(1-\alpha)]^{1/3}$
2	Loss of SO_3 (I)	$\log(g\alpha) = (-8.6041/T) \times 10^3 + 10.546$	165.7	$[-\ln(1-\alpha)]^{1/3}$
3	Loss of SO_3 (II)	$\log(g\alpha) = (-5.3585/T) \times 10^3 + 5.4791$	103.1	$[-\ln(1-\alpha)]^{1/3}$

like $Fe(OH)SO_4$ (539 kJ mol^{-1}) [6] and $Fe_2O(SO_4)_2$ (527 kJ mol^{-1}) [6]. However, the enthalpy change for water loss is much higher than the enthalpy change for water loss of $Fe(OH)SO_4$ (96 kJ mol^{-1}) [6].

The kinetic data for the thermal decomposition in various steps of the basic sulphates are presented in Table 5. The activation energies were calculated from the slopes of the regression equations given in Table 5. The kinetic models obtained through a computer program described earlier are also presented in the same table. It is interesting to note that the whole range of thermal decomposition follows Avrami's A_3 mechanism, which assumes random nucleation. The sulphate is lost in two steps, and therefore the kinetics are worked out for both the steps separately. As in the case of enthalpy changes, the activation energies for loss of SO_3 are much lower when compared to the lower basic sulphates, $Fe(OH)SO_4$ (560 kJ mol^{-1}) [7] and $Fe_2O(SO_4)_2$ (619 kJ mol^{-1}) [7]. The mechanism of decomposition is also different. The lower basic sulphates decomposed with D_1 mechanism, which assumes one-dimensional diffusion with a constant diffusion coefficient.

REFERENCES

1 M.S.R. Swamy, T.P. Prasad and B.R. Sant, J. Therm. Anal., 15 (1979) 307.

2 S. Mahapatra and T.P. Prasad, Indian J. Technol., 27 (1989) 447.

3 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans and Green, London, 3rd edn., 1962, pp. 287 and 309.

4 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans and Green, London, 3rd edn., 1962, p. 462.

5 C.G.R. Nair and P.M. Madhu Sudanan, Thermochim. Acta, 14 (1976) 373.

6 M.S.R. Swamy and T.P. Prasad, J. Therm. Anal., 20 (1981) 107.

7 T.P. Prasad, J. Therm. Anal., 31 (1986) 553.