HYDROLYTIC PRODUCTS OF Fe(III) AFTER OXIDATION OF Fe(II) BY CHLORATE

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Dedicated to Professor J. Klikorka on the occasion of his 60th birthday.

Ferrous sulphate was oxidized by potassium chlorate in the pH region 2—7 and at temperatures ranging from 298·1 to 323·1 K and various hydrolytic products of Fe(III) were separated and identified. The separated solid ferric products were analyzed using a combination of the chemical analysis, IR spectroscopy, X-ray diffraction, and electron microscopy. The following substances were found as major components of the products: $Fe_2O_3.n\ H_2O$ ("ferric gel"), $Fe_2O_3.n\ H_2O$ with bound SO_4^{2-} ions ("sulphogel"), α-FeO(OH), γ-FeO(OH) and Fe_3O_4. Their amount depends particularly on the pH and temperature of the reaction medium.

Aqueous systems of Fe(III) at pH values allowing their hydrolysis were studied many times at various conditions and from various points of view, e.g., in[1-4]. Solid hydrolytic products of Fe(III) can be formed, e.g., by introducing Fe^{3+}, most frequently in the form of a salt soluble in water[5], into an aqueous system in which all conditions, particularly the temperature and acidity, are preset and maintained constant, or by the so-called hydrothermal transformation, during which the previously formed substance is transformed into a form more stable under the given conditions (temperature, pressure, pH)[6,7]. The authors of the paper[8] prepared even α-Fe_2O_3 and Fe_3O_4 in the form of well defined colloidal particles using the hydrothermal decomposition of ferric chelate by triethanolamine.

However, the hydrolytic precipitation of Fe(III) can be accompanied also by other processes, e.g., it can be preceded by the oxidation-reduction formation of Fe(III) itself. In this case the reaction system is changed by the hydrolysis of Fe(III) and by the subsequent processes of the formation of final products (hydrolysis to mono- and dimers, the fast reversible growth of small polymers, the formation of slowly reacting large polymers, the solid-phase precipitation[1,9]) as well as by the oxidation-reduction formation of Fe(III) as demonstrated by the Fe^{2+} oxidation by chlorate according to the reaction (A).

The given system can be studied from various points of view, e.g., to determine the kinetics and to elucidate the mechanism of various proceeding processes or to

obtain solid Fe(III) products of the required composition. It is particularly important to find out the influence of the system properties and of the preparation conditions on the composition of the products. As far as these products are mostly composed of various modifications of ferric oxides and oxide-hydroxides, some of which can be used for the preparation of substances of a considerable practical importance (ferric pigments, magnetic recording materials), the most frequent aim of the studies of such systems is to master the so-called controlled preparation of products with certain required properties (type of the substance, modification, size of particles and its distribution, specific surface, magnetic properties, *etc.*).

We have studied the system comprising the oxidation-reduction formation of Fe(III) and its subsequent hydrolysis from the point of view of its kinetics[10] and − in this paper − also from the point of view of the preparation of solid ferric products. Only a detailed knowledge of the reaction mechanism and of all factors affecting it can form a basis for mastering the controlled reaction in the sense mentioned above.

EXPERIMENTAL

Solid ferric products were isolated from the reaction systems used for the kinetic studies of the $FeSO_4$ oxidation by potassium chlorate described in our previous paper[10]. The initial concentration of the reaction components was 0.05 mol dm^{-3} $FeSO_4$ and 0.15 mol dm^{-3} $KClO_3$ that allowed to obtain a sufficient amount of the solid products. The pH value was kept constant by addition of the Na_2CO_3 solution or − at high pH values − by addition of NaOH solution, the constant ionic strength was adjusted by the excess of $KClO_3$.

The formed precipitate of Fe^{3+} hydrolytic products was separated immediately after the reaction was finished by centrifugation and it was washed out by water until the amount of SO_4^{2-} ions in the liquid phase decreased under the value detectable by the reaction with Ba^{2+} ions. After the last centrifugation the precipitate was dehydrated by acetone, filtered and dried on air at the room temperature. The phase composition of these standardized products was determined by a combination of several methods — namely chemical analysis, molecular spectroscopy, X-ray diffraction and electron microscopy.

Chemical Analysis

Fe(III) was determined chelatometrically, SO_4^{2-} gravimetrically as $BaSO_4$ after all iron was oxidized to Fe^{3+} by HNO_3, precipitated by NH_4OH and removed by filtration. The content of Na^+ and K^+ was determined by flame photometry. The determined relative content of these compounds was compared with their theoretical content in known ferric oxides, oxide-hydroxides and sulphate-hydroxides.

Molecular Spectroscopy

The infrared spectra were measured with the gitter Beckmann IR 20 A spectrometer (USA) using tablets with TlBr. This medium was used due to the high refraction index of the measured substances. The spectra were qualitatively and semiquantitatively analyzed using the characteristic bands of the individual phases, the wavenumbers of which are listed in Table I.

X-Ray Diffraction

The X-ray diffraction patterns of crystalline products were obtained on the DRON 1 diffracto-meter (USSR), using the vanadium filtered Cr K_α radiation at the constant scan speed of $0.5°$/min. The interplanar spacing d-values calculated from the diffraction patterns, with regard to the intensities of the principal reflexions, were compared with the values for α-FeO(OH), γ-FeO(OH), Fe_3O_4 and $K[Fe_3(OH)_6(SO_4)_2]$ as given in the tables[17]. The integral intensities, expressed in the relative units $(0-100)$ with respect to the most intense reflexions, were determined for the individual reflexions. The participation of individual components in the solid products was estimated by the comparison of their principal reflexions.

Electron Microscopy

The micrographs of the solid product samples were taken with the transmission electron micro-scope TESLA BS 242 E at the direct magnification of 10 000. The particle shapes observed on the micrographs were ascribed according to their morphology using the comparison with crystals of several ferric oxides and oxide-hydroxides described in the published litera-ture[6,18,19,20].

RESULTS AND DISCUSSION

Oxidation of Fe^{2+} by the chlorate anion in the acidic medium can be described by the equation

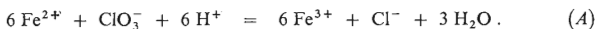$$6\,Fe^{2+} + ClO_3^- + 6\,H^+ = 6\,Fe^{3+} + Cl^- + 3\,H_2O. \qquad (A)$$

TABLE I
Wavenumbers (ν) of the characteristic IR absorption bands for several Fe(III) oxides and oxide-hydroxides

Substance	ν, cm^{-1}	Assignment according to
α-FeO(OH)	790, 890	11
γ-FeO(OH)	740, 1 020, 1 150	12
$Fe_2O_3 . n\,H_2O$	425, 580, 1 360	13
	1 553, 1 650	
Fe_3O_4	380, 575	14
SO_4^{2-} in $Fe_2O_3 . n\,H_2O . SO_4$ }	1 060, 1 115	15
$K[Fe_3(OH)_6(SO_4)_2]$	1 080, 1 181	16

Among the reaction products at pH > 2 a precipitate containing Fe(III) was observed that was formed by the subsequent hydrolysis of Fe(III) according to the overall reaction

$$m \, Fe^{3+} + n \, H_2O \; \rightleftharpoons \; Fe_m(OH)_n^{3m-n} + n \, H^+ . \qquad (B)$$
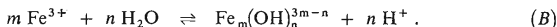
Because the phase analysis of the solid products containing Fe(III) formed in the reaction system at various pH and temperature values revealed different compositions of these products the effect of these reaction medium parameters on the solid product composition was studied in detail.

First of all the reproducibility of the composition of the prepared products had to be verified. It has been shown that at the same pH and temperature values their composition is identical within the accuracy limits of the identification methods used. The product composition did not change significantly even if Na_2CO_3 was used instead of NaOH for maintaining the constant pH value.

Results of the chemical analysis of the solid products obtained by the oxidation of $FeSO_4$ by chlorate at pH = 3, 4, 5, 6, and 7 and at the temperatures of 298·1, 313·1, and 323·1 K are given in Table II.

From Table II it follows that the chemical analysis alone allowed to distinguish three groups of products. The group *a* contains products with the lowest content of Fe(III) and with the highest content of SO_4^{2-}, products with the intermediate content of Fe(III) and SO_4^{2-} belong to the group *b*, and those in the group *c* have the highest content of Fe(III) and the lowest content of SO_4^{2-}. The determined content of Na^+ and K^+ was negligible in comparison with other components, except of the product prepared at pH 5 and 298·1 K, in which approximately 2% of K^+ were found.

These (and other) groups have also been found by other methods — infrared spectroscopy, X-ray diffraction, and electron microscopy. It was shown that the group *a* products are formed by the hydrated ferric oxide containing bound SO_4^{2-} ions (so-called "sulphogel")[13], that the products of the group *b* are mixtures of α- and γ-FeO(OH) in various ratios, and that the triiron tetraoxide contaminated by α- or γ-FeO(OH) is the main product of the group *c*. Moreover, two other products (denoted by *p*) have been identified, containing α-, γ-FeO(OH), and the "sulphogel". In the product prepared at pH 5 and 298·1 K the "sulphogel" is replaced by $K[Fe_3.(OH)_6(SO_4)_2]$, *i.e.* by the ferric potassium hydroxide-sulphate which is known as the mineral "jarosite". These two products are transient forms between groups *a* and *b*.

It has been further proved that there are no substantial differences between the results of these methods. In most cases the conformity of results increases the reliability of the total phase analysis. It is evident that the phase analysis of so complex mixture of substances with similar composition and properties must be performed
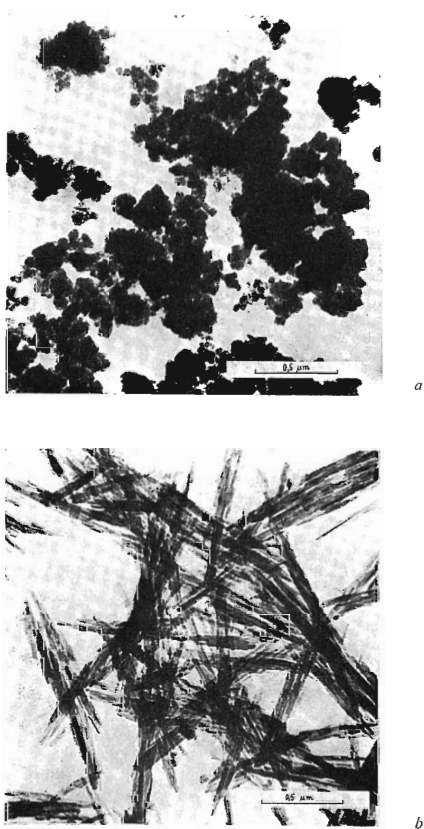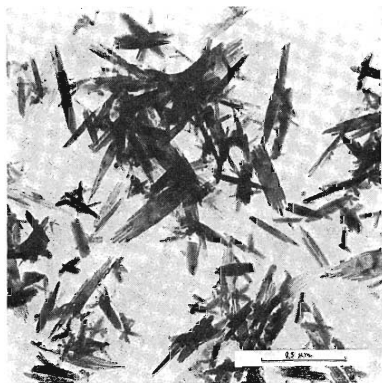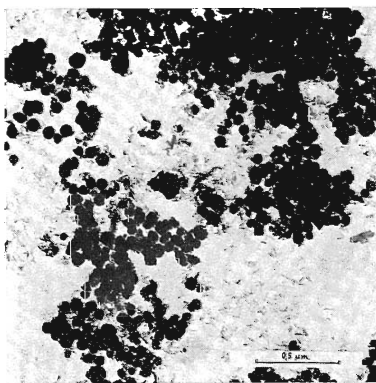
FIG. 2
Electron micrographs of several typical Fe(III) solid products. Magnification 10 000 times. $[Fe^{2+}]_0 = 0.05$ mol dm^{-3}, $[ClO_3^-]_0 = 0.15$ mol dm^{-3}, N_2 inert atmosphere. a pH 3, 313·1 K — amorphous phase; b pH 6, 298·1 K — γ-FeO(OH); c pH 6, 313·1 K — α-, γ-Fe(OH); d pH 7, 323·1 K — Fe$_3$O$_4$ with α-FeO(OH)

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by a combination of several methods. If this combination is properly chosen the advantages of the individual methods can complement each other. For instance, the quantitative participation of individual phases can be found, besides the X-ray diffraction and Mössbauer spectroscopy, rather rapidly and simply also from the infrared spectra. However, the precision of the determination depends in a great extent on the composition of the compounds under investigation; for instance, in the mixtures of α-Fe_2O_3 and α-$FeO(OH)$ and γ-$FeO(OH)$, respectively, the results are more precise (the relative deviation $\pm 5\%$) than in the mixture with $Fe_2O_3 \cdot n\,H_2O$ as the major component (relative deviation $\pm 15-20\%$). On the other hand, the infrared spectroscopy, in contrast to all other methods (except the chemical analysis), indicates the presence of SO_4^{2-} with very high sensitivity. Only the IR spectroscopy and X-ray diffraction proved the presence of the above-mentioned ferric potassium

TABLE II

Chemical analysis of solid products. $[Fe^{2+}]_0 = 0.05$ mol dm^{-3}, $[ClO_3^-]_0 = 0.15$ mol dm^{-3}, N_2 inert atmosphere; a group of products containing the amorphous phase; b mixtures of α- and γ-$FeO(OH)$; c Fe_3O_4; p transient products between groups a and b

pH	T, K	Group	Chemical analysis, %^{a}		Content of Fe^{3+} and SO_4^{2-} corresponds to
			Fe^{3+}	SO_4^{2-}	
3	298·1		43·67	14·06	
	313·1	a	44·25	12·85	$Fe_2O_3 \cdot n\,H_2O$–SO_4
	323·1		50·27	8·14	
4	298·1		43·74	14·19	
	313·1	p	53·40	5·85	$FeO(OH)$–$Fe_2O_3 \cdot n\,H_2O$–SO_4
	323·1	b	58·04	3·45	$FeO(OH)$–$Fe_2O_3 \cdot n\,H_2O$
5	298·1	p	49·66	10·76	$FeO(OH)$–$Fe_2O_3 \cdot n\,H_2O$–SO_4
	313·1		60·30	3·20	
	323·1		59·40	2·35	
6	298·1	b	59·43	1·40	$FeO(OH)$–$Fe_2O_3 \cdot n\,H_2O$
	313·1		58·64	1·35	
	323·1		58·28	0·94	
7	298·1		58·95	0·73	
	313·1	c	63·49	0·29	Fe_3O_4–$FeO(OH)$
	323·1		64·52	0·23	

^{a} The content of Na^+ and K^+ is negligible.

hydroxide-sulphate $K[Fe_3(OH)_6(SO_4)_2]$ in the product formed at pH 5 and 298·1 K. Similarly, in the product formed at pH 7 and 313·1 K the electron microscopy did not prove the presence of α-FeO(OH) that was found by all other methods. This discrepancy is most probably caused by the irregular distribution of individual phases in the mixture which is most conspicuously manifested in the observation of a small part of a very small sample as is the case in electron microscopy. On the other hand this method is capable to identify only few grains of a certain phase if they fall into the viewing field of the microscope while for the IR spectroscopy and/or X-ray diffraction this amount can be lower than their sensitivity limit. For instance, in contrast to all other methods only the electron microscopy proved the presence of a small amount of an amorphous phase (most probably of the "ferric gel") in the product prepared at pH 7 and 298·1 K. However, the phase analysis of solid products carried out by the above-mentioned methods gave a substantially good agreement of the results.

The solid product composition obtained by the combination of the results of various methods of phase analysis is given in Fig. 1. In this figure the abundance of individual phases of products is expressed by the part of the rectangular area, corres-
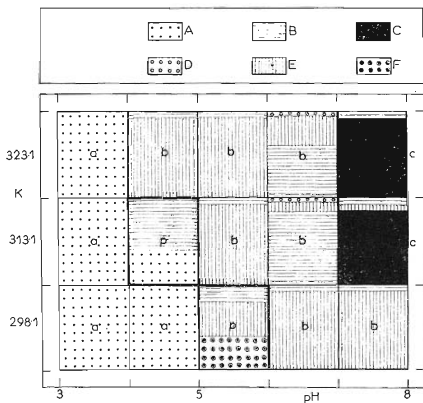

FIG. 1

Composition of solid products as a function of pH and temperature. $[Fe^{2+}]_0 = 0{\cdot}05$ mol dm^{-3}, $[ClO_3^-]_0 = 0{\cdot}15$ mol dm^{-3}, N_2 inert atmosphere. A $Fe_2O_3 \cdot n\,H_2O$–SO_4^{2-}; B α-FeO(OH); C Fe_3O_4; D $Fe_2O_3 \cdot n\,H_2O$; E γ-FeO(OH); F $K[Fe_3(OH)_6(SO_4)_3]$

ponding to the given product formed at the given temperature and acidity. From Fig. 1 it follows that at 298·1 K and at the pH value increasing from 3 (at pH 3 and at all temperatures only the pure amorphous "sulphogel" is formed) to 4 the abundance of the sulphogel decreases. The increase of temperature affects unfavourably the formation of this amorphous phase; the formation of crystalline α- and γ-FeO(OH) is preferred at pH 4. The fact that the amounts of the formed γ-FeO(OH) at pH 5 (at 313·1 and 323·1 K) and at pH 6 and 7 (at 298·1 K) are similar is rather remarkable. A change of pH at the temperature of 313·1 K causes the replacement of the α-FeO. .(OH) phase by the γ-FeO(OH) phase; finally, the pure Fe_3O_4 is formed at pH 7. A rather abrupt change of the product composition is observed at 323·1 K if pH is changed from 5 to 6, when about 60% of α-FeO(OH) is formed instead of nearly pure γ-FeO(OH). A nearly pure γ-FeO(OH) is formed at five combinations of the temperature and pH while the formation of α-FeO(OH) in the mixture is limited only to the pH 4 (313·1 K) and pH 6 (323·1 K); nearly pure α-FeO(OH) is formed only at pH 6 (313·1 K). The two highest values of pH and temperature in Fig. 1 represent the region of the exclusive formation of Fe_3O_4.
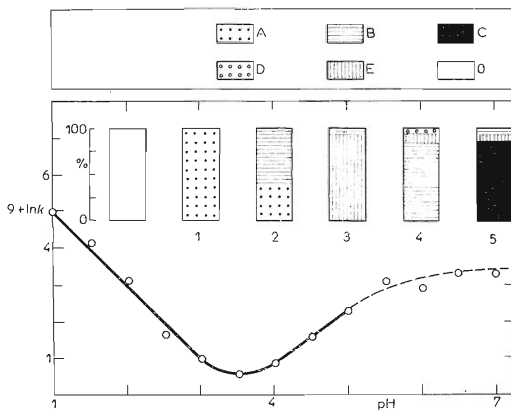

Fig. 3

The logarithm of the rate constant as a function of pH and the composition of solid products as a function of pH at the temperature of 313·1 K. $[Fe^{2+}]_0 = 0.05$ mol dm^{-3}, $[ClO_3^-]_0 = 0.15$ mol dm^{-3}, N_2 inert atmosphere. A $Fe_2O_3 \cdot n\, H_2O–SO_4^{2-}$; B α-FeO(OH); C Fe_3O_4; D $Fe_2O_3 \cdot n\, H_2O$; E γ-FeO(OH). 0 no sediment; 1 $Fe(H_2O)_x^{2+}$; 2 $Fe^{2+} \rightleftarrows Fe(OH)^+$; 3 $Fe(OH)^+$; 4 $Fe(OH)_2$; 5 $Fe(OH)_2$, green rust

These results show the complex effect of the temperature and acidity on the participation of individual phases in the solid product.

The electron micrographs are the most illustrative document on the nature of solid products. Fig. 2* shows typical products from the groups *a*, *b*, and *c*. A typical product of the group A, prepared at pH 3 and 298·1 K, is given in Fig. 2*a*. It is easy to distinguish the agglomerates of amorphous particles of the hydrated ferric oxide $Fe_2O_3.n\ H_2O$ (so-called "ferric gel") or of $Fe_2O_3.n\ H_2O$ with SO_4^{2-} (so-called "sulphogel"). Figs 2*b* and 2*c* present the products of the group *b*, prepared at pH 6 and at temperatures 298·1 K and 313·1 K, respectively. In Fig. 2*b* one can observe the elongated "grass-like" particles of the well developed γ-FeO(OH) and a small amount of tiny needles of α-FeO(OH). Fig. 2*c* demonstrated the mixture of α- and γ-FeO(OH) and of a small amount of an amorphous phase. γ-FeO(OH) is present in the form of elongated plates irregularly frayed on opposite ends while the well developed needles with sharp ends belong to the so-called "needle-like" α-FeO(OH). However, this micrograph does not reflect the prevailing amount of α-FeO(OH) as found by the IR spectroscopy and X-ray diffraction. The product on Fig. 2*d*, prepared at pH 7 and 323·1 K, is typical for the group *c*. It contains triiron tetraoxide — dark, in several cases well developed hexagonal particles on the micrograph — as well as the so-called needle-like α-FeO(OH) (light, tiny, and thin sticks).

Together with the preparation reactions of the described solid products also their kinetics has been simultaneously studied in detail as described in our previous paper[10]. To establish a possible relation between the reaction kinetics and the nature of products the dependence of the logarithm of the rate constant of the Fe^{2+} oxidation by the chlorate anion on pH was correlated with the composition of the simultaneously formed solid products, as shown in Fig. 3.

The kinetic calculations and the following considerations on the mechanism of Fe^{2+} oxidation at various values of pH, as described in detail in our previous paper[10], have shown that at the low values of pH (at pH ~ 3) Fe^{2+} is predominantly oxidized in the form of the hydrated ion $[Fe(H_2O)_x]^{2+}$. Beginning from approximately pH 3·5, when the equilibrium $Fe^{2+} \rightleftharpoons Fe(OH)^+$ starts to play a role, Fe^{2+} is oxidized also in the form of $Fe(OH)^+$. At pH 5 this equilibrium is already considerably shifted towards the right-hand side and from pH 6 most of Fe^{2+} in the given system is already oxidized in the form of the precipitate $Fe(OH)_2$. In our previous paper the change of the slope of the logarithm of the rate constant on pH in the vicinity of pH 3·5 was also explained by the gradual hydrolysis of Fe^{2+}. These results may also play a certain role in the evaluation of the effect of pH on the formation and composition of the final solid products.

Fig. 3 demonstrates that a different composition of the final product can be correlated with different regions of pH and therefore also with different forms of the

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* See insert facing page 1072.

oxidized Fe^{2+}. Moreover, at pH 7 a temporary formation of a green-blue precipitate, in the published literature currently denoted as the "green rust"[21], was observed. The nature of this intermediate was not studied in detail in this paper but this problem has been dealt with, *e.g.*, by the authors of papers[21,22]. The effect of pH on the formation of the ferric hydrolytic products in an aqueous medium, which comprises mainly the processes of olation and oxolation[1], followed by the formation of linear chains and by the crystallization of the final products, was already discussed elsewhere[5,9]. In spite of this fact it can be stated that these processes are not yet completely elucidated. According to the results of this study it seems highly probable that the nature of the final product containing Fe(III) is — along with other effects — affected also by the initial state of Fe^{2+} that depends first of all on the acidity, *i.e.*, by the fact whether Fe^{2+} is oxidized either in the form of the ions $[Fe(H_2O)_x]^{2+}$ or $Fe(OH)^+$, or in the form of $Fe(OH)_2$.

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