Action of Ammonium Fluoride Solutions on ' Iron(III) Hydroxide ' Gel

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X-Ray diffraction, fluorine and thermal analysis show that, when reacted with an aqueous solution of ammonium fluoride, freshly precipitated ' iron(III) hydroxide ' gel is partially transformed into triammonium hexafluoroferrate(III) and not hydrated iron(III) fluoride oxide, $Fe(O)F,nH_2O$, as had been previously concluded by V. Frei. The triammonium hexafluoroferrate(III) replaces the gel and, being white, causes the suspension to change colour from dark brown to varying shades of tan depending on the fraction of unreacted gel. The proportions of unreacted gel and $[NH_4]_3[FeF_6]$, remaining after reaction has ceased, depend on the initial concentration of ammonium fluoride used; even a concentration as high as 10M does not transform the gel completely. If the temperature is raised, however, complete conversion is possible and pure $[NH_4]_3[FeF_6]$ results. Monitoring of the pH during reaction at room temperature indicates that equilibrium is established within 5 min. Aluminium hydroxide gel behaves similarly towards ammonium fluoride solution, except that it is always completely transformed to $[NH_4]_3[AlF_6]$.

METALS in oxidation state III commonly form stable hydroxide oxides with the formula $M^{3+}O^{2-}OH^-$. Since F^- and OH^- have almost equal radii in ionic crystals, fluoride oxide analogues might be expected to occur. Their heats of formation compared with those of the hydroxide oxides would depend considerably on the contribution of hydrogen bonding to the lattice. A few such fluoride oxides[1,2] have been prepared by high-temperature reaction between the oxide and the fluoride but none by solution methods. The reported preparation[3] of the hydrate of iron fluoride oxide, $Fe(O)F,nH_2O$, offers the possibility of producing Fe(O)F by controlled dehydration; Fe(O)F produced by a low-temperature method under conditions normally leading to α-Fe(O)OH would be expected to have a structure similar to that of the latter. The structure of α-Fe(O)OH depends to a considerable extent on hydrogen bonding between the ions O^{2-} and OH^- and so the possibility of Fe(O)F with a similar structure, but without the contribution of hydrogen bonding to the lattice energy, would be of interest. We have reinvestigated the preparation of $Fe(O)F,nH_2O$ as part of a programme to synthesize Fe(O)F by a low-temperature method.

It is well known that the gelatinous precipitate of ' iron(III) hydroxide,' produced by raising the pH of an aqueous solution of an iron(III) salt, will age to the well defined crystalline compound α-Fe(O)OH. Frei[3] concluded that, if, instead of ageing, this gel is treated with a concentrated solution of NH_4F, replacement of OH^- by F^- occurs and the fluoride analogue of the hydroxide oxide is formed, but with an ill defined water content, which may be expressed by the formula $Fe(O)F,nH_2O$. Frei did not observe an *X*-ray diffraction pattern from this product, and so his conclusion rests entirely on evidence of the iron to fluoride ratio obtained by chemical analysis. Our experiments, however, do not bear out this conclusion. We observed that the ' iron(III) hydroxide ' gel was transformed into solid $[NH_4]_3[FeF_6]$ to an extent which depends on the NH_4F concentration, and that no fluoride oxide was formed. A preliminary investigation of the action of NH_4F solution on aluminium hydroxide gel was carried out for comparison since, in situations where redox reactions are absent, Al^{3+} behaves like Fe^{3+}. The reaction was entirely similar, the analogous product $[NH_4]_3[AlF_6]$ being formed.

EXPERIMENTAL

Samples of ' iron(III) hydroxide ' gel were prepared by adding aqueous ammonia to 1M-iron(III) nitrate solution (10 cm³) until the pH reached 8·5.† The gelatinous precipitate was then filtered off and washed with water. Each sample was treated with ammonium fluoride solution (20 cm³) of different concentrations and stirred for varying periods of time. One set of reactions was carried out at 20 °C for periods of 5, 12, and 30 min and another set at 90 °C for 30 and 240 min. (It is to be noted that Frei did not state either the temperature or time of reaction, but implied that his experiments were carried out at room temperature and terminated after a few minutes.) Unless otherwise stated, laboratory grade reagents were used throughout. Frei used NH_4F concentrations of 1, 3, 5, and 7M and stated that 7M gave complete conversion to $Fe(O)F,nH_2O$. We carried out the reaction with 5, 7, and 10M-NH_4F solutions and as a control we also used water instead of NH_4F in one set of experiments.

The pH was monitored during all runs at 20 °C and was found to increase to a constant value after *ca.* 5 min, in agreement with Frei (Figure 1). The kinetics of the reaction, however, were not studied. The residue after reaction was filtered off, washed with ethanol and diethyl ether, and allowed to dry at room temperature. Water was not used for washing in case any substitution of OH^- was reversed. Experiments were also carried out using aluminium as the metal ion. The preparation of the gel and the reaction procedure used was exactly analogous to that in the iron experiments. Ammonium fluoride solutions of concentrations 5, 7, and 10M were treated with aluminium hydroxide gel at room temperature for 30 min and at 90 °C for 240 min.

Analysis of fluorine was carried out by two procedures according to whether the residue after reaction was completely or partially soluble in excess of water. In the soluble products, fluorine was determined by dissolving in water and titrating with lanthanum(III) nitrate solution using a selective-ion electrode (Orion Research Inc.) in

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† 1M = 1 mol dm⁻³.

[1] P. Hagenmuller, J. Portier, J. Cadiou, and R. de Pape, *Compt. rend.*, 1965, **260**, 4768.

[2] B. L. Chamberland and A. W. Sleight, *Solid State Comm.*, 1967, **5**, 765.

[3] V. Frei, *Coll. Czech. Chem. Comm.*, 1962, **27**, 782.

conjunction with a calomel reference electrode and digital voltmeter. Determinations on products containing insoluble constituents were carried out by heating with silicon at 900 °C.[4] The SiF_4 thus produced was decomposed by passing through water. After neutralization with aqueous ammonia, the liberated F^- ion was titrated with $La(NO_3)_3$ solution as before. This method of determining fluorine in insoluble materials was checked on PbF_2 of extra pure grade (B.D.H., minimum assay 99%). Determinations on four samples of the standard yielded values in the range 15·25—15·75% by weight (mean 15·51 ± 0·13%). The theoretical F content of PbF_2 assuming 100% purity is 15·5%. The titration procedure was frequently checked with an 0·01M standard NaF solution. The error in the fluorine determinations using the SiF_4 method is thus 0·2% or less, in agreement with the value of Portier and Roux. The error in the determinations carried out directly on[4] soluble products is of course lower than this and arises from the accuracy of the volume measurements during titration. For simplicity the higher error of 0·2% is quoted throughout.

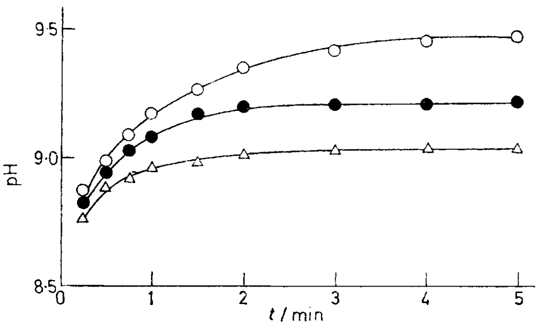

FIGURE 1 Variation of pH of aqueous solutions of ammonium fluoride during reaction with 'iron(III) hydroxide' gel. Measurements were taken over a period of 30 min and in each case the pH remained constant after 5 min. $[NH_4F]$ = 5 (△), 7 (●), and 10M (○)

The products of all reactions were examined by *X*-ray diffraction on a Nonius–Guinier–de Wolff camera using Fe-K_α radiation. As this camera contains monochromating and beam-focusing facilities it is capable of detecting crystalline constituents in amounts less than 1%, depending on the degree of particle-size broadening of the lines and the relative atomic-scattering factors of the constituent elements. Bragg angles were measured to a precision of ±0·05° which corresponds to a variation in *d* values ranging from ±0·5% at 10×10^{-10} m to ±0·05% at $1{\cdot}5 \times 10^{-10}$ m. These values were corrected for film shrinkage using aluminium ammonium bis(sulphate) hydrate as an internal standard.

Thermal analyses were carried out on a Linseis thermoanalyser, which was accurate to ±0·25 mg. Sample weights in the range 40—50 mg were heated at 10 °C min^{-1} in flowing nitrogen and t.g.a., d.t.g., and d.t.a. traces recorded simultaneously.

RESULTS

Colour.—The starting material for these experiments, the gelatinous precipitate of 'iron(III) hydroxide,' was typically dark brown. During reaction with 10M-NH_4F solution at 90 °C the suspension of this gel changed from dark brown to white. After drying, the white residue was found to be completely free from any traces of brown colour. The products of reaction under other conditions displayed varying colours intermediate between brown and white. During the filtration stage, some separation of colour into white and shades of brown could be observed, indicating lack of homogeneity in such products. There was no colour change in reactions with white aluminium hydroxide.

X-Ray Diffraction.—With the exception of the product obtained when pure water was substituted for NH_4F solution, the products of all the 'iron(III) hydroxide' experiments showed the *X*-ray reflections of $[NH_4]_3[FeF_6]$.

TABLE 1

Comparison of *d* values and intensities of the white product reflections with those of $[NH_4]_3[FeF_6]$

			$[NH_4]_3[FeF_6]$ *		White product		
					Observed		Calc.†
h	*k*	*l*	$10^{10}d$/m	I/I_1	$10^{10}d$/m	I/I_1	$10^{10}d$/m
1	1	1	5·29	100	5·25	100	5·26
2	0	0	4·58	61	4·56	90	4·55
2	2	0	3·24	45	3·224	90	3·221
3	1	1	2·76	6	2·749	10	2·747
2	2	2	2·65	8	2·632	10	2·630
4	0	0	2·28	29	2·276	60	2·277
4	2	0	2·04	11	2·038	30	2·037
4	2	2	1·86	16	1·857	40	1·860
3	3	3	1·75	14	1·754	40	1·754
5	1	1					
4	4	0	1·61	9	1·610	30	1·610
5	3	1	1·54	9	1·539	30	1·540
6	0	0	1·52	6	1·517	10	1·518
4	4	2					

The salt $[NH_4]_3[FeF_6]$ is face-centred cubic. The unit-cell parameter a_0, calculated from observed *d* values of the white product, was found to be $(9{\cdot}110 \pm 0{\cdot}008) \times 10^{-10}$ m. This may be compared with the value of $9{\cdot}10 \times 10^{-10}$ m reported in the J.C.P.D.S. index. The intensities in column 5 were estimated visually.

* From card no. 5–223 of the J.C.P.D.S. index. † From $a_0 = 9{\cdot}110 \times 10^{-10}$ m.

These were identified by comparing their accurately measured *d* values with those listed for this salt on card no. 5–223 in the J.C.P.D.S. index.[5] Table 1 shows a typical set of such values from the product of a 10M-NH_4F reaction at 90 °C which other analytical evidence showed to be $[NH_4]_3[FeF_6]$. The J.C.P.D.S. values are listed alongside for comparison. The intensity of these reflections increased with increasing concentration of ammonium fluoride used in the reaction, whilst the background (arising from an amorphous component) decreased. No reflections of any other crystalline material were observed in any of the products, except that in 90 °C runs at low NH_4F concentrations the faint pattern of α-Fe(O)OH was observed, indicating ageing before reaction.[6] These reflections were markedly broadened, indicating that the average crystallite size was considerably less than that of triammonium hexafluoroferrate(III), whose reflections were only slightly broadened. It was noted that whenever $[NH_4]_3[FeF_6]$ was detected by *X*-ray powder diffraction colourless poorly formed isotropic crystals could always be seen under an optical microscope. In complete reactions these occurred either separate from the brown amorphous regions or as particles adhering to them.

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[4] J. Portier and J. Roux, *Chim. Analyt.*, 1968, **50**, 390.

[5] Joint Committee on Powder Diffraction Standards, Swathmore, Pennsylvania, U.S.A.

[6] H. Remy, 'Treatise on Inorganic Chemistry,' Elsevier, 1956, p. 274; see also G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' Academic Press, 1965, p. 1499.

All reactions of ammonium fluoride with aluminium hydroxide gel gave products which were identified as $[NH_4]_3[AlF_6]$ from *X*-ray powder-diffraction photographs by comparison of the *d* values with those listed on card no. 3–122 in the J.C.P.D.S. index.[5] This salt is isostructural with its iron analogue and so the diffraction patterns are similar.

Thermal Analysis.—Figure 2(*b*) shows a typical thermogram of the white product produced by treating ' iron(III) hydroxide ' with 10M-NH_4F at 90 °C. It was found to be identical to that from pure triammonium hexafluoroferrate(III) obtained by Shinn *et al.*[7] The thermogram of the product from a 7M-NH_4F reaction at room temperature [Frei's optimum conditions for conversion to $Fe(O)F,nH_2O$] is shown in Figure 2(*c*) and it was found to contain all the features of the thermograms of pure triammonium hexafluoroferrate(III) [Figure 2(*b*)] and ' iron(III) hydroxide ' gel [Figure 2(*a*)]. The relative heights of the thermogravimetric steps belonging to individual components in a mixture is a measure of their proportions. It was observed that the proportions of the two components, as assessed from their respective step heights, correlated with the colour gradation in the different products. The lighter the brown colour of the product, the higher were the steps of the (*b*) thermogram in relation to the single step of that in (*a*).

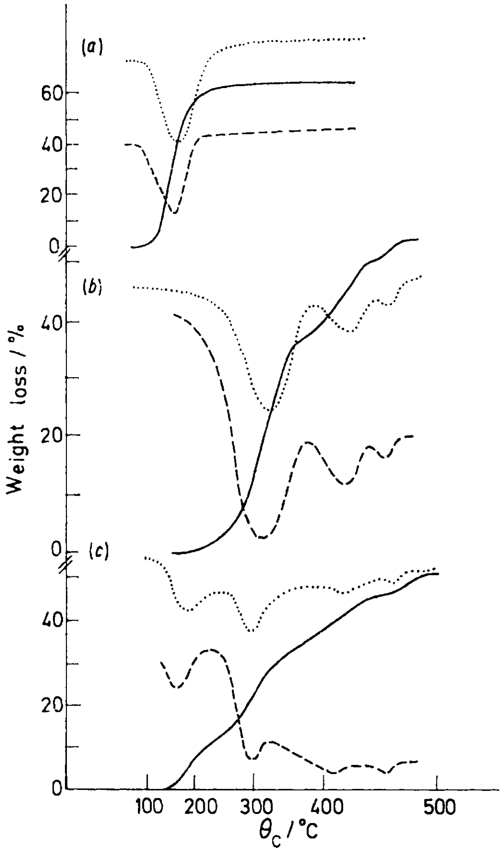

FIGURE 2 Thermograms of (*a*) ' iron(III) hydroxide ' gel, (*b*) the product of reaction of 10M-NH_4F solution with the ' gel ' at 90 °C for 240 min (identified as pure triammonium hexafluoroferrate(III) by *X*-ray diffraction and chemical analysis), and (*c*) the product of reaction of 7M-NH_4F solution with the gel at 20 °C for 12 min; (*c*) is a combination of (*a*) and (*b*), indicating that the residue contains triammonium hexafluoroferrate(III) and some unreacted gel. (· · ·), d.t.g.; (——), t.g.a.; and (– – – –), d.t.a.

Chemical Analysis.—Triammonium hexafluoroferrate(III) is moderately soluble in water (four determinations yielded an average value of 7·4 g per 100 g of water at 25 °C), but as may be expected it is much less so in concentrated NH_4F solution. The gel, on the other hand, is insoluble and so the two constituents of the product may be easily separated and their proportions determined by weighing. This was carried out by placing weighed amounts of the products in water (100 cm^3) and stirring for 1 h. After filtration, washing with water, ethanol, and then diethyl ether, and drying at room temperature, the loss in weight was found (Table 2). A thermogram of one of the washed insoluble portions was found to be identical to that of unreacted gel, *i.e.* (*a*) in Figure 2. The Table shows that only reaction with 10M-NH_4F at 90 °C gives a completely soluble product, and that an increase in concentration and time increases the proportion of soluble component. Solubility tests on the aluminium products showed them all to be completely soluble.

TABLE 2

Percentage soluble constituent in products from the reaction of ' iron(III) hydroxide ' gel with NH_4F

$[NH_4F]$/M	5	7	10
t/min at 20 °C			
5	17·2	37·2	57·3
12	31·6	48·1	77·4
30	50·4	65·2	85·9
t/min at 90 °C			
30	42·5	89·6	100·0
240	58·4	76·4	100·0

The ratio F : Fe = 1·0 : 1 is obtained if the percentage of the soluble constituent, $[NH_4]_3[FeF_6]$, is *ca.* 30%, assuming that the insoluble constituent conforms to the ideal formula $Fe(OH)_3$.

After separation the constituents of one of the mixtures were also analysed for fluorine, two determinations being carried out in each case. No fluorine could be detected in the washed insoluble portion, whilst the fluorine content in the soluble constituent yielded a mean value of 50·8%. The calculated value for $[NH_4]_3[FeF_6]$ is 50·9%. The completely soluble white product was found to contain 50·6% by weight of fluorine.

Thus the *X*-ray diffraction, thermal and chemical analyses indicate that the soluble white product is triammonium hexafluoroferrate(III), and that the brown products of the experiments are mixtures of unreacted gel and this salt in proportions as indicated in Table 2. There was no evidence to indicate that the action of NH_4F solutions on ' iron(III) hydroxide ' produces the fluoride oxide or any other product whether crystalline or amorphous.

DISCUSSION

It would appear that Frei's optimum conditions for the product to which he assigned the formula $Fe(O)F,nH_2O$ fortuitously produced a mixture containing the unreacted gel and $[NH_4]_3[FeF_6]$ in the right proportions to yield an F : Fe ratio of *ca.* 1·0 : 1. From our results it is apparent that under the same conditions, the

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[7] D. B. Shinn, D. S. Crockett, and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 1927.

7M-NH_4F concentration would require a reaction time less than 5 min to yield this ratio. Furthermore, the results indicate that had Frei used a higher concentration than 7M for either extended periods of time or at higher temperatures he would have obtained products with a fluorine content much too high for the formula $Fe(O)F,nH_2O$. Complete conversion to $[NH_4]_3[FeF_6]$ in his experiments would have been possible only with NH_4F solutions of concentration 3M or above, the former concentration yielding exactly the stoicheiometric amount for complete conversion. (Since we used the same volumes of reacting solutions, there was excess of NH_4F in all our experiments.)

One difficulty in explaining Frei's observations remains. He observed no *X*-ray reflections in any product. The sharp intense reflections of the relatively large crystallites of $[NH_4]_3[FeF_6]$, however, should certainly have been observable in his Debye–Scherrer camera, despite its much lower sensitivity compared to a Guinier camera. Frei did not state the type of *X*-ray radiation used. One cannot exclude the possibility that the photographs were taken with Cu-*K* radiation which is absorbed by compounds containing iron, thus lowering the intensity of their diffraction patterns and increasing the background through fluorescence. In such a case the diffraction patterns would not usually be observed.

The conversion of 'iron(III) hydroxide' gel to $[NH_4]_3[FeF_6]$ may be formulated as in equation (1).

$$FeO_x(OH)_{3-2x} + 6NH_4F + xH_2O \longrightarrow [NH_4]_3[FeF_6] + 3NH_4OH \quad (1)$$

The formula $FeO_x(OH)_{3-2x}$ for 'iron(III) hydroxide' represents its non-stoicheiometry with respect to water. This equation explains the observed pH changes and the different terminal values of the pH obtained for different concentrations of NH_4F.

It is of interest to compare the behaviour of 'iron(III) hydroxide' with that of aluminium hydroxide in aqueous NH_4F solutions. Berzelius [8] found that on boiling freshly precipitated aluminium hydroxide gel with an aqueous solution of NH_4F a white powder was formed. This white powder was analysed as $[NH_4]_3[AlF_6]$ by von Helmolt.[9] With the aid of *X*-ray diffraction as a means of identification, we have corroborated these observations on aluminium hydroxide, as previously described in the Experimental and Results sections. Thus the iron and aluminium systems are, as might be expected, very similar in their behaviour towards solutions of NH_4F.

It is not clear, however, what the mechanism of the reaction is. There are two ways in which the product may be formed. The first is a solid-state reaction which would require diffusion of both NH_4^+ and F^- into, and simultaneously the diffusion of OH^- out of, the solid phase. Diffusion in the gel would be facilitated by its very disordered and open structure. The product on the other hand possesses a considerably close-packed lattice which, in the initial stages, would form a protective skin on the gel particles and inhibit further reaction. This mechanism is therefore very unlikely. The second and most likely possibility is that 'iron(III) hydroxide' is continuously dissolved and reprecipitated as $[NH_4]_3[FeF_6]$. This may even take place within the pores of the gel. Indeed in the disordered gel it may be difficult or even semantic to distinguish between reaction in the solid or in solution. Optical microscopy supports the second mechanism. At intermediate stages of reaction the product was observed to occur as individual crystals either separate from or adhering to the brown amorphous regions but never as a layer or skin enclosing them. In this mechanism both the solubility of the gel and its open porous structure are important factors controlling the rate of reaction. It may be significant in this connection that α-Fe(O)OH, which has a well ordered and close-packed structure and lower solubility, showed only slight traces of $[NH_4]_3[FeF_6]$ after treatment with NH_4F solutions even after long reaction times under the most favourable conditions.

All previous work on the NH_4^+–Fe^{3+}–F^- system has been put in doubt by Cox and Sharpe [10] who showed that the only product obtained from an aqueous solution when the ratio $NH_4^+ : Fe^{3+}$ exceeded 3 : 1 was a cubic phase, which on recrystallization from very dilute hydrofluoric acid had the formula $(NH_4)_{2\cdot6}FeF_{5\cdot6},0\cdot4H_2O$. Our products, perhaps, also contained some water which we did not determine, but they analysed as F : Fe *ca.* 6 : 1. Our higher ratio may be due to the fact that the product was formed in high concentrations of NH_4F whilst Cox and Sharpe's products were recrystallized from water, *i.e.* at relatively low F^- concentrations. Cox and Sharpe observed that for ratios of NH_4 : Fe less than 3 : 1 no other product was formed. It is not surprising therefore that in our investigations we did not notice $[NH_4]_2[FeF_5]$ or $[NH_4][FeF_4]$ even as intermediates.

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[4/730 *Received*, 10*th April*, 1974]

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[8] J. J. Berzelius, *Annalen*, 1824, **1**, 41.

[9] H. von Helmolt, *Z. anorg. Chem.*, 1893, **3**, 127.

[10] B. Cox and A. G. Sharpe, *J. Chem. Soc.*, 1954, 1798.