[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Constitution of β Iron Oxide Monohydrate[1]

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In addition to the two iron oxide monohydrates, α and γ $Fe_2O_3{\cdot}H_2O$, it is claimed[2] that upon slow hydrolysis of not too dilute ferric chloride solutions, a yellow precipitate is formed which has a structure different from that of the two oxides. Schikorr[3] found this product to have an x-ray pattern identical with that described by Böhm but different from that of FeOCl. Stirnemann[4] prepared the latter product in a pure state by hydrolysis of concentrated ferric chloride solutions at temperatures between 270 and 410° and studied its properties. Weiser and Milligan[5] found that upon hydrolysis of various iron salts $\alpha Fe_2O_3{\cdot}1H_2O$ was formed, ferric chloride being the only salt yielding the yellow precipitate which was named by them[6] β iron oxide hydrate. The latter contains variable amounts of chloride[6] depending upon the method of preparation, and treatment of the product. Irrespective of the chloride content, Weiser and Milligan[6] found identical x-ray pictures for various products, indicating, according to them, that the precipitate is ferric oxide with more or less adsorbed chloride and not a basic ferric salt. It is suggested that the chloride stabilizes the lattice. The results of our own work are contrary to the conclusions of the above authors and are more in agreement with those obtained by Goldsztaub.[7] It may be mentioned that the latter's paper was published after our work had been brought to conclusion. On the basis of extensive investigations, Goldsztaub concluded that only two iron oxide monohydrates exist: α FeO(OH) (goethite) and γ FeO(OH) (lepidocrocite). The latter product was also obtained by treatment of large crystals of FeOCl with water, and it was shown by x-ray analysis that lepidocrocite and FeOCl have the same structure, OH^- and Cl^- being able to replace one another in the two products. From the above, one would conclude that the so-called β oxide monohydrate actually consists of mixed crystals of lepidocrocite and FeOCl. In the present work it is shown that upon shaking of the β oxide monohydrate with dilute hydrochloric acid, in the presence of large amounts of alkali chloride, the chloride ion penetrates slowly into the lattice of the solid. With other acids in the presence of their alkali salts only a slight adsorption was found on the α and β oxide monohydrates. Similarly, on shaking the α oxide with dilute hydrochloric acid and alkali chloride, only an adsorption was found.

Preparations Used

β-$Fe_2O_3{\cdot}H_2O$.—Two samples of this oxide were prepared according to the directions of Schikorr[3] and of Weiser and Milligan[6] with a slight modification in the washing procedure.

Product 1.—Two liters of 0.1 *M* ferric chloride solution was hydrolyzed on the steam-bath at an average temperature of 55° for four days. A yellow precipitate settled out, which, when packed tight, had a reddish-brown appearance. It was found that washing the product with water resulted in immediate peptization. With the aid of the centrifuge the precipitate was washed with 1 *N* ammonium chloride, until the wash liquid did not give a test for iron with thiocyanate in acid medium. The washing was continued with 1 *N* ammonia until the wash liquid was chloride free (20 washings with 50-ml. portions). The nature of the precipitate appeared to change from a finely divided state into a granular form. It was then washed 14 times with 50-ml. portions of conductivity water. After the last washing peptization of the precipitate began to take place. It was finally washed three times with 95% alcohol, and several times with ether, made air dry by passing purified air through it and finally dried in an oven at 110° for two hours. It was allowed to remain exposed to pure air for several weeks before use. The product was tan-colored.

Product 2.—Four liters of 0.1 *M* ferric chloride was subjected to hydrolysis at 55° for twenty days. The precipitate was collected, and treated as described above.

α-$Fe_2O_3{\cdot}1H_2O$.—Four liters of 0.1 molar ferric nitrate was hydrolyzed at 65–70° for seven days. A finely divided yellow precipitate settled out. Since peptization took place with the first washing of the precipitate with water, it was washed with 1 molar ammonium nitrate until no test for iron was obtained with thiocyanate. Upon washing (centrifuge) with 1 *N* ammonia, the α oxide behaved quite differently from the β oxide. Whereas the latter was coagulated by ammonia, the α oxide became peptized after the fourth washing. The precipitate was then washed four times with conductivity water, four

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(1) This manuscript has been prepared from notes left by Benjamin Moskovitz, who died October 17, 1935. The work is part of the material which was intended to constitute the body of his thesis for the degree of Doctor of Philosophy.

(2) J. Böhm, *Z. anorg. allgem. Chem.*, **149**, 203 (1925); *Kolloid Z.*, **42**, 276 (1927); *Z. Krist.*, **68**, 567 (1929).

(3) G. Schikorr, *Kolloid Z.*, **52**, 25 (1930).

(4) E. Stirnemann, *Neues Jahrbuch f. Mineralogie*, **52A**, 334 (1925).

(5) H. B. Weiser and W. O. Milligau, *J. Phys. Chem.*, **39**, 25 (1935).

(6) H. B. Weiser and W. O. Milligan, THIS JOURNAL, **57**, 298 (1935).

(7) M. S. Goldsztaub, *Bull. Soc. Franc. de Mineralogie*, **58**, 6 (1935).

TABLE I

HYDROCHLORIC ACID

	With β Oxide (Product 1)		
Time of shaking	H^+ removed from solution in milli-equiv.	H^+ removed in %[a]	Fe^{+++} dissolved in milli-moles
10 minutes	0.10	4.8	0.005
2 hours	.15	7.2	.01
26 hours	.24	11.6	.0275
8 days	.28	13.2	.0665
44 days	.31	14.9	.146

	With α Oxide	
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %[b]
10 minutes	0.10	4.8
2 hours	.11	5.3
21 hours	.11	5.3
7 days	.11	5.3

[a] Solution 0.0209 N in HCl and 1 N in NaCl. [b] Solution 0.0209 N in HCl and 2 N in NaCl.

TABLE II

PERCHLORIC ACID[a]

	With β Oxide (Product 1)		
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %	Fe^{+++} dissolved in milli-moles
10 minutes	0.031	1.5	0.002
2 hours	.035	1.7	.004
25 hours	.035	1.7	.0125
35 days	.031	1.5	.0435

	With α Oxide	
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %
10 minutes	0.010	0.5
1 day	.010	.5
7 days	.010	.5

[a] Solution 0.0203 N in $HClO_4$ and 1 N in $NaClO_4$.

times with 95% alcohol and five times with ether. It was treated further as the β oxide. The final product was a very finely divided light yellow powder.

Procedure

0.4000 g. of the dry powder was shaken with 100 ml. of a solution that was approximately 0.02 N in acid (see tables), and 1 to 2 N in the sodium salt of the acid, for various periods of time. The large concentration of salt served two purposes. In the first place it prevented peptization of the adsorbent, and in the case of chloride, promoted the exchange of chloride ions from the solution with OH^- from the lattice. After the indicated time of shaking, the mixture was centrifuged, and the acid titrated, in 50 ml. of the clear supernatant liquid of filtrate, with 0.03 N sodium hydroxide, using methyl red as indicator and finishing the titration at boiling temperature. With longer times of shaking small amounts of iron oxide dissolved in the acid. This iron does not interfere in the titration, since at the end-point any dissolved iron salt has reacted quantitatively according to the equation: $FeCl_3 + 3NaOH \longrightarrow Fe(OH)_3 + 3NaCl$. In some cases the amount of dissolved iron was determined by collecting the precipitate at the end of the titration, dissolving it in hydrochloric acid, reducing the ferric iron with stannous chloride according to the standard procedure and finally titrating the ferrous iron with 0.02 N potassium dichromate with diphenyl benzidine sulfonate as indicator.

The results are given in the tables.

TABLE III

SULFURIC ACID[a]

	With β Oxide (Product 2)	
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %
10 minutes	0.0275	1.45
2 hours	.034	1.8
26 hours	.040	2.1
7 days	.040	2.1

	With α Oxide	
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %
10 minutes	0.038	2.0
2 hours	.072	3.8
25 hours	.091	4.8
7 days	.099	5.2

[a] Solution 0.0192 N in sulfuric acid and 0.95 N in Na_2SO_4.

TABLE IV

HYDROBROMIC ACID[a]

	With β Oxide (Product 2)	
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %
12 minutes	0.031	1.5
2 1/2 hours	.031	1.5
24 hours	.032	1.55
7 days	.032	1.55

	With α Oxide	
Time of shaking	H^+ removed in milli-equiv.	H^+ removed in %
12 minutes	0.054	2.6
2 1/2 hours	.054	2.6
24 hours	.054	2.6
7 days	.054	2.6

[a] Solution 0.0208 N in HBr and 1 N in NaBr.

Discussion

It is evident from the results that in all cases, except in the system β oxide–chloride, a final equilibrium state is reached after a relatively short time of shaking. This indicates that we are dealing with adsorption, and that adsorption equilibrium is attained quickly. The behavior of the β oxide–chloride system is in striking contrast with the others, and also with the α oxide–chloride system. Upon prolonged shaking, more and more acid is found to be removed from solution. Although in the initial stages of shaking undoubtedly a small percentage (about 2%) will be adsorbed, the continuous decrease of the hydrogen ion concentration must be attributed to an exchange between OH^- in the surface (and also in the interior of the product) and Cl^- from the solution

$$FeO(OH) + Cl^- \longrightarrow FeOCl + OH^-$$

In our experiments no final distribution equilibrium was to be expected, since during its preparation the β oxide had been subjected to a drastic perfection process. It may be safely predicted that under equilibrium conditions the ratio Cl : OH in the precipitate will increase with increasing chloride and hydrogen ion concentration in the solution.

$$\left(\frac{\mathrm{Cl}}{\mathrm{OH}}\right)_{\text{precipitate}} = K\left(\frac{\mathrm{Cl}^-}{\mathrm{OH}^-}\right)_{\text{solution}} = K'\{[\mathrm{Cl}^-][\mathrm{H}^+]\}_{\text{solution}}$$

The results show the care that must be exercised in the interpretation of "adsorption" experiments. In all cases mentioned above the "adsorption" of the hydrogen ions was measured, naturally an equivalent amount of anion also disappeared when the adsorbent did not contain adsorbed base.

$$\mathrm{FeO(OH)} + \mathrm{H}^+ + \mathrm{Cl}^- \longrightarrow \mathrm{FeO(OH)H}^+ \mid \mathrm{Cl}^-$$

A similar equivalent removal of hydrogen ions and anions is found when we are dealing with an exchange and subsequent neutralization of the hydroxyl ions sent into solution

$$\mathrm{FeO(OH)} + \mathrm{Cl}^- \longrightarrow \mathrm{FeOCl} + \mathrm{OH}^-$$
$$\mathrm{OH}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{H_2O}$$

The results obtained allow the following conclusions to be drawn: (1) FeOCl and β FeO(OH) (β $Fe_2O_3 \cdot 1H_2O$) are isomorphous, and may form mixed crystals over a wide range of Cl : OH ratios. (2) The β oxide is not iron oxide monohydrate, β $Fe_2O_3 \cdot 1H_2O$, but has the constitution FeO(OH). (3) The conclusion of Weiser and Milligan[6] that the yellowish precipitate obtained by slow hydrolysis of ferric chloride solutions contains more or less chloride adsorbed is not warranted. The precipitate is a mixed crystal of FeOCl and β FeOOH, the composition of which depends upon experimental conditions. Upon washing with ammonia more or less of the chloride in the precipitate is replaced by hydroxyl.

From Table IV it follows that on shaking of the β oxide with hydrobromic acid adsorption equilibrium is attained very quickly, but that no bromide ion enters the lattice of the oxide. Although the bromide ion has about the same size as the chloride ion it apparently does not fit in the lattice of β FeO(OH). This finding is in harmony with the fact discovered by Weiser and Milligan[5] that upon hydrolysis of ferric bromide not the β but the α oxide is formed. From the results in Tables I and III it is apparent that the β oxide dissolves faster in a solution that is 0.02 *N* in hydrochloric acid and 1 *N* in sodium chloride than in a solution containing corresponding amounts of perchloric acid and sodium perchlorate.

Summary

Upon prolonged shaking of so-called β ferric oxide monohydrate with dilute hydrochloric acid in a sodium chloride solution a continuous decrease of the acid concentration is found. The results indicate that the β oxide is not an oxide monohydrate but has the structure β FeO(OH) which is isomorphous with FeOCl and that these two form mixed crystals.

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The Configuration of the Azide Ion

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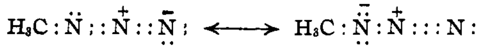
In 1925 it was shown that the azide ion in the azides of sodium and potassium is linear and possesses a center of symmetry.[2] The collinearity of the azide group in organic compounds, however, was not settled until the electron diffraction work on methyl azide[3] and the recent crystal structure determinations of cyanuric triazide[4,5] revealed definitely that the N_3 group is linear but not centro-symmetric like the N_3^- ion. The symmetry of the azide ion as ascertained from x-ray data was independently supported by Raman spectra of the azide ion in aqueous solution.[6]

This difference between the N_3 group and the N_3^- ion can be explained readily. In methyl azide, for example, the following two resonating



$$\mathrm{H_3C}:\ddot{\mathrm{N}}::\overset{+}{\mathrm{N}}::\underset{..}{\overset{-}{\mathrm{N}}}: \longleftrightarrow \mathrm{H_3C}:\underset{..}{\overset{-}{\ddot{\mathrm{N}}}}:\overset{+}{\mathrm{N}}:::\mathrm{N}:$$

structures were found to represent satisfactorily the configuration of the azide group.[3,4,5]

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[1] National Research Fellow.

[2] Sterling B. Hendricks and Linus Pauling, THIS JOURNAL, **47**, 2904 (1925).

[3] L. O. Brockway and Linus Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933).

[4] E. W. Hughes, *J. Chem. Phys.*, **3**, 1 (1935).

[5] I. E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935).

[6] A. Langseth, J. Rud Nielson and Utoff Sørensen, *Z. physik. Chem.*, **B27**, 100 (1934).