Thermal Reactions of the Mixed-valence Iron Fluorides, $Fe_2F_5 \cdot nH_2O$

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The thermal reactions of $Fe_2F_5 \cdot 7H_2O$ and $Fe_2F_5 \cdot 2H_2O$ have been studied using a combination of thermogravimetric and differential thermogravimetric analysis and by differential scanning calorimetry. The initial dehydration of $Fe_2F_5 \cdot 7H_2O$ near 100 °C is shown to be a complex process which leads to a fluoride-deficient phase of nominal composition $Fe_2F_5 \cdot 2H_2O$. Further heating leads to a product at the hemihydrate level. Isothermal dehydrations lead to two distinct high-temperature phases, but the formation of these materials is accompanied by both oxidation and fluoride loss. Vacuum dehydration of $Fe_2F_5 \cdot 7H_2O$ leads to a fully mixed-valence monohydrate phase, which was previously prepared by dehydration in an HF atmosphere. Dehydration of the authentic crystalline $Fe_2F_5 \cdot 2H_2O$ is seen to be distinguishable from the second-stage dehydration of $Fe_2F_5 \cdot 7H_2O$. Thermogravimetric analyses, thermodynamic measurements, and the kinetic parameters extracted from the several thermal techniques demonstrate that these two forms of ' $Fe_2F_5 \cdot 2H_2O$ ' differ significantly in their thermal reactions.

In 1958 Brauer and Eichner reported [1] that the reaction of iron powder with hot concentrated hydrofluoric acid led to a yellow crystalline material of composition $Fe_2F_5 \cdot 7H_2O$. This material could be thermally dehydrated to a red trihydrate and, at higher temperatures, to a blue-grey anhydrous material. Since colour changes of this sort in a mixed-valence material are suggestive of interactions among the metal ions, we initiated studies [2-4] of the electronic, magnetic, and structural behaviour of these systems.

Although the preparation of the yellow heptahydrate was straightforward using Brauer and Eichner's method,[1] we were unable to reproduce the anhydrous material, and it was apparent that the red material was nominally a dihydrate rather than a trihydrate.[4] In order to identify the phases which could actually be formed, we have investigated the thermal behaviour of these materials in some detail, and find that they are much more complicated than originally reported.[1] While this work was in progress, two reports [5,6] on the thermal decomposition of the heptahydrate have appeared. Although certain aspects of our work are in agreement with these reports, there are significant differences as well, and one of the purposes of this paper is to clarify these differences. We have examined these materials using thermogravimetric analysis (t.g.a.), differential thermogravimetric analysis (d.t.g.a.), and differential scanning calorimetry (d.s.c.). These measurements, combined with chemical analyses and *X*-ray powder patterns of the products derived from the thermal reactions of $Fe_2F_5 \cdot 7H_2O$, have allowed us to both identify these products and determine aspects of the thermodynamics and apparent kinetic parameters for their formation.

RESULTS AND DISCUSSION

The Initial Dehydration of $Fe_2F_5 \cdot 7H_2O$.—Figure 1 shows a typical tracing of the t.g.a. curve observed for $Fe_2F_5 \cdot 7H_2O$ under conditions of inert gas flow (N_2 or He) and slow heating rates (2 °C min^{-1}). It may be seen that under these conditions two major thermal processes exist. The first of these (*ca.* 80—130 °C) has a weight change corresponding to the loss of approximately five molecules of water of hydration, and suggests formation of the dihydrate $Fe_2F_5 \cdot 2H_2O$. Although Brauer and Eichner reported [1] that the dehydration proceeded to a trihydrate level, it is clear both from this t.g.a. work and other published reports [5-7] that a dihydrate formulation is more appropriate.

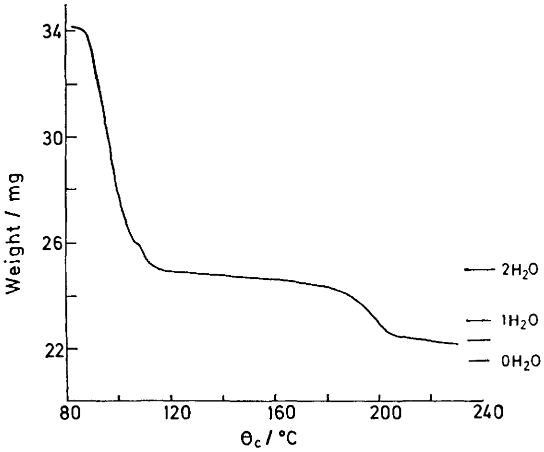

FIGURE 1 Thermogravimetric analysis of $Fe_2F_5 \cdot 7H_2O$ in a helium atmosphere, scan rate 2 °C min^{-1}

Close examination of Figure 1 demonstrates that this process is clearly not a simple dehydration. In particular, there is a distinct shoulder present at *ca.* 110 °C. The position and structure of this shoulder are sensitive to several experimental variables. Slow heating rates ($\leqslant$5 °C min^{-1}) are necessary to attain resolution of this shoulder, and the process is also better resolved when using samples with smaller crystallite size. There is no evidence of this shoulder in the thermograms reported by Gallagher and Ottaway,[6] but this is probably a result of the conditions used (10 °C min^{-1} heating rate). Charpin and Macheteau [5] employed conditions similar to our own, and the shoulder is clearly present in their published thermogram, although no comment is made concerning it. Although the magnitude of this shoulder is variable, it typically corresponds to a weight loss of *ca.* 2—3%.

The complexity of this first dehydration process is shown more clearly by derivative t.g.a. Figure 2 represents a d.t.g.a. scan of $Fe_2F_5{\cdot}7H_2O$ at a heating rate of 10 °C min^{-1}. Even at these high heating rates the shoulder observed by t.g.a. is well resolved, appearing as a distinct process at *ca.* 135 °C. Furthermore, the curve for the major (low-temperature) process is quite asymmetric, suggesting complexity in that process as well. Some complexity is expected, since the transformation from $Fe_2F_5{\cdot}7H_2O$ {formulated[2] as $[Fe(OH_2)_6]^{2+}$-$[FeF_5(OH_2)]^{2-}$} to $Fe_2F_5{\cdot}2H_2O$ (which contains water bound to Fe^{2+} only [3]) requires loss of water from both Fe^{2+} and Fe^{3+}. These two processes, at least, would be expected to occur at different temperatures and hence lead to some fine structure in the d.t.g.a.

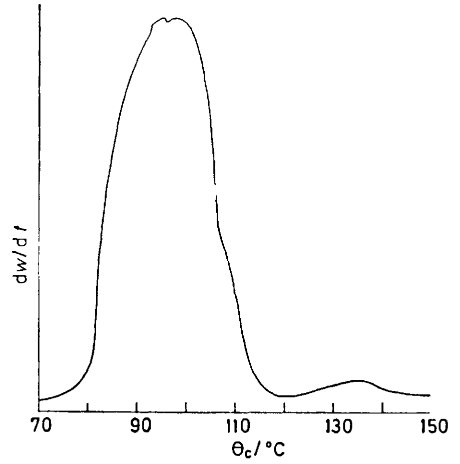

FIGURE 2 Differential thermogravimetric analysis of $Fe_2F_5{\cdot}7H_2O$ (initial dehydration only) in a helium atmosphere, scan rate 10 °C min^{-1}

Although the loss in weight between 70 and 150 °C is conveniently represented as a transformation of the heptahydrate to the dihydrate, several lines of evidence indicate that dehydration is accompanied by hydrogen fluoride evolution. We have observed HF in the mass spectrum of the evolved gases, and have, at least semiquantitatively, measured the extent of HF evolution following trapping of the t.g.a. effluent gas in a polypropylene trap at −196 °C. Acid in this effluent was determined by titration with Na[OH], and fluoride was determined using a fluoride-specific electrode. Although the quantities of evolved HF (*ca.* 0.3 mol per formula weight) measured in this fashion are consistent with the analytical determinations on the solid product, their low precision and accuracy preclude quantitative use. The most compelling evidence in favour of a fluorine-deficient iron fluoride product is elemental analysis of the product. The product obtained by heating $Fe_2F_5{\cdot}7H_2O$ to the expected dihydrate level (representing a loss of 27.1% of the original sample weight) has an *X*-ray powder diffraction pattern identical to that of the authentic dihydrate (*i.e.* the crystalline dihydrate produced directly [3] from the reaction of Fe and HF in refluxing HF). However, the elemental analysis quite clearly demonstrates a substantial deficiency in fluorine, the average fluorine to iron ratio being 2.33 ± 0.05 : 1. Thus, in a typical case we find 46.1% Fe and 35.3% F (estimated uncertainty in the analyses is ±0.5 for each element) compared to theory for $Fe_2F_5{\cdot}2H_2O$: Fe, 46.0; F, 39.1%. There is evidence from other published reports for this fluoride deficiency. Sakai and Tominaga report [7] analytical data supporting a ratio F : Fe = 2.41 : 1. Although the ratio reported by Charpin and Macheteau [5] is not fluorine-deficient (2.53 : 1), the estimated errors are rather large. Gallagher and Ottaway [6] report no analytical data on the dihydrate. However, their analytical method for fluoride in the heptahydrate required an initial dehydration. They reported that unless the dehydration were performed in an HF atmosphere the method gave inconsistent results, an observation compatible with fluoride loss upon normal dehydration.

Vacuum Dehydration of $Fe_2F_5{\cdot}7H_2O$.—A thermogravimetric scan of $Fe_2F_5{\cdot}7H_2O$ obtained under a dynamic vacuum shows (Figure 3) the onset of dehydration at *ca.* 60 °C, rather than at 80 °C. In addition there is a weight change corresponding to the loss of approximately six molecules of water between 60 and 110 °C, but above this temperature interval a smooth and apparently continuous decomposition of the sample appears to occur. No evidence of a shoulder is observed at any point in the thermogravimetric scan, suggesting that the mechanism of solid-state decomposition may be different for samples treated under reduced pressure. We have sought routes to this apparent monohydrate under conditions which would minimize the decomposition noted above 110 °C. Samples of $Fe_2F_5{\cdot}7H_2O$ were placed in an Abderhalden apparatus under vacuum at 78 °C. After several hours a purple-grey product formed at the approximate monohydrate weight level. Chemical analyses demonstrate that this material is fully mixed-valent and slightly fluoride-deficient. Charge balance must then be maintained by either oxide or hydroxide, leading to an approximate (average) formu-

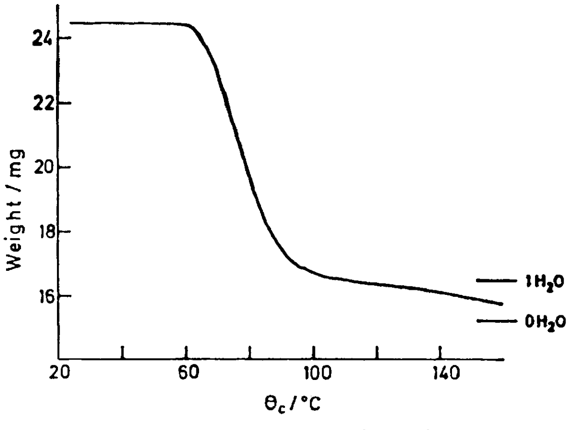

FIGURE 3 Thermogravimetric analysis of $Fe_2F_5{\cdot}7H_2O$ *in vacuo*, scan rate 1 °C min^{-1}

lation $Fe_2F_{4.8}(OH)_{0.2}\cdot H_2O$ (Found: F, 40.6; Fe, 50.8; Fe^{2+}, 26.7. Calc.: F, 40.7; Fe, 49.8; Fe^{2+}, 24.9%). Interestingly, *X*-ray powder diffraction studies show that this monohydrate is isomorphous with a purple-grey phase produced [6] by the isothermal decomposition of $Fe_2F_5\cdot 7H_2O$ at 90 °C in flowing HF. Although the authors of this study have described the phase (called A′ by them) as an ' anhydrous ' product, they have no analytical support for this formulation. It is suggested, on the basis of our studies, that they have produced an authentic, mixed-valence monohydrate, $Fe_2F_5\cdot H_2O$. As in the case of the ' dihydrate ' prepared by dehydration of the heptahydrate in inert atmospheres, it appears that a range of stoicheiometries may be accommodated within a particular structural phase. Thus, a range of solid solutions may exist here in which $Fe_2F_5\cdot H_2O$ is merely a limiting case. In view of the reported dark colour of this iron fluoride hydrate, complete characterization of its chemical and physical properties would be interesting. Continued vacuum thermolysis for several days at 78 °C leads to an increase in the fluorine deficiency and to oxidation of some of the Fe^{2+}.

The Second-stage Dehydration of $Fe_2F_5\cdot 7H_2O$.—Starting at about 180 °C, a second major thermal process occurs in the dehydration of $Fe_2F_5\cdot 7H_2O$ (Figure 1). A plateau is attained at about 220 °C after this process is completed, although a slow but continuous weight loss is observed at higher temperatures. A visual examination of the product shows that it has a distinct yellow to light gold colour which darkens as the thermolysis is continued until a brown product is produced at elevated temperatures (>300 °C). As can be seen in Figure 1, the weight loss during this thermal process (180—220 °C) corresponds to the formation of a nominal hemihydrate. Repeated measurements of this weight loss lead reproducibly to the formal loss of 6.5 ± 0.1 mol of water. This may be contrasted to the report by Gallagher and Ottaway [6] that the material at the same point is the fully anhydrous Fe_2F_5 and to the reported formation of a monohydrate by Charpin and Macheteau.[5,*] Of course, this overall process requires care in interpretation, since it is not a simple dehydration. As mentioned above, the first stage of the thermolysis involves HF evolution, and the second stage (see below) involves both fluoride loss and iron oxidation.

Gallagher and Ottaway [6] described the formation of an ' off-white ' product at 200 °C which quickly turned purple-grey as the temperature was increased to 220 and then 250 °C. *X*-Ray powder diffraction patterns of the products of thermal scans (N_2 flow, 10 °C min^{-1}) allowed them to identify these products as mixtures of two distinct phases which they called A and B. A low-temperature phase (B) appeared to maximize at about 200 °C, and a higher-temperature phase (A) maximized at about 250 °C. We have found that the low-temperature phase (B) is produced by isothermal dehydration. Reaction conditions of 170 °C for 8 h in a helium flow were chosen, in part because similar conditions were reported [5] to lead to a monohydrate having the powder pattern of phase B. *X*-Ray powder patterns reveal that the material we prepare under these conditions is predominantly phase B, but phase A′ (the material prepared by vacuum dehydration at 78 °C) is also present. Continued heating at 170 °C appears to involve the slow oxidation of this phase A′ to phase B. Although we have not been able to prepare phase B in pure form, weight-loss and analytical data suggest that it is a fully oxidized, fluoride-deficient anhydrous material. Although analytical data were adequate to demonstrate that all iron was present as Fe^{3+} and that the F : Fe ratio was less than 2.5 : 1, the exact composition of this material, which is undoubtedly a mixed oxyfluoride, could not be determined.

In agreement with Gallagher and Ottaway,[6] we find that thermolysis at higher temperatures leads to the transformation of phase B to phase A. For example, heating in a He flow at 220 °C for 75 min produces a weight loss corresponding to the formation of the anhydrous Fe_2F_5. The gold coloured product formed at this point exhibits powder patterns characteristic of a mixture of phases A and B. Continued heating under these conditions for 14 h leads to a weight loss beyond that of the nominal anhydrous complex, and a powder pattern characteristic of phase A. We are forced to conclude that the ' blue platelets ' formulated as Fe_2F_5 by Brauer and Eichner [1] are not accessible by thermal dehydration of $Fe_2F_5\cdot 7H_2O$.

In summary, our findings concur with the more general belief that the materials $Fe_2F_5\cdot 7H_2O$ and $Fe_2F_5\cdot 2H_2O$ exist as well defined compounds, although the latter must be produced either by the direct preparation described by Brauer and Eichner [1] from HF and Fe or by a modification thereof which we have previously described.[3] The thermal dehydration of $Fe_2F_5\cdot 7H_2O$ is a complex process which occurs in two major stages. Both stages are accompanied by solid-state reactions which result in the liberation of HF when thermolysis is effected under inert atmospheres. It is possible to identify at least three lower hydrates according to *X*-ray diffraction information: phases A, A′, and B, although only phase A′ may be isolable in pure form.[6]

Dehydration of the Crystalline Dihydrate, $Fe_2F_5\cdot 2H_2O$.—As reported previously,[3] we have prepared and structurally characterized the authentic dihydrate, $Fe_2F_5\cdot 2H_2O$. Unlike the species prepared by thermal dehydration of the heptahydrate, this material suffers from no fluoride deficiency. Although these two materials give identical *X*-ray powder patterns, their analytical formulations and thermal behaviour are distinct. Figure 4 shows a t.g.a. (N_2, 5 °C min^{-1}) of the crystalline dihydrate, and it is seen to differ from the second-stage dehydration of the heptahydrate in two ways. First, the dehydration proceeds to the fully anhydrous level. Unlike the second-stage dehydration of the heptahydrate, there is no indication of a stable ' hemihydrate ' stage. Second, the dehydration of the crystalline dihydrate occurs at signifi-

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[*] Although prepared by an isothermal dehydration at 170 °C, it is clear from *X*-ray powder patterns that this material is identical to those which both we and Gallagher and Ottaway [6] report.

cantly higher temperatures. The inflection point of the weight-loss curve in Figure 4 is *ca.* 245 °C, whereas the comparable point in Figure 1 is *ca.* 195 °C. This difference is due in part to the higher crystallinity of the authentic dihydrate, and, in fact, a thorough grinding of the compound lowers the inflection point by *ca.* 20 °C. Even under these conditions, however, the dehydration occurs at a significantly higher temperature than for the analogous process in the thermolysis of the heptahydrate. The difference in behaviour between these two forms of the dihydrate is further manifested by the thermodynamic and kinetic parameters of the dehydration, and will be discussed in more detail below. Not surprisingly, *X*-ray powder patterns demonstrate that the ultimate products of the thermal decomposition of both of these forms of the dihydrate are the same. (Of course, *X*-ray powder measurements might not detect small amounts of another species, or larger amounts of such a species if formed in an amorphous state.)

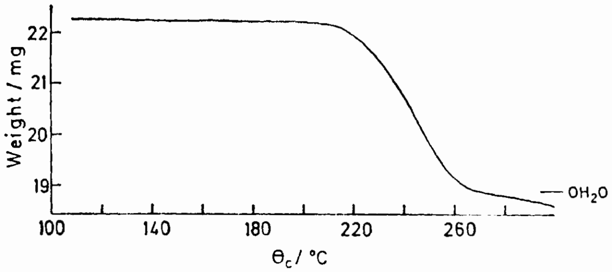

FIGURE 4 Thermogravimetric analysis of the crystalline dihydrate, $Fe_2F_5{\cdot}2H_2O$, in a nitrogen atmosphere, scan rate 5 °C min^{-1}

Thermodynamics of Dehydration.—Both stages of the dehydration of $Fe_2F_5{\cdot}7H_2O$ are endothermic processes, as determined by both d.t.a. and d.s.c. The enthalpy of the low temperature (<150 °C) process is measured by d.s.c. to be 66 ± 2 kcal * mol^{-1}. This number compares favourably with expectations, given typical values [8] of 12—13 kcal mol^{-1} for the enthalpy of dissociation of water in crystalline hydrates. For a pure dehydration of $Fe_2F_5{\cdot}7H_2O$ to $Fe_2F_5{\cdot}2H_2O$, then, an enthalpy of *ca.* 62.5 kcal mol^{-1} is expected, in rather good agreement with the experimental result. As noted above, this process is not a pure dehydration, but both the small amount of HF liberated, as well as the expected similarity in enthalpies of bonding to the metal centre for both H_2O and HF, suggest that the observed value should not differ significantly from expectations based purely on H_2O loss.

D.s.c. data substantiate the difference between the two different forms of the ' dihydrate '. As noted previously, the second-stage dehydration of $Fe_2F_5{\cdot}7H_2O$ *via* t.g.a. proceeds to a nominal hemihydrate level. Assuming, again, that this process represents a pure dehydration, it corresponds to the loss of 1.5 mol of water, and the expectation of an enthalpy for the process of *ca.* 19 kcal mol^{-1}. The experimental value, ΔH = 16 kcal mol^{-1}, is in reasonable agreement. More important than the absolute value is the comparison with the authentic crystalline dihydrate. This latter material was shown to proceed to the anhydrous level, corresponding to the loss of 2.0 mol of water. The expected enthalpy for the dehydration of the crystalline dihydrate is then *ca.* 25 kcal mol^{-1}, close to the experimental value, determined by d.s.c., of 27 kcal mol^{-1}. D.s.c., like t.g.a., thus clearly distinguishes these two materials which have been referred to as the dihydrate, $Fe_2F_5{\cdot}2H_2O$.

Kinetics of Dehydration.—Although the kinetic parameters of gaseous or solution reactions are typically examined at a series of constant temperatures, much the same information is available in a single thermogravimetric or thermoanalytical scan. Thus, in principle, a single t.g.a. or d.s.c. experiment provides both activation energy and order of reaction, and certain advantages accrue when all of this information can be attained using a single sample in a single experiment.[9] In this work we have used four distinct methods to evaluate activation energies, three based on thermogravimetry and one based on d.s.c.

Various methods for determining kinetic parameters from non-isothermal t.g.a. measurements have been proposed. The basic assumption in all of these methods is that the rate of a solid-state reaction [equation (1)] is proportional to some power function of the fraction, α, of material remaining [equations (2) and (3)]. The methods differ in the means of dealing with the resulting

$$\text{Solid (A)} \longrightarrow \text{Solid (B)} + \text{Gas} \quad (1)$$

$$d\alpha/dT = k(1-\alpha)^n \quad (2)$$

$$k = Ae^{-E/RT} \quad (3)$$

differential equation. Some approaches require information only from the t.g.a. curve (integral methods) while others require in addition the derivative of the t.g.a. curve (differential methods). It is also possible to determine kinetic parameters independently using d.s.c.

Coats and Redfern [10] have pointed out that there are four reasonable reaction orders for a solid-state process such as described by equation (1). For a zero-order process they have derived equation (4). A plot of the left-hand side of the equation against the reciprocal of

$$\log\left[-\log\frac{(1-\alpha)}{T^2}\right] = \log\left(\frac{AR}{aE}\right)\left(1-\frac{2RT}{E}\right) - \frac{E}{2.3RT} \quad (4)$$

the absolute temperature should give a line whose slope is related to the activation energy. From the intercept, the pre-exponential factor can be determined as well. The Coats and Redfern method requires data only from the t.g.a. curve. For meaningful reaction orders n of $\frac{1}{2}$, $\frac{2}{3}$, and 1, equation (5) is used in the same way.

$$\log\left[\frac{1-(-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\left(\frac{AR}{aE}\right)\left(1-\frac{2RT}{E}\right) - \frac{E}{2.3RT} \quad (5)$$

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* Throughout this paper: 1 cal = 4.184 J.

A somewhat more general treatment has been given by Freeman and Carroll[9] [equation (6)]. Using both the t.g.a. and d.t.g.a. curves, it is possible using equation (6) to determine the activation energy as well as an

$$\frac{\Delta[\log(\mathrm{d}\alpha/\mathrm{d}t)]}{\Delta[\log(1-\alpha)]} = n - \frac{E}{2.3RT}\left\{\frac{\Delta(1/T)}{\Delta[\log(1-\alpha)]}\right\} \quad (6)$$

apparent reaction order, n.

A somewhat less general treatment, but one which is useful in its simplicity, has been suggested by Tang.[11] This method assumes a first-order process [equation (7)].

$$\log\left[\frac{\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)}\right] = \log A - \frac{E}{2.3RT} \quad (7)$$

The Tang treatment, which is of the differential category, provides an independent check on the integral Coats and Redfern first-order method. Quite independently, d.s.c. provides a second approach to kinetic parameters for solid-state reactions. One approach has been described by Rogers and Smith.[12] Their method allows for either calculating the activation energy and reaction order, or specifying a reaction order. While there is no clear advantage to any particular one of the above mentioned treatments, agreement between them provides some confidence that the resulting activation energy is characteristic of the material, rather than of the data analysis. It should be emphasized that the 'order of reaction', α, has no intrinsic meaning in a solid-state decomposition, but is rather a mathematical smoothing device. Furthermore, the errors inherent in the determination of activation energies from thermogravimetric data are rather large (see the Table). Nonetheless, the configuration used on the TGS-1 thermobalance is such that a very close approximation to equilibrium conditions is achieved and, in general, we are able to extract kinetic parameters that are in very close agreement with isothermal data, even at heating rates much higher than those used here.

Activation enthalpies for dehydration steps[a]

Calculation method	$\Delta E^{\ddagger}$/kcal mol^{-1} [b]		
	$Fe_2F_5\cdot 7H_2O \longrightarrow$ '$Fe_2F_5\cdot 2H_2O$'	'$Fe_2F_5\cdot 2H_2O$' $\longrightarrow$ 'Fe_2F_5'	$Fe_2F_5\cdot 2H_2O \longrightarrow Fe_2F_5$
Freeman–Carroll	29 (11)	54 (4.5)	31 (2.9)
Tang	42 (11)	47 (2.9)	27.6 (1.4)
D.s.c.	27 (see text)	54	36

[a] '$Fe_2F_5\cdot 2H_2O$' represents the product formed upon the low-temperature dehydration of $Fe_2F_5\cdot 7H_2O$ and is to be distinguished from the authentic crystalline dihydrate prepared directly from Fe and HF. [b] Estimated standard deviations are given in parentheses.

The activation energies derived using these non-isothermal kinetic methods are presented in the Table for three distinct processes. The interpretation of these data requires some prudence. In the case of the first-stage dehydration, *e.g.* $Fe_2F_5\cdot 7H_2O \longrightarrow$ '$Fe_2F_5\cdot 2H_2O$', reaction orders calculated using the Freeman–Carroll technique[9] are highly variable, falling in a range *ca.* 0.3—5.0 for different samples and experiments. By contrast, reaction orders for both the second-stage dehydration and the dehydration of the crystalline dihydrate, which appear to be relatively clean processes, tend to lie in a fairly limited range near 1. The complexity of the first dehydration of the heptahydrate is also reflected in the rather large uncertainties associated with the activation energies. The values in the Table represent averages of at least six experiments, and for this process values of specific experiments are highly dependent on experimental conditions (*e.g.* heating rate, crystallite size). Figure 5 shows kinetic data for this process evaluated by the Coats and Redfern method for an experiment involving low heating rates. In this case, the data have been treated assuming a first-order reaction. The presence of two straight-line segments demonstrates resolution of the two major processes, and may be compared to the t.g.a. data reported above. Activation energies calculated for the two steps are 21.6 and 79.4 kcal mol^{-1}, and indicate clearly that values calculated in the absence of this resolution will have little meaning.

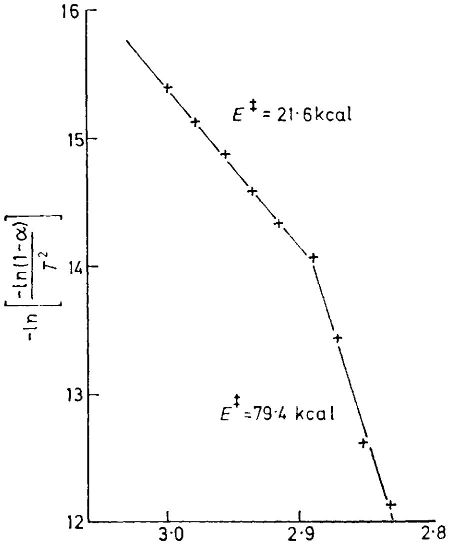

FIGURE 5 First-order kinetics for the initial dehydration of $Fe_2F_5\cdot 7H_2O$ using the Coats and Redfern method

Kinetic parameters evaluated from both the second-stage dehydration of the heptahydrate and the dehydration of the crystalline dihydrate show a much better precision, suggesting that these dehydrations are relatively simple processes. Furthermore, activation energies calculated by different methods from thermogravimetric data are in reasonable agreement with activation energies calculated from d.s.c. data, so that we feel confident of these values. There is, however, a large difference between activation energies for the chemical processes, being *ca.* 50 kcal mol^{-1} for the second-stage dehydration of the heptahydrate and *ca.* 32 kcal mol^{-1} for the dehydration of the crystalline dihydrate. This difference further substantiates the observation, from t.g.a. and enthalpic measurements, that these two processes, although nominally equivalent, are in fact quite distinct.

In summary, this work has shown that the thermal reactions of the mixed-valence iron fluorides are much more complex than previously reported. In particular, the initial dehydration of $Fe_2F_5\cdot7H_2O$ has been shown to be a multistep reaction, and to involve some loss of hydrogen fluoride as well as loss of water. The material prepared in this dehydration, nominally $Fe_2F_5\cdot2H_2O$, is seen to differ significantly from the authentic dihydrate prepared by an alternative route. Several other phases of lower water content are formed at higher temperatures, their specific distribution depending upon the detailed experimental conditions.

EXPERIMENTAL

Materials.—The compounds $Fe_2F_5\cdot7H_2O$ and $Fe_2F_5\cdot2H_2O$ were prepared as described previously (refs. 2 and 3 respectively). Total iron was determined by permanganate titration following tin(II) chloride reduction or spectrophotometrically with *o*-phenanthroline following hydroxylamine reduction. Iron(II) was determined spectrophotometrically with *o*-phenanthroline and iron(III) was determined by difference. Fluoride was determined using an Orion 94–01 fluoride-ion specific electrode. Prior to measurement, samples were treated with Orion total-ionic-strength adjustment buffer in order to eliminate problems of fluoride complexation with either protons or iron. The accuracy of fluoride determinations performed in this way was periodically checked using potentiometric lanthanum titrations.

Thermal Analysis Equipment.—The differential scanning calorimetry (d.s.c.), thermogravimetric (t.g.a.), and differential thermogravimetric (d.t.g.a.) curves were obtained from a Perkin-Elmer DSC-1b differential scanning calorimeter and TGS-1 thermal balance. Heating rates of 2—10 °C min^{-1} were employed, using 3—6 mg of powdered sample in an aluminium oxide microcrucible in a helium atmosphere. T.g.a. curves were also obtained using a DuPont 900 thermal analyzer coupled to a DuPont 950 thermogravimetric analyzer. In this case larger samples (*ca.* 20—30 mg) on platinum pans were used, in either helium or nitrogen atmospheres and at heating rates of 2—10 °C min^{-1}.

TGS-1 *Thermobalance.*—Teflon needles valves replaced the screw-cap closures on the gas inlet and tareloop of the TGS-1 in order to provide improved conditions for a pure He atmosphere within the balance bottle A small platinum heater was used in the modified furnace mount assembly after the suggestions of Etter and Smith.[13] Room-temperature vulcanizing silicon elastomer was used to seal the furnace screw-cap closures.

Microcrucibles (Mettler) were used to replace the platinum sample pans provided by Perkin-Elmer. These crucibles were made of hot pressed Al_2O_3 (*ca.* 150 mg in weight). This allowed for small size sample (3—6 mg). In order to obtain the maximum thermal equilibrium, helium was used as the inert gas. Although the rated range of the Cahn RG balance is 20 μg full scale (0.1 μg sensitivity), in practical terms the 0.4 mg range (0.4 μg sensitivity) represents a maximum sensitivity of this system. Either a Texas Instrument 2 channel recorder (Servo Riter II, 1 mV range) or a multiplexed 4 channel Heath recorder was used to record the output from the Cahn RG balance.

The derivative of the primary (unattenuated) t.g.a. signal was fed into a Cahn Mark II time derivative computer (classical RC differentiation) and the output of this device was recorded on the second channel of the TI recorder or a second multiplex channel on the Heath recorder (1 or 10 mV respectively). The approximate ranges on the time derivative computer were calibrated by determining weight loss due to diffusion of water vapour from a Kneudsen cell at a controlled temperature. The balance weight ranges were calibrated class M (N.B.S.) standard 10 mg weights.

Temperature calibrations of the thermal balance were obtained by means of the Curie-point magnetic transitions. Over the temperature range of 100—500 °C the observed and actual temperature agreed to within ±1 °C (He atmosphere, 10 °C min^{-1} or less heating rate).

Sample Loading Procedure.—The sample crucible was first heated to a temperature of *ca.* 800 °C in air, then allowed to cool to room temperature, and suspended from the balance. The mass dial of the RG balance was adjusted so that zero deflection was noted on a recorder scale when the atmosphere of helium had been re-established in the balance chamber. The sample was then loaded on the balance, being protected from the atmosphere by increasing the flow of helium. When the sample was in place and the hangdown tube was returned to its normal position, the helium flow was maintained at 20 cm^3 min^{-1} for *ca.* 5 min, at which time the balance chamber again contained a pure helium atmosphere. Then the sample weight could be obtained directly from the recorder. Activation energies obtained by the methods described above are in agreement with published data on the dehydration of $Ca[C_2O_4]\cdot2H_2O$ and $Zn[C_2O_4]\cdot2H_2O$, even though smaller samples were used in this study (10 *vs.* 100 mg).

X-Ray Powder Diffraction.—*X*-Ray powder diffraction patterns were obtained with the Straumanis technique using vanadium-filtered Cr radiation ($\lambda_{mean} = 2.290\,9$ Å). The high-temperature phases A, B, and A′ were identified by comparison of powder data to those reported for these phases by Gallagher and Ottaway.[6]

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