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FLUOROFERRIC HEXAFLUOROSILICATES OBTAINED IN THE REACTION OF $Fe(OH)_3$ WITH H_2SiF_6 AND IN THE OXIDATION OF $FeSiF_6$ WITH H_2O_2

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SUMMARY

The title reactions were found to proceed in solution with formation of a mixture of the complexes $(FeF)SiF_6$ and $(FeF_2)_2SiF_6$ with an average atomic ratio $F/Fe \simeq 1.6$. Partial reactions involved in equilibria in the reaction system are proposed and discussed.

INTRODUCTION

Since 1913, when Recoura [1] stated that $Fe_2(SiF_6)_3$, formed initially in the reaction of $Fe(OH)_3$ with H_2SiF_6, decomposes instantly into $Fe_2F_2(SiF_6)_2$, there have been no further reports on this subject. As solutions of Fe(III) in H_2SiF_6 are of some significance in various technological processes [2-4], it was of interest to learn in what form trivalent iron exists in the presence of SiF_6^{2-} - ions.

EXPERIMENTAL

The reagents used were:

a) fluorosilicic acid, H_2SiF_6 (144 g/l, 1 M), of commercial grade;

b) ferric hydroxide freshly precipitated by the action of NH_3.aq on a solution of $FeCl_3$, and then thoroughly washed with warm water;

c) ferrous silicofluoride, $FeSiF_6$, obtained by dissolving steel shavings in H_2SiF_6 (1 M) at ca. 90°C until hydrogen evolution stopped and the pH rose to ca. 6. After filtration to remove excess iron and residue, the solution was allowed to stand for several days, then the precipitated silica gel was separated. The supernatant solution after analysis for its Fe and F content was used in the oxidation experiments. The solution contained Fe(II) 52.8 g/l, 0.94 M (by the $KMnO_4$-method), or 53.0 g/l, 0.95 M (by the EDTA method after oxidation Fe(II) to Fe(III) with H_2O_2) and F as H_2SiF_6 142 g/l, 0.98 M (by the alkalimetric method).

d) perhydrol, 30% H_2O_2 com. grade.

The reaction of H_2SiF_6 (1 M) with $Fe(OH)_3$ (added to the acid all at once) was carried out at 80-90°C with continuous stirring (3 hr) in a flask equipped with a reflux condenser. The molar ratio of reactants $H_2SiF_6:Fe(OH)_3$ = 1:2 employed is such as would yield FeF_3 (by analogy to AlF_3) if this were possible, according to equation (1). Changes in the solution were followed by Fe (with $KMnO_4$) and SiF_6^{2-} (as K_2SiF_6) determinations. The results obtained are given in Table 1.

The oxidation of $FeSiF_6$ solution (1 M, pH ~ 6) was initially attempted by bubbling oxygen over a period of several hours. It proved however that the reaction does not go to completion and is enhanced after ca. 40% of Fe(II) had been turned into Fe(III), probably due to self-acidification of the solution. Therefore perhydrol, 30% H_2O_2, was employed in all the experiments as an effective oxidizer for bivalent Fe-ions in the presence of SiF_6^{2-}-ions. After addition H_2O_2, the solution, initially green in colour, turned instantly to brownish-red, and its pH decreased from the original value of ca. 6 to ca. 1.2 - 1.3, some silica gel being formed. After decomposing the excess H_2O_2 by boiling, the silica was filtered off, washed thoroughly with hot water, dried and weighed. Oxidations with H_2O_2 were performed also with mixtures composed of 0.33 M $FeSiF_6$ with 0.67 M H_2SiF_6 and 0.67 M $FeSiF_6$ with 0.33 M H_2SiF_6. The experimental data are given in Table 3.

RESULTS AND DISCUSSION

The reaction of H_2SiF_6 with $Fe(OH)_3$, which was followed at 80°C and 90°C by chemical analysis, proceeded as given in Table 1

TABLE 1. The course of the reaction of H_2SiF_6 (1 M) with $Fe(OH)_3$ in 1:2 molar ratio

Temp. °C	Reaction time min	Chem.anal. of soln., M Fe^{3+}	SiF_6^{2-}	$a=\frac{FeF_n^{3-n}}{SiF_6^{2-}}$	Compn. calcd.,mole % $FeFSiF_6$ x	$(FeF_2)_2SiF_6$ (100-x)	$\frac{nF}{FeF_n}$
1	2	3	4	5	6	7	8
80	0	0	1.0	0			
	30	-	0.86	-			
	60	-	0.69	-			
	120	-	0.58	-			
	180	0.83	0.57	1.46	54	46	1.63
90	0	0	1.0	0			
	10	-	0.79	-			
	30	-	0.76	-			
	60	-	0.64	-			
	300	1.06	0.62	1.71	29	71	1.83

The experimental data show (col. 3 and 4) that the reaction stops after decomposition of ca. 40% of the acid and when 0.8-1.1 moles of $Fe(OH)_3$ (of 2 moles used originally, i.e. 40-53%) have passed into solution, giving Fe/SiF_6 molar ratios = 1.5 and 1.7 (col. 5), respectively.

Considering various possible hypothetical pathways, as expressed by the equations:

$$3\ H_2SiF_6 + 6\ Fe(OH)_3 \longrightarrow 6\ FeF_3 + 3\ SiO_2 + 12\ H_2O \qquad (1)$$

$$5\ H_2SiF_6 + 6\ Fe(OH)_3 \longrightarrow 3\,(FeF_2)_2SiF_6 + 2\ SiO_2 + 14\ H_2O \qquad (2)$$

$$7\ H_2SiF_6 + 6\ Fe(OH)_3 \longrightarrow 6\,(FeF)SiF_6 + SiO_2 + 16\ H_2O \qquad (3)$$

$$9\ H_2SiF_6 + 6\ Fe(OH)_3 \longrightarrow Fe_2(SiF_6)_3 + 18\ H_2O \qquad (4)$$

the following degrees of decomposition of the reactants used and concentrations of the constituents in solution may be calculated (Table 2).

TABLE 2. Decomposition (%) of reactants in the system H_2SiF_6 (1 M) - $Fe(OH)_3$ (m.r. 1:2) and their contents in solutions after the reactions (1) - (4)

Reaction	Degree of decompn., %		Compn. of soln., M theoret.		$\frac{FeF_n^{3-n}}{SiF_6^{2-}}$
No	$Fe(OH)_3$	H_2SiF_6	Fe^{3+}	SiF_6^{2-}	
1	100	100	2.0	0	∞
2	60	40	1.20	0.60	2.0
3	42.8	14.3	0.86	0.86	1.0
4	33.3	0	0.67	1.0	0.67

The reactions (1) and (4) may be eliminated because of the extreme inconsistency in the experimental data for the F/SiF_6 ratio and the degree of decomposition of the reactants.

Total agreement between the data found (Table 1) and calculated (Table 2) is obtained by assuming that reactions (2) and (3) proceed together in proportions given by the expression:

$$x = 100\ (2 - a)$$

where: x - mole % of $(FeF)SiF_6$ in mixtures with $(FeF_2)_2SiF_6$ and a = the FeF_n / SiF_6 molar ratio in solution found experimentally.

From the data shown in Table 1, equilibrium between FeF^{2+} and FeF_2^+ ions seems to establish very slowly and prolonged heating of the reaction system at higher temperature increases the proportion of FeF_2^+.

The oxidation of $FeSiF_6$ (1 M) with 10% excess of H_2O_2 (30%), was found to proceed smoothly at either temperature with precipitation of silica gel. The observation made with 1 mole solutions of SiF_6^{2-} containing 0.33, 0.67 and 1 gm.-ion of Fe(II), with the balance consisting of H^+ ions, are summarized in Table 3.

As is seen, in all cases oxidation results in SiO_2 precipitation independent of the content of free acid (col. 4). This fact allows us to exclude the formation of $Fe_2(SiF_6)_3$, despite

TABLE 3. The effect of the oxidation of $FeSiF_6$-H_2SiF_6 solns. (1 M) with H_2O_2 (30%)

Run no.	Parent solution M H_2SiF_6	Parent solution M $FeSiF_6$	Silica ppt. after oxidation $SiO_2/FeSiF_6$	x-value in eqn. (7)	$\frac{nF}{FeF_n}$ acc.to(7)	Proportion of FeF^{2+} mole %	Proportion of FeF_2^+ mole %
1	2	3	4	5	6	7	8
1	0.67	0.33	0.270	-0.080	1.54	46	54
2	0.33	0.67	0.260	-0.040	1.52	48	52
3	0.0	1.0	0.272	-0.088	1.54	46	54

the fact that in runs 1 and 2 appropriate amounts of free H_2SiF_6 were present, as required by the equation:

$$2\ FeSiF_6 + H_2SiF_6 + H_2O_2 \longrightarrow Fe_2(SiF_6)_3 + 2\ H_2O \tag{5}$$

Precipitation of silica may however be explained on the basis of the following equation:

$$12\ FeSiF_6 + 6\ H_2O_2 + x\ H_2SiF_6 \longrightarrow$$
$$6(x+1)(FeF)SiF_6 + 3(1-x)(FeF_2)_2SiF_6 + 3(1-x)SiO_2 + 2(x+3)H_2O \tag{7}$$

Variations of the $FeSiF_6$ content in the parent solution within a total of 1 mole of ($FeSiF_6$ + H_2SiF_6) apparently remain without any influence on the quantity of silica precipitated, which amounts to 0.26-0.27 moles SiO_2 per one mole of $FeSiF_6$ used (col. 4). This figures make it possible to find x-values in eqn. (7) for runs 1-3 and, further, to estimate the mean composition of FeF_n-cations in solutions oxidized. Negativity of x-values means that oxidation of $FeSiF_6$ proceed with liberation of x moles H_2SiF_6 per mole $FeSiF_6$ independent of its presence in runs 1 and 2. It explains the observable drop of pH from 6 to ca. 1.2 in the case of oxidation of $FeSiF_6$ solution in the absence of the acid (run 3).

As is seen from Table 3, the trivalent iron exists in the resulting solutions in the form of FeF^{2+} and FeF_2^+-cations in almost equal proportions (col. 7 and 8) defined by an F/Fe atomic ratio of ca. 1.5 (col. 6) independent of the conditions used. This figure is comparable with the value of 1.6 for the reaction of H_2SiF_6 with $Fe(OH)_3$ (Table 1, col. 8) and with data found recently by Russian workers [5] for H_2SiF_6 (~0.2 M): Fe (III) ≃ 1, while studying the system H_3PO_4-H_2SiF_6-Fe(III). It differs, however, from that presented by Recoura [1], for his compound with an nF/FeF_n ratio of 1.0. This author stated that he had been unsuccessful in isolating FeF-silicofluoride from solution. In fact, evaporation on boiling and at 50°C gave a fine white crystalline residue with an Fe content of ca. 30% and SiO_2 of 2%, which by the X-ray method, proved to be $FeF_3.3H_2O$. This leads to the tentative conclusion that the compounds considered are not stable as solids and decompose with evolution of SiF_4:

$$(FeF)SiF_6 + (FeF_2)_2SiF_6 + 9\ H_2O \longrightarrow 3\ FeF_3.3H_2O + 2\ SiF_4 \quad (8)$$

Further, it seemed interesting to compare the experimental results presented in this paper with theoretical ones which could be predicted from the equilibria of partial reactions. In the light of literature data [6] concerning the instability constants of complexes involved in the reaction systems under study, the following steps and partial processes must be considered:

1) equilibria existing in H_2SiF_6 and $FeSiF_6$ solutions:

$$H_2SiF_6 \longrightarrow 2\ H^+ + SiF_6^{2-} \quad (9)$$

or $$FeSiF_6 \longrightarrow Fe^{2+} + SiF_6^{2-} \quad (10)$$

$$SiF_6^{2-} \rightleftharpoons SiF_4 + 2\ F^- \qquad pk_1 = 6.0 \quad (11)$$

$$SiF_4 + 2\ H_2O \rightleftharpoons SiO_2 + 4\ HF \quad (12)$$

$$HF \rightleftharpoons H^+ + F^- \qquad pk_2 = 3.17 \quad (13)$$

2) neutralization or oxidation producing Fe^{3+} ions:

$$Fe(OH)_3 + 3\ H^+ \longrightarrow Fe^{3+} + 3\ H_2O \quad (14)$$

$$2\ Fe^{2+} + H_2O_2 \longrightarrow 2\ Fe^{3+} + 2\ OH^- \quad (15)$$

3) formation of fluoroferric complexes, disturbing equilibria (13), (12) and (11), with precipitation of silica:

$$Fe^{3+} + F^- \rightleftharpoons FeF^{2+} \qquad pk_3 = 5.28 \quad (16)$$

$$FeF^{2+} + F^- \rightleftharpoons FeF_2^+ \qquad pk_4 = 4.02 \quad (17)$$

$$FeF_2^+ + F^- \rightleftharpoons FeF_3 \qquad pk_5 = 2.76 \quad (18)$$

4) establishing equilibria between FeF_n, H^+ and F^--ions:

$$FeF_n^{3-n} + H^+ \rightleftharpoons FeF_{n-1}^{4-n} + HF \qquad pk'_{FeF_n} \tag{19}$$

Considering FeF_n and HF as complexes of fluoride ligands, in which Fe^{3+} and H^+ - ions are competetive ligand acceptors, the following approximate relation can be evolved between the instability constants pk' of the FeF_n complexes and pH [7]:

$$pk'_{FeF_n} = pk_{FeF_n} - pk_{HF} + pH \tag{20}$$

when: $pH \ll pk_{HF}$.

For pH values of 1.2 - 1.3 which are displayed by solutions after "neutralization" or oxidation if no further acid is added, the following figures are obtained from the expression (20) for particular fluoroferric complexes:

FeF^{2+}: $pk'_3 = 5.28 - 3.17 + 1.25 = 3.36$

FeF_2^+ : $pk'_4 = 2.10$

FeF_3 : $pk'_5 = 0.84$

Decreasing the pH in solution, e.g., by using excess H_2SiF_6 acid, would result in lowering these figures, but the range in which this factor may vary is rather limited. In turn, the concentration of F^--ions is limited by the equilibrium with SiF_6^{2-} ions (eq. (11)), as can be seen from the equation derived from the equilibrium equation (11):

$$[F] = 10^{-1.89}\sqrt[3]{[H_2SiF_6]} \tag{21}$$

It is readily found from the above figures or from the equilibrium equations (16) - (18), after inserting $[F] = 10^{-1.89}$ (for H_2SiF_6 = 1 M), that Fe (III) species should remain in the proportions:

$$Fe : FeF : FeF_2 : FeF_3 = 1 : 10^{3.36} : 10^{5.46} : 10^{6.30}$$

or $FeF : FeF_2 : FeF_3 = 1 : 126 : 871$

As is seen, FeF_3 should contribute nearly up to 90% in mixture with the other species. This is however inconsistent with there being no FeF_3 molecules in the solutions investigated and with the existence of only FeF^{2+} and FeF_2^- ions in almost equal proportions determined by the atomic ratios F/Fe = 1.5-1.8. Departure of the experimental results obtained from the theoretical data evolved are supposedly brought about by the high concentrations of solutions considered.

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