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METHOD OF OXIDIZING FERROUS SALTS INTO FERRIC SALTS IN THE PRESENCE OF A GAS CONTAINING FREE OXYGEN

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The present invention relates to a method of oxidizing ferrous salts into ferric salts in the presence of air, products obtained thereby and applications thereof.

It is a well-known fact that ferric salts form oxidizing agents which are of considerable interest for the solving of numerous problems, both of inorganic and of organic chemistry. They allow for instance transforming mercaptans into bisulfides, o-nitrobenzaldoxime into o-nitrobenzoic aldehyde, indoxyl into indigo, phenylhydrazoaldoximes into azo derivatives, hydrogen sulfide into sulfur and the like.

When used for such applications, the ferric salts are reduced into ferrous salts and it is obvious that the use of ferric salts as oxidizing reagents would be of a considerable interest if it were possible to regenerate the ferrous salts thus obtained into ferric salts. It is known furthermore that ferrous salts are transformed in the presence of air into ferric salts through an oxidizing reaction which may be written out for instance:

$$FeCl_2+HCl+\tfrac{1}{4}O_2=FeCl_3+\tfrac{1}{2}H_2O$$

It is one object of the present invention to provide a method which relates to the obtention of ferric salts the reduction of which leads to the formation of ferrous salts which are readily regenerated, so as to return into the state of ferric salts.

Our improved method resides in the following features:

If we add to a solution of ferrous salts certain organic amino-acids such as those which are obtained through the controlled hydrolysis of albuminoid substances and if air is caused to pass through the solution, there is obtained a sparingly soluble ferric salt which separates out of the liquid phase as it is being formed, which prevents the oxidation reaction from being limited by chemical equilibrium. The ferric salt separates out as a highly subdivided deposit and there is obtained finally a suspension which may serve as an oxidizing agent to the same extent and in the same manner as a solution of a ferric chloride, sulfate or the like salt.

In particular, if it is desired to treat such a suspension with sulfuretted hydrogen, the iron redissolves and forms a ferrous compound, while the sulfur is precipitated. The amino-acid is redissolved together with the iron. It may be assumed without this theory limiting by any means the scope of the present invention that the following reactions are obtained:

Oxidation: $FeX_2+HOOC.R.NH_2+\tfrac{1}{4}O_2$ (Amino-acid)

$=FeX_2OOC.R.NH_2+\tfrac{1}{2}H_2O$ (Insoluble complex salt)

(the atoms of iron and nitrogen in the complex salt being probably bound together through a covalence).

Reduction:

$$FeX_2.OOC.R.NH_2+\tfrac{1}{2}H_2S=FeX_2+HOOC.R.NH_2+\tfrac{1}{2}S$$

(X=Cl, $\tfrac{1}{2}SO_4$, etc.)

When applying this method, it is possible to resort to various amino-acids, those obtained through partial hydrolysis of albuminoid substances such as albumin, globulin, gelatine, keratin, etc. The hydrolysis may be

performed through the action of an acid, an alkaline substance or an enzyme on the albuminoid material. It is to be understood, however, that the reference to "amino-acids" means conventional amino-acids and not, for instance, hydroxy-amino acids.

In order that the oxidizing reaction of the ferrous salt may be obtained speedily, it is necessary to provide for an intimate contact between the solution of ferrous salt and oxygen. This may be obtained by introducing air through a porous plate or else by resorting to a column including a filling and in which the solution flows downwardly and the air upwardly, etc. Excellent results have been obtained particularly through the incorporation of air into a solution of a ferrous salt to obtain a fine-bubbled froth remaining stable for a time sufficient for the oxidation to be performed. It is possible, to this end, to introduce into the solution a reagent adapted to modify the surface pressure of the latter without reacting on the iron salts. But it is also possible to use an amino-acid constituted by a derivative having a large frothing power, for instance a substance obtained through alkaline hydrolysis of wool or comminuted horn material which allows resorting to the same reagent both for the insolubilization of the ferric ions and for the obtention of frothing properties in the solution.

EXAMPLE

A mixture is prepared which contains 10% by weight of ferrous sulfate and 5% by volume of a solution obtained through alkaline hydrolysis or hydrolysis with calcium hydroxide of comminuted horn material after which the solution is neutralized with sulfuric acid and filtered. The mixture comprising a solution containing 20% of dry material is caused to froth to an extent such that 100 cu. cm. supply 3 liters of froth. Said froth is kept at 40° C. during ten minutes, after which it is urged into a mechanical froth breaker to be destroyed therein.

We obtain thus a suspension of the ferric salt and analysis shows that 80% of the ferrous ions are transformed into ferric ions.

The suspension of a ferric compound thus obtained may serve for executing various organic or inorganic oxidations. If care is taken to select a stable amino-acid such as that obtained through hydrolysis of comminuted horn material, it may be regenerated indefinitely.

It is possible, in particular, to resort to such a suspension for the oxidation of sulfuretted hydrogen into sulfur and it should be remarked that it is not necessary in such a case to oxidize concentrated sulfuretted hydrogen.

It is also possible to treat through an excess amount of a suspension of a ferric salt industrial gases containing sulfuretted hydrogen and, in such a case, the gas is completely stripped of its sulfur and we obtain a suspension of sulfur in a solution of a ferrous salt and of an amino-acid. Said sulfur may be recovered through any known method such as filtration, centrifugation, extraction through a solvent, melting under pressure and the like, said means being applied separately or in combination. The ferric reagent is then regenerated through oxidation by air.

While we have disclosed several embodiments of the present invention, it is to be understood that these embodiments are given by example only and not in a limiting sense, the scope of the present invention being determined by the objects and the claims.

What we claim is:

1. A method of oxidizing inorganic ferrous salts into ferric salts comprising the steps of

adding to a solution of said ferrous salts an amino-acid containing a carboxylic group and an amino group connected with the same carbon atom,

subjecting said solution to a gas containing free oxygen, resulting in soluble ferrous salts and in insoluble ferric salts, thereby obtaining an aqueous suspension of insoluble ferric salts, to function as an oxidizing reagent.

2. The method, as set forth in claim 1, which includes as the step of subjecting said solution to a gas containing free oxygen, the steps of

forming a froth consisting of fine bubbles, the liquid phase of which consists of said aqueous solution of ferrous salts and said amino acid,

the gaseous phase of which consists of said oxygen containing gas, and

breaking said froth upon terminating the oxidation.

References Cited in the file of this patent

UNITED STATES PATENTS

1,888,186	Stoll et al.	Nov. 15, 1932
2,462,124	Neuberg et al.	Feb. 22, 1949
2,772,146	Pippig	Nov. 27, 1956
2,819,950	Patton	Jan. 14, 1958
2,831,885	Kroll et al.	Apr. 22, 1958
2,890,233	Opfermann	June 9, 1959

OTHER REFERENCES

King et al.: "The Fundamentals of College Chemistry," 2nd edition (1954), pages 222, 223 and 515.