

Note

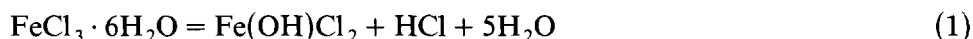
SOLID-STATE HYDROLYSIS OF IRON(II) SULPHATE HEPTAHYDRATE

SIPRA MAHAPATRA and T.P. PRASAD

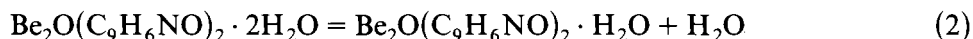
Regional Research Laboratory, Bhubaneswar-751 013 (India)

(Received 9 September 1987)

There are certain salts such as iron chloride, magnesium chloride and aluminium chloride whose hydrates evolve hydrochloric acid on heating as a result of solid-state hydrolysis. The iron(II) chloride hexahydrate reaction may be written as



However, it is not generally known whether non-chloride mineral acid salts hydrolyse in the manner mentioned above. We may find examples of solid-state hydrolysis amongst some metal–organic compounds. For example, Sastri and Prasad [1] found that beryllium oxinate undergoes solid-state hydrolysis with the liberation of free oxine



Similar solid-state hydrolysis was observed earlier by Charles [2] in the case of barium oxinate tetrahydrate.

However, free liberation of sulphuric acid, as a result of solid-state hydrolysis, cannot be expected as the acid is non-volatile and only decomposes when heated to high temperatures. It appears that the sulphate readjusts itself as a part of the basic salt, e.g. in iron(II) sulphate heptahydrate. The formation of $\text{Fe}(\text{OH})\text{SO}_4$ has actually been observed [3,4] during the thermal decomposition of iron(II) sulphate heptahydrate, but it has not been attributed to the phenomenon of solid-state hydrolysis.

In this paper the results of the solid-state hydrolysis of iron(II) sulphate heptahydrate are given and are discussed from the thermodynamic point of view in order to throw some light on the mechanism of the reaction.

It may be noted that the formation of $\text{Fe}(\text{OH})\text{SO}_4$ has been observed in the case of other hydrates of iron(II) sulphate by Swamy et al. [4]. The heptahydrate was chosen for the present study as it is the most important salt. It is supposed that the observations made for the heptahydrate also apply to the other hydrates.

EXPERIMENTAL

Materials

The only material required for this investigation was the iron(II) sulphate heptahydrate. It was obtained by the following procedure. Reagent grade heptahydrate was dissolved in 2N analytical grade sulphuric acid to give a saturated solution at about 50°C. This was treated with high purity iron metal powder at the same temperature to reduce any ferric iron. A carbon dioxide atmosphere was maintained over the solution throughout. The solution was filtered hot and the filtrate was treated with absolute alcohol with stirring. The mixture was then allowed to cool to room temperature and the heptahydrate crystallised out. The crystals were filtered through a sintered glass funnel and washed several times with absolute alcohol. They were then dried under a stream of dry carbon dioxide.

The material thus obtained was analysed for free acid, iron(II), iron(III) and water of crystallisation by the methods described previously [3]. A typical analysis of the product is given in Table 1.

Apparatus

A furnace which can be maintained within $\pm 5^\circ\text{C}$ of the desired temperature was used. Flat bottomed glass dishes (height, 26 mm; diameter, 36 mm; wall thickness, 2 mm) were used for the heating experiments. The products obtained at various temperatures were examined by a Philips X-ray diffractometer.

Method

The material passing through an ASTM 60 mesh sieve but retained on a 100 mesh sieve was used in this investigation. One gram lots of the material were accurately weighed into several dishes and the material was spread

TABLE 1
Typical analysis of iron(II) sulphate heptahydrate

No.	Component	Analysis	
		Observed	Calculated
1	Water	7.02	7.00
2	Sulphate (SO ₄)	34.52	34.55
3	Free acid	Trace	—
4	Iron(II)	20.10	20.10
5	Iron(III)	Trace	—

uniformly in the dishes. These dishes, placed on a wire gauge, were inserted into the furnace maintained at a pre-determined temperature. Two dishes at a time were withdrawn at fixed intervals, cooled quickly and weighed. When the weight of the crucibles remained constant, the material from one dish was dissolved in dilute sulphuric acid and analysed for degree of oxidation by the standard dichromate method. The material in the other dish was examined for phase composition. The experiments were repeated at various temperatures in the range 60–300 °C.

RESULTS AND DISCUSSION

The X-ray data for the “constant weight condition” at various temperatures are presented in Table 2. From the intensities of the important *d* spacings, an approximate estimation was made of the amounts of various phases. On the basis of these estimations, the various phases are arranged in decreasing order of abundance in Table 3 together with percentage weight loss and percentage oxidation.

From the data it is evident that the constant weight condition is obtained after 48 h at 40 °C and after 23 h at 300 °C. The final product obtained at 300 °C was pure Fe(OH)SO₄. At other temperatures, mixtures of Fe(OH)SO₄ with the monohydrate and tetrahydrate were obtained.

The solid-state hydrolysis reaction leading to the formation of the hydroxy iron(III) sulphate, Fe(OH)SO₄, may be written as

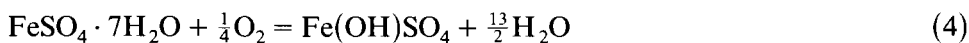


TABLE 2

Solid-state hydrolysis products at various temperatures under constant weight conditions (X-ray data)

No.	Temperature (°C)	<i>d</i> Spacings with probable assignment ^a
1	40	4.82(1), 3.45(1,2), 3.28(3), 3.15(1,2), 2.58(1), 2.52(1), 2.00(1,3)
2	60	4.82(1), 3.45(1,2), 3.28(3), 3.15(1,2), 2.58(1), 2.52(1), 2.00(1,3)
3	120	4.75(3), 3.59(3), 3.26(3), 3.21(3), 2.57(1), 2.29(3), 2.00(1,3), 1.84(3), 1.60(3), 1.56(3)
4	300	4.74(3), 3.55(3), 3.66(3), 2.33(3), 2.04(3), 1.99(3), 1.83(3), 1.63(3), 1.59(3), 1.56(3)

^a The numbers in parentheses refer to the following phases together with reference to ASTM cards: 1, FeSO₄·H₂O: 1-612; 2, FeSO₄·4H₂O: 1-201; 3, Fe(OH)SO₄: 21-428.

TABLE 3

Solid-state hydrolysis of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (data for constant weight conditions)

No.	Temperature (°C)	Time (h)	% wt. loss	% oxidation	Phases arranged in order of abundance
1	40	48	19.20	1.80	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}(\text{OH})\text{SO}_4$
2	60	48	36.00	19.50	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{OH})\text{SO}_4$
3	90	40	36.80	91.00	$\text{Fe}(\text{OH})\text{SO}_4$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
4	120	35	37.20	99.40	$\text{Fe}(\text{OH})\text{SO}_4$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
5	250	25	39.58	99.70	$\text{Fe}(\text{OH})\text{SO}_4$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$
6	300	23	42.30	100.00	$\text{Fe}(\text{OH})\text{SO}_4$

Assuming that the constant weight condition represents the equilibrium condition, the equilibrium constants at various temperatures were calculated using reaction (4) and the data of Table 3

$$K = \frac{[\text{H}_2\text{O}]^{13/2}}{[\text{O}_2]^{1/4}} \quad (5)$$

Table 4 gives the equilibrium constants obtained at various temperatures. A plot of $\log K$ vs. $1/T$ gave a straight line, whose equation was found to be

$$\log K = -0.39 \times 10^3/T + 14.95 \quad (6)$$

From eqn. (6), the heat of solid-state hydrolysis was found to be 3.73 kJ mol^{-1} and the entropy change was $34 \text{ cal K}^{-1} \text{ mol}^{-1}$. The entropy value appears to be very low when compared with the expected value of about $200 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the liberation of 6.5 moles of water in vapour form. Thus, it is obvious that the constant weight condition does not represent the equilibrium condition.

An examination of the results presented so far shows that even at temperatures as low as 40°C oxidation takes place leading to the formation of $\text{Fe}(\text{OH})\text{SO}_4$. The formation of the tetrahydrate and the monohydrate is

TABLE 4

Solid-state hydrolysis of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (equilibrium constants)

No.	Temperature (K)	Amount (mg) of		Moles of		K
		Oxygen	Water	Water	Oxygen	
1	333	13.68	200.10	0.43	11.12	6.06×10^{13}
2	363	13.99	204.54	0.44	11.36	7.91×10^{13}
3	393	14.14	206.76	0.44	11.49	9.17×10^{13}
4	523	15.04	219.99	0.47	12.22	1.98×10^{14}

also observed at this temperature. Thus under constant weight conditions at this temperature, one has a mixture of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and $\text{Fe}(\text{OH})\text{SO}_4$. It appears as if the constant weight condition occurs as a result of an end in dehydration which gives the impression that equilibrium has been reached. This is not the case as described above. The reason for this behaviour can be attributed to the build-up of a diffusional barrier. The same explanation also holds at higher temperatures.

The fact that $\text{Fe}(\text{OH})\text{SO}_4$ is formed at very low temperatures, throws some light on the existence of intermediate hydrates. It is possible that the intermediate hydrates are unstable and that their "stability" is only a result of diffusional barriers which prevent water vapour from being released. At low temperatures, the build-up of the product layer is slow and hence it takes more time to attain constant weight conditions. This time decreases as temperature is increased as the product layer builds up more quickly owing to the higher velocity of the reaction.

ACKNOWLEDGEMENTS

We thank Prof. P.K. Jena, Director, for his encouragement and for his permission to publish the results. One of us (S.M.) also thanks the Council of Scientific and Industrial Research for a Junior Research Fellowship.

REFERENCES

- 1 M.N. Sastri and T.P. Prasad, *Talanta*, 14 (1967) 481.
- 2 R.G. Charles, *J. Inorg. Nucl. Chem.*, 20 (1961) 211.
- 3 M.S.R. Swamy, T.P. Prasad and B.R. Sant, *J. Therm. Anal.*, 15 (1979) 307.
- 4 M.S.R. Swamy, T.P. Prasad and B.R. Sant, *J. Therm. Anal.*, 16 (1979) 471.