

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE CHEMICAL INSTITUTE OF THE FORSTLICHE HOCHSCHULE, HANN-MÜNDEEN, GERMANY]

GAMMA-FERRIC OXIDE HYDRATE

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RECEIVED OCTOBER 23, 1931

PUBLISHED MARCH 5, 1932

In an earlier communication one of the authors¹ has published results concerning the magnetic and crystallographic investigations of the products formed by the oxidation of ferrous bicarbonate solutions, and has shown further that γ -ferric oxide hydrate is formed on oxidizing ferrous ammonium sulfate solutions with iodates in the presence of thiosulfates.² Since this γ -hydrate is free from impurities and forms on dehydration ferromagnetic γ -ferric oxide, a new proof of the existence of a ferromagnetic cubic ferric oxide was established, which was still doubted by some authors despite the work of Sosman, Baudisch and Welo, Böhm, and others.

The x-ray photographs of the compounds which were obtained by the oxidation of ferrous bicarbonate solutions gave the diagram of the α -hydrate only. The compounds were also, in general, magnetically identical with one another. But some of the preparations, which were obtained by *slow oxidation* in air (weeks and months), not only showed differences among themselves, but also as compared with the compounds which were obtained by rapid oxidation (passing air through, or adding hydrogen peroxide). It was at that time suggested that a "ferrit" formation^{3,4} and also that the presence of a small amount of divalent iron, were responsible for these properties.

We therefore repeated this slow oxidation and found that the precipitate obtained was not homogeneous, but contained a mixture of α - and γ -hydrates. They can be separated from each other since the γ -hydrate is formed as a dark brown crust on the surface of the solution, while the α -hydrate is formed in the solution itself as a finely-divided yellow precipitate on the bottom of the vessel. On drying the preparations, however, a part of the γ -hydrate is changed into γ -oxide, which is in accordance with the increase of the magnetic susceptibility.

Schickor⁵ has recently described similar experiments, so that we can content ourselves with confirming his results, without bringing in further experimental material. He also makes the suggestion that an intermediate green labile ferrous-ferric complex is necessary for the formation of γ -ferric oxide hydrate.

Our further experiments, which were completed in the main by the

¹ Albrecht, *Ber.*, **62**, 1475 (1929).

² Hahn and Hertrich, *ibid.*, **56**, 1729 (1923).

³ Hilpert, *Z. anorg. Chem.*, **169**, 273 (1928).

⁴ Krause, *Ber.*, **42**, 2248 (1909); *Z. anorg. allgem. Chem.*, **197**, 301 (1931).

⁵ Schickor, *Z. anorg. allgem. Chem.*, **191**, 322 (1930).

end of 1929, but which have not yet been published for various reasons, were based on the following considerations.

One of us has shown in earlier work⁶ that in catalytic oxidations with the aid of iron salts, the oxygen used for the oxidation becomes temporarily activated, becoming coördinatively linked in an intermediate iron complex. Such "active" iron complexes could be identified.⁷ This supposition contradicts two other theories. Manchot, as the leading representative of one, stipulates the formation of an intermediate iron peroxide, while Wieland, as the supporter of the other, supposes the formation of intermediary hydrogen peroxide. An exact proof for the existence of either the one or the other is lacking at the present time,⁸ while the facts can be just as well explained by the aid of Baudisch's oxygen-complex theory, with the further advantage that complexes of which oxygen is a member are known with iron as well as with cobalt. If such a complex decomposes on further oxidation, one should expect that ferric oxide hydrate of another structure would be formed in this decomposition, as when, in the direct oxidation of a ferrous salt, the ferric salt formed decomposes by hydrolysis into ferric oxide hydrate and acid.

This theory explains the following experiment very well. If ferrous chloride solution is oxidized at ordinary temperatures (about 18°), whether quickly or slowly, only α -hydrate is formed. If, however, the oxidation is carried out *slowly* at a somewhat higher temperature (40–50°) while the solution is being stirred slowly (a saturated solution diluted to one-half), a considerable percentage of γ -hydrate is formed. At temperatures from 90–100° α -hydrate is obtained with slow as well as with rapid oxidation. The self-complex formation of ferrous chloride solution at higher temperatures has been shown as probable by other investigators,⁹ and Chandra¹⁰ has succeeded in isolating polynuclear ferrous-ferric complexes as their alkali salts by the partial oxidation of ferrous salt solutions.

An attempt was then made to obtain pure γ -oxide hydrate by oxidation following the addition of suitable complex-forming compounds to ferrous salt solutions. It has been shown that nitrogen-containing compounds are especially suitable, above all pyridine. As can be seen from the experimental part, it was possible to obtain pure γ -oxide hydrate by the addition of pyridine to ferrous chloride solutions. It has been shown, moreover, that not only the addition of a suitable complex-forming compound, but also the nature of the anions in the salt solution, is of impor-

⁶ Baudisch, *Naturwissenschaften*, **16**, 542 (1928); see also Baudisch and Welo, *J. Biol. Chem.*, **61**, 261 (1924).

⁷ *Biochem. Z.*, **232**, 35 (1931).

⁸ Cf. Abegg's "Handbuch der anorganischen Chemie," Vol. IV, 3d. ed., II, Teil B, pp. 8 *et seq.*

⁹ Abegg, *Z. Elektrochem.*, **10**, 77 (1904).

¹⁰ Chandra, *Inaugural dissertation*, Friedrich Wilhelm University, Berlin, 1913.

tance for the formation of γ -oxide hydrate; *i. e.*, it was impossible to obtain γ -oxide hydrate from ferrous sulfate or ferrous fluoride solutions. A γ -oxide formation from ferric nitrate solutions was not expected and not found, as the oxidizing power of nitric acid is too great for the formation of any kind of intermediate products with the desired properties.

In further preparations of γ -oxide hydrate, the addition of sodium azide to the ferrous chloride solutions was found to be of great advantage. The question as to whether this addition of sodium azide to the ferrous salt solutions forms a complex cannot be definitely answered from our experimental material. The red color of the solution points to the formation of an iron azide.¹¹ In oxidations at a higher temperature hydrazoic acid, which can be recognized by its odor, is given off abundantly. It is interesting to note that the formation of γ -hydrate does not commence until the solution is already partly oxidized, and the originally alkaline solution (P_H 8 to 10) has become weakly acid. The formation of γ -hydrate first starts from a P_H of 6.5 to *ca.* 2.0. It seems then that the formation of γ -hydrate is dependent also on the hydrogen-ion concentration, for it is always found that γ -hydrate is formed only in weakly acidic solutions (P_H 2–6.5). This observation is in agreement with that of Krause,⁴ who is of the opinion that his "metaferric hydroxide" ("eisenige Säure") with the isoelectric point P_H 5.2 is identical with the γ -hydrate.

Experimental Part

The purest iron powder, prepared by I. G. Farbenindustrie A.-G.¹² from iron-pentacarbonyl, was used in excess, being dissolved in the corresponding acid until the solutions reacted neutral to Congo paper. The oxidations were then made with these solutions.

Hydrochloric Acid Solutions.—The solutions were still more weakly acid (P_H 4 to 5). On oxidation by means of air, oxygen, or hydrogen peroxide, a yellow precipitate of α -hydrate separated out. On slower oxidation at a somewhat higher temperature with stirring, a mixture of α - and γ -hydrates was formed.

One hundred cc. of the concentrated ferrous chloride solution was diluted with 100 cc. of water and 20 cc. of the purest Merck pyridine added. A green precipitate came out which, however, dissolved upon shaking. On passing air or oxygen through the mixture an orange-red precipitate of γ -hydrate was formed. On the addition of pyridine the P_H of the solution rose to about 6–6.4 and then remained practically constant after the oxidation. The formation of γ -hydrate was proved by the fact that the precipitate was then free from divalent iron and gave a ferromagnetic ferric oxide on dehydration at 280–290°. If the solution to which pyridine had been added was then heated on the water-bath and air passed through, α -hydrate was formed. α -Hydrate was also formed on oxidizing the pyridine-containing solution with hydrogen peroxide. Changing the concentration of the solutions of ferrous chloride or of pyridine did not change the oxidation product. If an excess of pyridine was added to the solution, *i. e.*, 50 cc. of concentrated ferrous chloride solution and 50 cc. of pyridine, the

¹¹ Salomea Lorie, Inaugural dissertation, "Stickstoffwasserstoffsäure und ihre anorganischen Verbindungen," Zürich, 1912.

¹² At this point we should like to thank the I. G. Farbenindustrie A.-G. for their kind supply of the preparations used in this research.

solution solidified to a gray-green mass. An attempt to oxidize this gray-green mass with air or oxygen yielded no satisfactory results. Dark brown products are formed which are very difficult to wash free of chlorides and pyridine. If, however, the gray-green precipitate is shaken with much water before oxidizing, most of it goes into solution, forming a green color, and is oxidized to γ -hydrate by passing through air or oxygen.

If piperidine or ammonia was added to the ferrous chloride solution instead of pyridine, γ -hydrate was never formed, even under the same conditions as when pyridine was used.

When the ferrous chloride solution was added to a 10% sodium azide solution, the green solution became red and alkaline (P_H 10). Upon passing through air or oxygen a yellowish-red precipitate of α -hydrate was formed, the P_H changing meanwhile to neutral or weakly acidic. The filtrate from this precipitate was warmed on the steam-bath and more oxygen passed through. A yellowish-red precipitate of γ -hydrate was formed, the solution becoming colorless and strongly acid. The reaction was quantitative. If a large amount of sodium azide was added to the solution, the precipitate obtained on oxidation always contained chlorides and nitrogen. The following method of precipitation proved to be very satisfactory; 50 cc. of ferrous chloride solution (P_H 5) was added to 50 cc. of water and 20 cc. of 10% sodium azide solution poured in. The resulting red solution had a P_H of 8.9. After oxidation by passing oxygen through at water-bath temperature, the now colorless solution had a P_H of 2.4. The reddish-yellow precipitate was easily filtered and washed, then identified as γ -hydrate.

Analogous experiments on solutions containing excess of iron were carried out with hydrobromic, hydriodic, hydrofluoric, sulfuric and nitric acids.

Upon dissolving iron in nitric acid, an oxidation set in immediately, and upon precipitation with organic or inorganic bases red oxide hydrates were formed.

Moreover, no γ -hydrate was formed on oxidizing ferrous fluoride and ferrous sulfate under the same conditions as with the ferrous chloride, while in the cases of the bromide and iodide positive results were obtained. No doubt the ferrous bromide solution behaved in a manner exactly analogous to the ferrous chloride solution. On oxidation of the iodide solutions, the precipitates which formed always contained iodides.

Magnetic Measurements

The mass susceptibilities of a series of preparations made from iron chloride by oxidation in the presence of pyridine were determined.¹

No.	1	2	3	4	5
$\chi \times 10^6$	100	215	115	308	46
Moles of H_2O	1.22	...	2.50	1.52	1.73

All the preparations with the exception of preparation 5 contained divalent iron. This latter was dehydrated slowly at different temperatures and from time to time its water content and magnetic susceptibility were measured:

Time of heating, hrs.	$T, ^\circ C.$	$\chi \times 10^6$	Amp.	Moles of H_2O
20	110	30	1, 2, 3	1.76
6	140-185	33	1, 2	1.64
2	240-280	538	0.50	0.21
		335	1.00	
		218	2.0	

Time of heating, hours	T , °C.	$\chi \times 10^6$	Amp.	Moles of H_2O
2	205	121	1.00	1.41
		96	2.00	
		84	3.00	
2	195	209	0.50	1.37
		186	1.00	
		140	2.00	
2	200	506	0.50	1.40
		332	1.00	
		284	1.50	
24	200	1870	0.50	1.03

A sample of the original material was sealed off in a hard glass tube and heated under water for two hundred hours. The resulting product was bright red, still contained, after drying with acetone and ether, 1.1 mole of water and its magnetic susceptibility was $\chi = 40 \times 10^{-6}$.

Further, two compounds which had been prepared by oxidation at water-bath temperature in the presence of sodium azide were magnetically measured. Both were free from divalent iron, contained 2.4 and 2.1 moles of water, respectively, and their magnetic susceptibilities were 56 and 55×10^{-6} . Upon heating to 280–290° they became strongly ferromagnetic.

Summary

1. Under certain conditions ferrous bicarbonate solution is autoxidized to γ as well as α -ferric oxide hydrate.

2. The oxygen-complex theory of Baudisch was supported by the following new preparations of γ - $Fe_2O_3 \cdot H_2O$ and γ - Fe_2O_3 . (a) γ - $Fe_2O_3 \cdot H_2O$ is formed by air-oxidation of ferrous chloride solutions under conditions where auto-complex-formation is favored. (b) In presence of certain organic nitrogen-containing compounds, the oxidation of ferrous chloride solution with air forms quantitatively γ - $Fe_2O_3 \cdot H_2O$. (c) γ - $Fe_2O_3 \cdot H_2O$ is formed by air-oxidation of ferrous chloride solutions in presence of sodium azide and under a certain PH .

3. The newly synthesized $Fe_2O_3 \cdot H_2O$ preparations were magnetically measured.

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