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Coprecipitation of Titanium(IV) and Iron(III) Complex Salts from Peroxide–Fluoride Solutions

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Abstract—Because the salts $(NH_4)_3TiO_2F_5$ and $(NH_4)_3FeF_6$ are isostructural, precipitation of the titanium peroxy salt from the $(NH_4)_2TiF_6$–$(NH_4)_3FeF_6$–NH_4F–H_2O_2 system is accompanied by crystal-chemical substitution of ions. As a result of partial peroxolysis, the iron salt coprecipitates with ammonium peroxypentafluorotitanate. If the degree of precipitation is higher than 20%, TiO_2 samples of high whiteness can be prepared from the hydrolysis product isolated from such solutions, after annealing at 850°C.

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Separation of ammonium fluorotitanates(IV) and fluoroferrates(III) is one of the most important problems in the fluoride method for breakdown of titanium-containing raw materials with ammonium fluorides, which is now under development [1–3]:

$$FeTiO_3 + 12\,NH_4F + 0.25O_2 = (NH_4)_3FeF_6 + (NH_4)_2TiF_6 + 3.5H_2O + 7\,NH_3,$$

$$FeTiO_3 + 6\,NH_4HF_2 + 0.25O_2 = (NH_4)_3FeF_6 + (NH_4)_2TiF_6 + 3.5H_2O + NH_3.$$

A procedure is known for separation of titanium and iron, based on partial coprecipitation of ammonium oxofluorotitanates and iron compounds from ammonium fluoride solutions prepared by breakdown of titanium-containing raw materials. The precipitation occurs when pH is increased to 6.5–7.5 by adding an ammonia solution [4]. In so doing, the reaction volume increases, which is undesirable.

A study of the solubility in the $(NH_4)_2TiF_6$–$(NH_4)_3FeF_6$–NH_4F–H_2O system showed that, with an increase in the NH_4F concentration, the solubility of the titanium and iron complex salts decreases, but the Ti/Fe weight ratio in solution increases, reaching a maximum (3260) in 28.5% NH_4F solution [5]. In such solution, the solubility of $(NH_4)_2TiF_6$ decreases, compared to that in water, from 24.09 to 8.63 g/100 g, which results in undesirable dilution of the reaction mixture.

To look for better procedures for separation of Fe(III) from Ti(IV), we examined the effect of H_2O_2 on the behavior of the iron and titanium salts present simultaneously in the $(NH_4)_2TiF_6$–$(NH_4)_3FeF_6$–NH_4F–H_2O_2 system.

It is well known that fluoride ion can act as a stabilizing agent in hydrogen peroxide solutions [6]; in addition, fluoride ion exerts a buffer effect on solutions [7].

As noted in [6], the calculated and actual pH values of hydrogen peroxide solutions differ from each other because of the presence of CO_2 contributing to the total acidity of the solution. Therefore, the pH values that we obtained for 1.2–8.0% H_2O_2 solutions are lower than the theoretical values. Addition of ammonium fluoride to a hydrogen peroxide solution allows pH of the NH_4F–H_2O_2 system to be maintained in the range 5.96–6.90 owing to the buffer effect of the F^- ion. There is a linear correlation between pH and H_2O_2 concentration in NH_4F solutions, and with an increase in the ammonium fluoride concentration from 3.4 to 10.0% pH of the system slightly increases and becomes close to 7 (Fig. 1).

It is known that base hydrolysis of ammonium hexafluorotitanate in peroxide solutions at pH 4–5 is accompanied by formation and precipitation of $(NH_4)_3TiO_2F_5$ [8]. Therefore, addition of $(NH_4)_2TiF_6$ to the NH_4F–H_2O_2 system with pH close to 7 will lead to

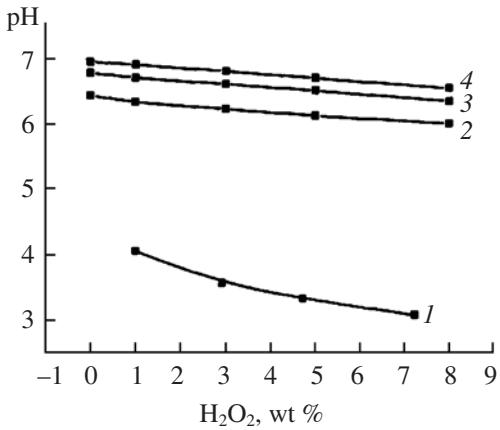

Fig. 1. Influence of H_2O_2 concentration on pH of the NH_4F–H_2O_2 system. NH_4F concentration, %: (*1*) 0, (*2*) 3.4, (*3*) 6.8, and (*4*) 10.0.

peroxolysis without adding an alkaline agent, according to reaction (1):

$$(NH_4)_2TiF_6 + NH_4F + H_2O_2 \rightarrow (NH_4)_3TiO_2F_5 + 2HF. \quad (1)$$

Under these conditions, the peroxolysis of the titanium salt occurs only partially, because the release of HF in the reaction leads to a decrease in pH of the solution to a value at which the peroxolysis stops. As seen from Table 1, after adding $(NH_4)_2TiF_6$ to the NH_4F–H_2O_2 system, pH of the solution decreases from 6.9–5.96 to 5.46–4.60.

The possibility of replacement of F^- by O_2^{2-} in the coordination sphere of titanium without adding an alkaline agent is provided by the stabilizing effect of NH_4F, resulting in formation of hydroperoxide ions in solution owing to proton transfer from H_2O_2 molecule to fluoride ion [scheme (2)], and also by the fact that pH of the solution corresponds to the onset of peroxolysis of the titanium salt:

Table 1. pH values of NH_4F–H_2O_2 solutions before and after peroxolysis of $(NH_4)_2TiF_6$ in them

H_2O_2, wt %	System 3.4 wt % NH_4F–H_2O_2		System 6.8 wt % NH_4F–H_2O_2		System 10 wt % NH_4F–H_2O_2	
	I	**II**	**I**	**II**	**I**	**II**
1.2	6.33	5.15	6.70	5.36	6.90	5.46
3.0	6.22	4.88	6.62	5.13	6.80	5.25
4.7	6.12	4.76	6.51	5.01	6.69	5.12
8.0	5.96	4.60	6.34	4.77	6.54	4.96

[a] (**I**) Initial NH_4F–H_2O_2 solution and (**II**) NH_4F–H_2O_2 solution after peroxolysis of $(NH_4)_2TiF_6$ in it.

$$H_2O_2 + F^- \rightleftarrows HF + OOH^-. \quad (2)$$

Thus, at comparable strength of the ligands F^- and O_2^{2-}, it is possible to control the ligand substitution and formation of mixed fluoroperoxy compounds of titanium.

When studying the $(NH_4)_2TiF_6$–NH_4F–H_2O_2 system, we found that the degree of peroxolysis of the starting ammonium fluorotitanate depends on the concentrations of H_2O_2 and NH_4F. According to reaction (2), an increase in the concentration of one of the components at a constant concentration of the other component shifts the equilibrium toward formation of the hydroperoxide ion. As a result, the weight of the precipitated $(NH_4)_3TiO_2F_5$ increases. In a solution containing 8.0% H_2O_2 and 10.0% NH_4F, the degree of peroxolysis of $(NH_4)_2TiF_6$ reaches a maximum. As a quantitative characteristic of the peroxolysis we chose the degree of precipitation (*A*, %) relative to the dissolved salt $(NH_4)_2TiF_6$ (Table 2).

We found that, when the peroxolysis was performed in the $(NH_4)_2TiF_6$–$(NH_4)_3FeF_6$–NH_4F–H_2O_2 system, iron salts coprecipitated with $(NH_4)_3TiO_2F_5$, which led to a decrease in the Fe(III) concentration in solution. As seen from Table 2, TiO_2 samples obtained from solutions with Ti/Fe > 3000 (by weight) have a whiteness of 94.1–97.6%. The high degree of separation of Fe from Ti is ensured by partial peroxolysis of solutions containing 6.8% NH_4F + 4.7 or 8.0% H_2O_2, or 10.0% NH_4F and any H_2O_2 concentration from the examined range. We believe that the factor responsible for the separation of Fe(III) from fluoride–peroxide solutions of Ti(IV) salts is that the compounds $(NH_4)_3TiO_2F_5$ and $(NH_4)_3FeF_6$ are isostructural. The peroxolysis of $(NH_4)_2TiF_6$ and formation of the complex compound $(NH_4)_3TiO_2F_5$ can be accompanied by heterovalent isomorphous substitution of a group of ions with close ionic radii ($R_{Ti^{4+}}$ 0.69 Å, $R_{Fe^{3+}}$ 0.67 Å), according to scheme (3) [9]:

$$Ti^{4+} + O_2^{2-} \rightarrow Fe^{3+} + F^-. \quad (3)$$

As a result, $(NH_4)_3FeF_6$ coprecipitates with $(NH_4)_3 \cdot TiO_2F_5$, and with an increase in the degree of peroxolysis of the starting titanium salt the precipitate weight and the probability of crystal-chemical substitution by scheme (3) will increase. This conclusion agrees with data of Table 2, which show that the separation of iron salts from titanium is the most efficient when the degree of precipitation *A* exceeds 22%.

Table 2. Characteristics of the $(NH_4)_2TiF_6$–$(NH_4)_3FeF_6$–NH_4F–H_2O_2 system and of hydrolysis products (HP) and TiO_2 samples obtained

NH_4F concentration, wt %	1.2 wt % H_2O_2				3.0 wt % H_2O_2				4.7 wt % H_2O_2				8.0 wt % H_2O_2			
	A, %	Ti/Fe	O_2^{2-}, % in HP	*W*, %	*A*, %	Ti/Fe	O_2^{2-}, % in HP	*W*, %	*A*, %	Ti/Fe	O_2^{2-}, % in HP	*W*, %	*A*, %	Ti/Fe	O_2^{2-}, % in HP	*W*, %
3.4	10.1	1000	2.6	72.9	10.7	1050	10.0	73.5	11.3	1220	15.0	74.3	11.4	1650	18.8	77.0
6.8	18.4	2280	2.7	90.6	21.4	2770	10.2	92.6	22.2	3550	15.5	96.4	26.1	3880	20.8	97.4
10.0	27.0	3120	2.7	94.1	29.6	3400	10.8	95.2	33.0	3610	15.7	96.9	33.6	3940	22.3	97.6

This assumption could be confirmed by proving that the hydrolysis of $(NH_4)_3FeF_6$ in the NH_4F–H_2O_2 system starts at higher pH values than the peroxolysis of $(NH_4)_2TiF_6$. Therefore, we performed potentiometric titration of $(NH_4)_3FeF_6$–NH_4F–H_2O_2 solutions with 0.1 M ammonia solution. It is known [10] that the hydrolysis with ammonia of an aqueous solution of the complex iron fluoride salt formed by addition of ammonium fluoride to a FeF_3 solution to an $NH_4F : F_3$ ratio of 3 : 1 is accompanied by precipitation of iron hydroxide on reaching pH 5.5 and is complete at pH ~7.2. As a result, $Fe(OH)_3$ is precipitated virtually completely with a stoichiometric amount of ammonia. If $Fe(OH)_3$ is precipitated from solutions with $NH_4F : FeF_3 > 3 : 1$, an excess of hydroxide ions is required, increasing with an increase in the excess amount of ammonium fluoride.

Figure 2 shows the potentiometric titration curves with NH_4OH of solutions prepared by dissolving $(NH_4)_3FeF_6$ in water and in solutions of 8.0% H_2O_2, 3.4 or 6.8% NH_4F, 1.2% H_2O_2 + 3.4 or 6.8% NH_4F, and 8.0% H_2O_2 + 6.8% NH_4F.

As we showed, the hydrolysis of a saturated solution of $(NH_4)_3FeF_6$ in H_2O starts immediately in the course of dissolution, when the pH of the initial solution is 4.86. On adding NH_4OH, the solution becomes yellow, and at pH 5.21 a reddish-brown precipitate starts to form. Further addition of ammonia leads to a slow increase in pH, and at pH 7.18 the hydrolysis is complete.

The potentiometric titration curve of a solution of $(NH_4)_3FeF_6$ in 8.0% H_2O_2 lies below the titration curve in water. On adding the first milliliter of the ammonia solution, pH sharply increases, and a reddish-brown precipitate is formed, which immediately dissolves, and the solution becomes orange-red. On adding 3 ml of the ammonia solution, the ascent of the curve becomes less steep, and pH at the moment of precipitate formation changes insignificantly. The potential jump corresponding to the end of titration is observed at pH 7.32.

In titration of $(NH_4)_3FeF_6$ in 3.4 and 6.8% NH_4F solutions, the hydrolysis starts at pH 7.32 and 7.97, and in solutions with the same NH_4F concentration in the presence of 1.2 and 8.0% H_2O_2, at lower pH values, 7.12 and 7.52, respectively (cf. curves *3* and *4*, *5* and *6*). At the same NH_4F concentration, the hydrol-

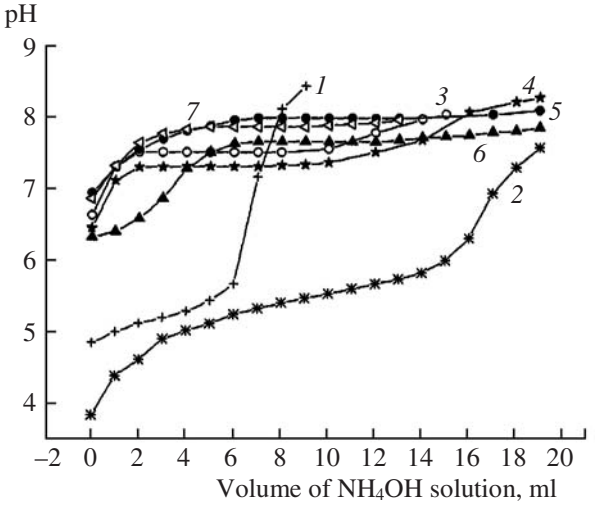

Fig. 2. Potentiometric titration of the $(NH_4)_3FeF_6$–NH_4F–H_2O_2 system with a 0.1 M NH_4OH solution: (*1*) 3.6×10^{-4} mol of $(NH_4)_3FeF_6$ in H_2O, (*2*) 5.1×10^{-4} mol of $(NH_4)_3FeF_6$ in 8.0% H_2O_2, (*3*) 2.5×10^{-4} mol of $(NH_4)_3FeF_6$ in 3.4% NH_4F, (*4*) 2.7×10^{-4} mol of $(NH_4)_3FeF_6$ in 3.4% NH_4F and 1.2% H_2O_2, (*5*) 1.6×10^{-4} mol of $(NH_4)_3FeF_6$ in 6.8% NH_4F, (*6*) 3.3×10^{-4} mol of $(NH_4)_3FeF_6$ in 6.8% NH_4F and 8.0% H_2O_2, and (*7*) 2×10^{-4} mol of $(NH_4)_3FeF_6$ in 6.8% NH_4F and 1.2% H_2O_2.

ysis of $(NH_4)_3FeF_6$ starts at lower pH values in solutions with a higher H_2O_2 concentration (curves *6* and *7*). For example, in solutions containing 6.8% NH_4F and 1.2% H_2O_2, the hydrolysis starts at pH 7.78, and in a solution with 6.8% NH_4F and 8.0% H_2O_2, at pH 7.52.

The higher the NH_4F concentration, the larger excess of ammonia should be added to the solution to precipitate Fe(III) salts (this is associated with the buffer effect of fluoride ions). Experiments show that even at a large excess of ammonia the iron precipitation is incomplete. The end point in the titration curves is lacking. Figures 1 and 2 show that hydrolysis of $(NH_4)_3FeF_6$ in the NH_4F–H_2O_2 system starts at pH values that are higher than the pH values of the starting solutions with the same concentrations of ammonium fluoride and hydrogen peroxide. Therefore, after dissolution of $(NH_4)_2TiF_6$ in the $(NH_4)_3FeF_6$–NH_4F–H_2O_2 system, the titanium salt undergoes peroxolysis, whereas the iron salt is not hydrolyzed.

The solution purified to remove Fe(III) was then subjected to hydrolysis with ammonia, with isolation of the hydrolysis product (HP). It is known [11] that, at the molar ratio $H_2O_2/Ti < 2$, the HP (**I**) consists of a mixture of titanium oxy- and peroxyfluorides $(NH_4)_2 \cdot TiOF_4$, $(NH_4)_3TiOF_5$, and $(NH_4)_3TiO_2F_5$, whereas at the molar ratio $H_2O_2/Ti > 2$ the HP (**II**) consists only of peroxofluorotitanates $(NH_4)_3TiO_2F_5$ and $(NH_4)_3Ti \cdot (O_2)_2F_3$. The higher the H_2O_2/Ti ratio, the higher the weight fraction of $(NH_4)_3Ti(O_2)_2F_3$ in the precipitate. Therefore, hydrolysis of solutions with 1.2 and 3.0% H_2O_2 results in precipitation of product **II**, whereas from solutions with 4.7 and 8.0% H_2O_2 product **II** is precipitated. According to X-ray phase analysis, the compounds $(NH_4)_3TiOF_5$, $(NH_4)_3TiO_2F_5$, and $(NH_4)_3Ti(O_2)_2F_3$ are isostructural. Therefore, the presence of particular compound can be confirmed by determining the weight fraction of peroxide oxygen in precipitates **I** and **II** [$(NH_4)_3TiO_2F_5$ contains 14.0 wt %, and $(NH_4)_3 \cdot Ti(O_2)_2F_3$, 28.7 wt % O_2^{2-}].

Thus, when introducing hydrogen perpoxide into the $(NH_4)_2TiF_6$–$(NH_4)_3FeF_6$–NH_4F–H_2O system, partial base hydrolysis of ammonium fluorotitanates can be replaced by partial peroxolysis occurring under these conditions without adding ammonia, i.e., without dilution of the solution. By so doing, Ti(IV) and Fe(III) can be separated. The pyrohydrolysis of the titanium hydrolysis products isolated from the purified solutions yields TiO_2 samples of high whiteness, 94.1–97.6% (Table 2).

EXPERIMENTAL

To prepare solutions, we used chemically pure grade $(NH_4)_2TiF_6$, analytically pure grade NH_4F, medical grade 40% H_2O_2, and analytically pure grade 25% NH_4OH. $(NH_4)_3FeF_6$ was prepared as described in [12].

The hydrogen peroxide concentration was determined by permanganatometric titration, and the ammonium fluoride concentration, by titration with a 0.5 N NaOH solution in the presence of Formalin [13].

The concentrations of Ti(IV) and Fe(III) in solutions were determined by atomic emission spectroscopy with inductively coupled argon plasma on a Plasmoguant 110 device. The pH measurements and potentiometric titrations were performed with an I-500 pH-meter in the termal compensation mode at 25ºC using a combined electrode (Hanna). The compositions of solid samples were studied by X-ray phase analysis on a D8 ADVANCE diffractometer (CuK_α radiation). The whiteness (W) of TiO_2 samples was calculated from the reflection coefficients ρ_λ [14]. The reflection coefficients were measured with a U 3010 spectrophotometer relative to MgO reference (100%). Titanium dioxide samples were compacted in pellets 35 mm in diameter under a pressure of 1.5 MPa.

In H_2O_2 solutions of a known concentration (1.2, 3.0, 4.7, and 8.0%), after adding the required amount of NH_4F to prepare solutions of concentrations 3.4, 6.8, and 10.0%, we dissolved $(NH_4)_3FeF_6$ with stirring for ~1 h to obtain a solution saturated at room temperature. To 25 g of the resulting solution, we added $(NH_4)_2TiF_6$, first in the amount corresponding to the solubility of the titanium salt at the given NH_4F concentration [5]. Then, after separating the yellow precipitate of $(NH_4)_3TiO_2F_5$ formed in the process, we added a further amount of $(NH_4)_2TiF_6$ and performed the dissolution for ~1 h to obtain a saturated solution. The resulting solution was hydrolyzed to pH 9 with 25% NH_4OH. The hydrolysis product was filtered off and subjected to stepwise pyrohydrolysis at temperatures of up to 450ºC and then to annealing in a dry atmosphere at 850ºC as described in [11]. The final product was titanium dioxide of anatase structure.

REFERENCES

1. Tsaur, Y., Pong, T.K., Besida, J., O'Donnell, T.A., and Wood, D.G., *Ind. Eng. Chem. Res.*, 2002, vol. 41, no. 19, p. 4841.

2. Gregor, Mc., Robert, A., and Rodionov, A., Austrian Patent Appl. 2 005 100 939, 2006, *Chem. Abstr.*, 2006, vol. 144, abstract 470 674n.
3. Andreev, A.A., D'yachenko, A.N., and Kraidenko, R.I., in *Sbornik trudov II Mezhdunarodnogo sibirskogo seminara ISIF-2006 "Sovremennye neorganicheskie ftoridy"* (Proc. II Int. Siberian Workshop ISIF-2006 "Modern Inorganic Fluorides"), Tomsk, 2006, p. 17.
4. Usol'tseva, T.I., Gordienko, P.S., and Goncharuk, V.K., RF Patent 2 182 886, 2000, *Byull. Izobret*., 2002, no. 15.
5. Bakeeva, N.G., Gordienko, P.S., and Pashnina, E.V., *Khim. Tekhnol.,* 2007, no. 9, p. 389.
6. Schumb, W.C., Satterfield, Ch.N., and Wentworth, R.L., *Hydrogen Peroxide*, New York: Reinhold, 1955.
7. Nikolaev, N.S. and Buslaev, Yu.A., *Zh. Neorg. Khim.,* 1959, vol. 4, no. 3, p. 543.
8. Chernyshov, B.N., Didenko, N.A., Bukvetskii, B.V., Gerasimenko, A.V., and Kavun, V.Ya., *Zh. Neorg. Khim*., 1989, vol. 34, no. 9, p. 2179.
9. Urusov, V.S., *Soros. Obraz. Zh*., 1996, no. 11, p. 54.
10. Novoselova, A.V., *Zh. Obshch. Khim.*, 1945, vol. 16, nos. 4 –5, p. 509.
11. Gordienko, P.S., Didenko, N.A., Bakeeva, N.G., Pashnina, E.V., and Botsul, A.I., *Khim. Tekhnol*., 2003, no. 6, p. 2.
12. Moriya, K., Matsuo, T., Suga, H., and Seki, S., *Bull. Chem. Soc. Jpn*., 1977, vol. 50, no. 8, p. 1920.
13. Kiseleva, E.K., *Analiz ftorsoderzhashchikh soedinenii* (Analysis of Fluorine Compounds), Leningrad: Khimiya, 1966, p. 65.
14. Belen'kii, E.F. and Riskin, I.V., in *Khimiya i tekhnologiya pigmentov* (Chemistry and Technology of Pigments), Leningrad: Khimiya, 1974, p. 60.