THERMAL ANALYSIS OF IRON(II) SULPHATE HEPTAHYDRATE IN AIR

III. THERMAL DECOMPOSITION OF INTERMEDIATE HYDRATES

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Iron(II) sulphate hydrates (hexa- through mono-) have been prepared and their thermal decomposition behaviours have been studied in air by isothermal and dynamic thermal analysis methods. The results show that their behaviours are similar to that of the heptahydrate. The stepwise loss of water molecules is accompanied by oxidation. Under a restricted supply of oxygen, the anhydrous sulphate is oxidized directly to $Fe_2O(SO_4)_2$ without the formation of $Fe(OH)SO_4$. When free exchange with oxygen is allowed, $Fe(OH)SO_4$ is formed, which in turn decomposes to $Fe_2O(SO_4)_2$. The decomposition of $Fe_2(SO_4)_2$ to iron(III) oxide and sulphur oxides appears to occur via two independent paths — one direct and other through iron(III) sulphate.

We earlier [1] reported results on the thermal decomposition of iron(II) sulphate heptahydrate. It was shown that under dynamic and isothermal conditions the tetrahydrate, the monohydrate, the anhydrous sulphate, the hydroxysulphate and the oxosulphate are formed as intermediate compounds. Further it was observed that the formation of the intermediate hydrates is invariably accompanied by oxidation, the extent of oxidation being larger at higher temperatures. Thus, special methods must be adopted to obtain the intermediates. In this communication we present results on the thermal decomposition of various intermediate hydrates prepared by the methods described previously [2].

Experimental

Materials: Procedures for the preparation of tetra- and monohydrates have already been described [2]. To prepare the other intermediate hydrates, the heptahydrate was subjected to evacuation over fused calcium chloride till the theoretical weight loss for the desired hydrate was obtained. It was then immediately subjected to thermal analysis.

Apparatus/Equipment: As in our previous communication [1].

Procedure: Dynamic and isothermal thermal analyses were carried out as described earlier [1].

Results and discussion

Dynamic thermal analysis

The thermal behaviours of the intermediate hydrates have been found to be similar to that of the heptahydrate, except for small differences. These hydrates also lose water in a stepwise manner, with the formation of the intermediate
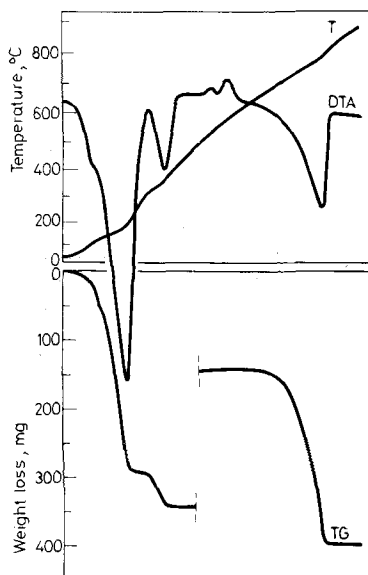

Fig. 1. Thermoanalytical curves of $FeSO_4 \cdot 6 H_2O$

$Fe_2O(SO_4)_2$ from the anhydrous salt. As for the heptahydrate, $Fe(OH)SO_4$ is not formed in these cases either. Similarly as in the case of the heptahydrate, an inflection is found around 100° for the hexa- and pentahydrates, and the weight gain due to oxidation falls short of the theoretical value for the same reason, viz. oxidation during dehydration. Figures 1 — 3 present typical thermal analysis curves in crucibles, and Tables 1 and 2 give the thermal and weight loss data. The X-ray data are presented in Table 3. From Figs 1 — 3 it is evident that the thermal behaviour is similar in all cases, except for the progressive change in the shape of the peak. The first peak, in the region of 180°, becomes progressively smaller, and the peak in the region of 360° becomes progressively larger as compared to the first peak. This is because the first peak represents the loss of all molecules of water except one, and the second peak always represents the loss of this single, last molecule. In fact, the second peak represents the decomposition of the monohydrate formed from the other hydrates. Of all the hydrates, the monohydrate appears to be the most extremely hygroscopic, as is evident from the peak in the region of
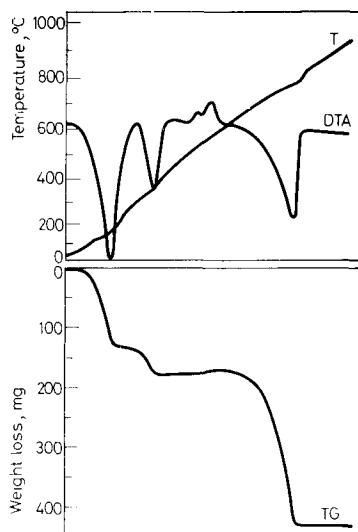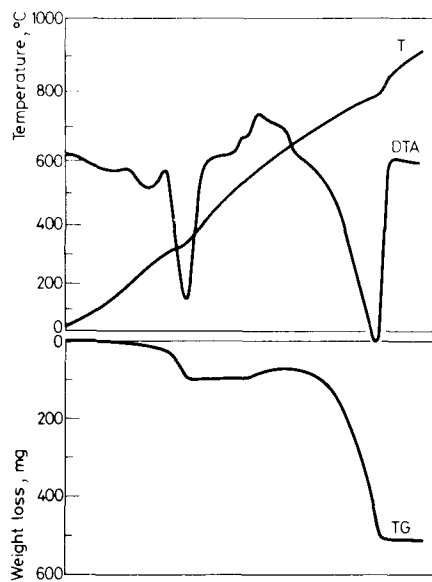
Fig. 2. Thermoanalytical curves of $FeSO_4 \cdot 4 H_2O$

Fig. 3. Thermoanalytical curves of $FeSO_4 \cdot H_2O$

Table 1

Thermal data on thermal decomposition of intermediate hydrates of iron(II) sulphate

No.	Event	Temperature, °C					
		$FeSO_4 \cdot 6 H_2O$	$FeSO_4 \cdot 5 H_2O$	$FeSO_4 \cdot 4 H_2O$	$FeSO_4 \cdot 3 H_2O$	$FeSO_4 \cdot 2 H_2O$	$FeSO_4 \cdot H_2O$
1.	Stability of the hydrate	up to 50	up to 50	up to 80	up to 80	up to 80	up to 100
2.	Formation of tetrahydrate	100*	100*	—	—	—	—
3.	Stability of monohydrate	200—300	220—280	200—300	200—300	170—300	260—300
4.	Stability of anhydrous sulphate	380—520	380—520	400—500	360—500	370—500	360—500
5.	Oxidation to $Fe_2O(SO_4)_2$	520—600	520—600	500—600	500—600	500—620	500—620
6.	Stability of $Fe_2O(SO_4)_2$	600—640	600—640	600—650	600—640	620—660	620—640
7.	Decomposition of $Fe_2O(SO_4)_2$	640—820	640—840	650—820	640—820	660—850	640—840

* Inflection

Table 2

Weight loss/gain data in thermal decomposition of intermediate hydrates of iron(II) sulphate

No.	Event	% Weight loss/gain											
		$x = 6$		$x = 5$		$x = 4$		$x = 3$		$x = 2$		$x = 1$	
		Theor.	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.	Theor.	Obs.
1.	$FeSO_4 \cdot x\,H_2O \rightarrow FeSO_4 \cdot 4\,H_2O + (x-4)\,H_2O$	13.85	1.73	7.44	1.39	—	—	—	—	—	—	—	—
2.	$FeSO_4 \cdot x\,H_2O \rightarrow FeSO_4 \cdot H_2O + (x-1)\,H_2O$	34.61	33.48	29.75	29.45	24.10	23.30	17.48	18.55*	9.60	7.60	ab-sorbed mois-ture	2.11
3.	$FeSO_4 \cdot H_2O \rightarrow FeSO_4 + H_2O$	10.59	9.54	10.59	9.01	10.59	9.00	10.59	8.94	10.59	9.70	10.59	9.90
4.	$2\,FeSO_4 + 1/2\,O_2 \rightarrow Fe_2O(SO_4)_2$	+5.26	+0.96	+5.26	+1.26	+5.26	+1.00	+5.26	+0.89	+5.26	+1.70	+5.26	+2.80
5.	$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2\,SO_3$	50.00	49.42	50.00	48.87	50.00	49.10	50.00	49.65	50.00	49.60	50.00	49.40
6.	$2\,FeSO_4 \cdot x\,H_2O + 1/2\,O_2 \rightarrow Fe_2O_3 + 2\,SO_3 + 2x\,H_2O$	69.23	69.26	66.94	66.65	64.30	63.90	61.17	62.25	57.80	56.80	52.90	53.10

* Absorbs water quickly during weighing, etc.

250°, due to the loss of water molecules. The shape of the exothermic peak in the 520−600° region undergoes a marked change in shape from the hexa- to the monohydrate.

From the above results it is evident that, when heated in air, any hydrate of iron(II) sulphate undergoes decomposition accompanied by oxidation. The hexa- and pentahydrates show an inflection point around 100°, which corresponds to the formation of the tetrahydrate. However, the weight loss data fail to show the formation of the tetrahydrate, even though X-ray powder diffraction data indicate its presence. The reason for the failure of the weight loss measurements to reveal the tetrahydrate may be attributed to the fusion of the specimen, resulting in the retention of liberated but unvolatilized water in $FeSO_4 \cdot 4 H_2O$, as in the case of the case of the heptahydrate [1, 3]. The exothermic peak, as for the heptahydrate, lies in the region of 500−600° and is split into two. The shape of the second split peak appears to depend on the nature of the hydrate studied. Under the conditions of the experiment, the anhydrous sulphate is converted directly into the oxosulphate, and the formation of hydroxysulphate is not observed. This is similar to the observation made in the case of the heptahydrate. Thus, all hydrates of iron(II) sulphate display similar thermal decomposition characteristics.

Isothermal analysis

Our isothermal experiments, confirmed by X-ray diffraction data (Table 3), indicate the formation of both the hydroxysulphate and the oxosulphate in all cases.

Table 3

X-ray diffraction data*

| No.	Temperature, °C	„d" values with probable assignments
1.	90	4.95(1), 4.79(2), 3.43(1), 3.26(2), 3.16(1), 2.58(1), 2.50(1), 2.00(1,2), 1.64(2), 1.59(2), 1.54(3).
2.	300	4.74(2), 3.55(2), 3.26(2), 2.33(2), 2.04(2), 1.99(2), 1.83(2), 1.63(2), 1.59(2), 1.56 (2).
3.	380	4.74(2), 3.55(2,4), 3.26(2), 2.49(4), 2.28(4), 1.98(2), 1.83(2), 1.63(2), 1.59(2), 1.55(2).
4.	420	4.98(4), 4.36(4), 3.57(4), 3.19(4), 3.14(4), 2.72(4), 2.49(4), 2.39(4), 2.28(4), 1.84(2,4,5).
5.	440	5.98(6), 4.35(4), 3.66(5), 3.56(4), 2.28(4), 1.99(6), 1.85(5,6), 1.70(5), 1.61(5,6), 1.49(5,6), 1.46(5,6).

Note: The numbers in parentheses in column 3 represent the following compounds, along with reference to ASTM cards:
   (1) $FeSO_4 \cdot H_2O$: 1−612;   (2) $Fe(OH)SO_4$: 21−428;   (3) $FeSO_4$: 1−703;   (4) $Fe_2O(SO_4)_2$: (5) α-Fe_2O_3: 13−534; (6) $Fe_2(SO_4)_3$: 18−652
* Data on the monohydrate. Other hydrates have identical results

Thus, it appears that $Fe(OH)SO_4$ is formed under good exchange of oxygen at lower temperatures (90–330°). At higher temperatures (>400°), the hydroxysulphate loses water to form the oxosulphate (minor amounts, however, formed at lower temperatures [1]).

The non-formation of the hydroxysulphate during dynamic thermal analysis may be explained as in the case of the heptahydrate [1]. In crucibles under dynamic conditions there is no free exchange with oxygen, due to the copious evolution of water at the lower temperatures where the formation of the hydroxysulphate is favoured, and so the monohydrate formed is preferentially dehydrated to the anhydrous salt instead of being oxidized to $Fe(OH)SO_4$. At higher temperatures, however, the situation alters and exchange with atmospheric oxygen takes place, resulting in the oxidation of the anhydrous salt to the oxosulphate. The oxosulphate now decomposes to iron(III) oxide and sulphur trioxide, as represented by the equation:
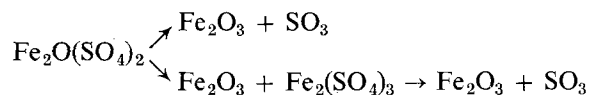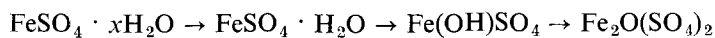
$$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2 SO_3 \tag{1}$$
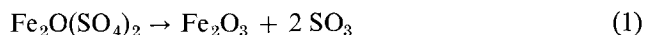
As the X-ray data indicate lines due to $Fe_2O(SO_4)_2$ (Table 3) at a temperature of 440°, and since no sulphur oxide fumes were observed at this temperature, it is felt that $Fe_2O(SO_4)_2$ also undergoes decomposition at the same time, partially to $Fe_2(SO_4)_3$, which in turn decomposes to Fe_2O_3 and SO_3:

$$3 Fe_2O(SO_4)_2 \rightarrow 2 Fe_2(SO_4)_3 + Fe_2O_3 \tag{2}$$
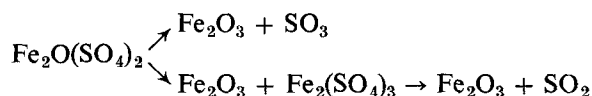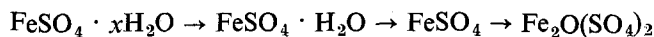
$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3 SO_3 \tag{3}$$
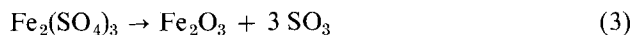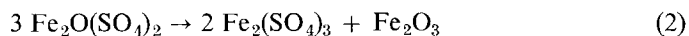
It may be noted that at the temperature of these reactions (640–850°) SO_3 is not stable and partially decomposes to SO_2, giving rise to a mixture of SO_2 and SO_3.

From the foregoing discussion it is evident that the hydrates of iron(II) sulphate (hexa- through mono-) undergo thermal decomposition in a manner similar to that of the heptahydrate. The dehydration takes place with oxidation to hydroxy- and oxosulphates depending on the experimental conditions. When free exchange with oxygen is allowed (as in isothermal studies), the dehydration – oxidation – decomposition path proceeds as:

$$FeSO_4 \cdot xH_2O \rightarrow FeSO_4 \cdot H_2O \rightarrow Fe(OH)SO_4 \rightarrow Fe_2O(SO_4)_2$$

$$Fe_2O(SO_4)_2 \begin{cases} \nearrow Fe_2O_3 + SO_3 \\ \searrow Fe_2O_3 + Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + SO_3 \end{cases}$$

Under a restricted supply of oxygen, the dehydration – oxidation – decomposition path proceeds as:

$$FeSO_4 \cdot xH_2O \rightarrow FeSO_4 \cdot H_2O \rightarrow FeSO_4 \rightarrow Fe_2O(SO_4)_2$$

$$Fe_2O(SO_4)_2 \nearrow^{\displaystyle Fe_2O_3 + SO_3}_{\displaystyle \searrow Fe_2O_3 + Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + SO_2}$$

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References

1. M. S. R. SWAMI, T. P. PRASAD and B. R. SANT, J. Thermal Anal., 16 (1979) 471.
2. M. S. R. SWAMI, T. P. PRASAD and B. R. SANT, J. Thermal Anal., 15 (1979) 307.
3. N. SH. SAFIULLIN, E. B. GITIS and N. M. PANASENKO, J. Appl. Chem. USSR, 42 (1969) 1842.

RÉSUMÉ — On a préparé les sulfates hydratés de fer (II), depuis l'hexa- jusqu'au monohydrate, et on a étudié leur comportement lors de la décomposition thermique par les méthodes de l'analyse thermique, en régime isotherme et dynamique, dans l'air. Les résultats montrent que leur comportement est similaire à celui de l'heptahydrate. La perte, par étapes, des molécules d'eau est accompagnée d'une oxydation. Si l'apport d'oxygène est limité, le sulfate anhydre est oxydé directement en $Fe_2O(SO_4)_2$, sans formation de $Fe(OH)SO_4$. Si l'échange libre avec l'oxygène est permis, il se forme $Fe(OH)SO_4$ qui, à son tour, se décompose en $Fe_2O(SO_4)_2$ La décomposition de $Fe_2O(SO_4)_2$ en oxyde de fer (III) et en oxydes de soufre semble avoir lieu par deux voies indépendantes: l'une directe et l'autre par l'intermédiaire du sulfate der fer (III).

ZUSAMMENFASSUNG — Eisen(II)-sulphathydrate von Hexa- bis Monohydrat wurden hergestellt und ihre thermische Zersetzung in Luft durch die isotherme und dynamische Thermoanalyse untersucht. Die Ergebnisse zeigen, daß ihr Verhalten dem der Heptahydrate ähnlich ist. Der stufenweise Verlust von Wassermolekülen ist von einer Oxidation begleitet. Bei beschränkter Sauerstoffzufuhr wird das wasserfreie Sulphat unmittelbar zu $Fe_2O(SO_4)_2$ oxidiert, ohne Bildung von $Fe(OH)SO_4$. Wenn freier Austausch mit Sauerstoff ermöglicht wird, wird $Fe(OH)SO_4$ gebildet, das dann zu $Fe_2O(SO_4)_2$ zerfällt. Die Zersetzung von $Fe_2O(SO_4)_2$ zu Eisen(III)oxid und Schwefeloxiden scheint auf zwei unabhängigen Wegen zu erfolgen — einem direkten Weg und einem über Eisen(III)sulphat.

Резюме — Получены гидраты (от гекса до моно) сульфата железа и изучено их термическое разложение в атмосфере воздуха изотермическим и динамическим термическим методами. Результаты показали, что поведение их подобно гептагидрату. Ступенчатая потеря молекул воды сопровождается окислением. При ограниченном доступе кислорода безводный слуьфат окисляется прямо до $Fe_2O(SO_4)_2$ без образования $Fe(OH)SO_4$. При свободном доступе кислорода, сначала образуется $Fe(OH)SO_4$, который затем окисляется до $Fe_2O(SO)_2$, разложение которого до окиси трехвалентного железа и трехокиси серы протекает двумя независимыми путями — один прямой, а другой — через сульфат железа(III).