COMPLEX TYPES INVOLVED IN THE CATALYTIC OXIDATION OF THIOL ACIDS

BY MAXWELL SCHUBERT

The study of the chemistry of the heavy metal complexes of thiol acids which in previous work[1] has been concerned with thioglycolic acid and cysteine and their compounds with cobalt has now been extended to include complexes of iron and of a thiol compound with no free carboxyl group, that is, thioglycolic ester. This extension makes possible a more detailed and clearer view on the probable mechanism of the catalytic oxidation of thiol acids to disulfide acids in the presence of iron salts by oxygen, noticed by Mathews and Walker and by Warburg and Sakuma.

The iron complexes are of particular interest as being the actual intermediate compounds involved in this catalytic process. The reaction is best shown by the addition of a trace of iron salt to a solution of thioglycolic acid or cysteine at a P_H of 8 to 9. A red color develops with the thioglycolic acid while a violet color appears in the case of cysteine. When the dissolved oxygen has been used up this color gradually fades. Simultaneously some of the thiol acid is transformed to disulfide, but as long as there remains any thiol acid the color may be regenerated by shaking the mixture with air. A time finally comes when this color can no longer be regenerated because the thiol acid has been completely oxidized to the disulfide.

There have been two attempts to work out the mechanism of this catalytic process in detailed steps, the first by Michaelis,[2] the second by Cannan and Richardson.[3] Both theories were based on measurements made on solutions of the complexes, of such physico-chemical properties as reduction potentials, reduction capacity and reaction kinetics. In each case the catalysis was imagined as occurring in three steps: first, a formation of a ferrous complex of the thiol acid; second, an oxidation of this complex by means of oxygen to a ferric complex, which is the cause of the red or violet color observed in the catalytic process; third, an autoreduction of this ferric complex in which the iron is reduced to a divalent condition while the thiol sulfur is oxidized to disulfide with simultaneous breaking up of the complex and fading of the color.

The theory that will be presented in the present paper is similar in outline but differs in the constitution of the complexes assumed as intermediate steps and attempts to present the whole picture in greater detail. The

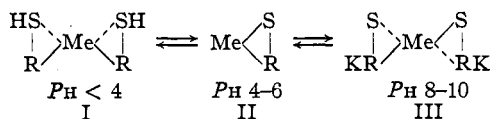[1] THIS JOURNAL, **52**, 4418 (1930); **53**, 3851 (1931).

[2] L. Michaelis, *J. Biol. Chem.*, **84**, 777 (1929).

[3] Cannan and Richardson, *Biochem. J.*, **23**, 1242 (1929).

evidence is based on the types of complex actually isolated in crystalline condition from solutions containing iron and thiol acid in which the catalysis could occur if exposed to the air and from similar solutions containing cobalt in place of iron in which no catalysis can occur.

The constitution and relations of the iron complexes can be brought out most clearly by a description of an actual experiment. If an air-free solution of ferrous iron and twice as many mols of thioglycolic acid be mixed in an atmosphere of hydrogen and air-free potassium hydroxide be added drop by drop, there soon develops a yellow color. On further slow addition a yellow crystalline precipitate appears. This has the composition $Fe(SCH_2COO)\cdot1.5H_2O$. As the potassium hydroxide addition is continued the yellow precipitate dissolves, giving a deep orange to orange-red solution. From this solution a crystalline product has been isolated having the composition $Fe(SCH_2COOK)_2$. The P_H at this stage is in the veronal range or about 9, as will be shown in the experimental section. Finally, if enough potassium hydroxide be added, ferrous hydroxide precipitates and the orange-red color disappears. The same sequence of changes occurs when thioglycolic acid is replaced by cysteine or when iron is replaced by cobalt, the colors being, of course, different. In all these changes the metal always remains divalent as air is rigorously excluded.

This series of changes can be formulated as follows. After enough alkali has been added to bring about ionization of the carboxyl group of the thiol acid and before the appearance of the first yellow color in the solution, it is probable that the normal, and to a certain extent complex, salt I is

$$
\begin{array}{ccc}
\underset{R}{\overset{HS}{>}}Me\underset{R}{\overset{SH}{<}} & \rightleftharpoons \quad Me\underset{R}{\overset{S}{<}} & \rightleftharpoons \quad \underset{KR}{\overset{S}{>}}Me\underset{RK}{\overset{S}{<}} \\
P_H < 4 & P_H\ 4\text{-}6 & P_H\ 8\text{-}10 \\
I & II & III
\end{array}
$$

formed. Further addition of alkali causes ionization of the thiol group to begin and this is facilitated by the tendency of the iron to combine with sulfur. The result is the precipitation of II in which the groups responsible for solubility are not free. That this compound should dissolve on further addition of alkali is very striking. The only way this can be made understandable is to take account of the further ionization of the thiol group and the preference of the iron to combine with sulfur rather than with oxygen. The deep orange-red solution which forms about P_H 9 then must contain the complex in the form III. I and III differ in the distribution of primary and secondary valence bonds and II is the transition state between them, separable because of its insolubility.

This is a point of considerable theoretical importance from the point of view of the structure of these complexes and a little further consideration will be required to see if it has any meaning at all because of the general opinion that in complex ions there is no distinction between primary and
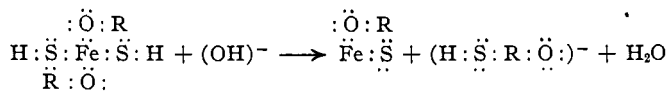
secondary valence links.   In the case of symmetrical complex ions such as ammonium or ferrocyanide, there seems to be no difference between primary and secondary bonds.   This probably means that the electron pair between the central atom and each coördinating group is held similarly and the electric charge of the ion is not localized at any particular hydrogen or cyanide group but is distributed over the ion as a whole.

On the octet scheme thioglycolic acid is written $H:S:\ddot{C}:C:\ddot{O}:H$, which

(with H above C and $H:\ddot{O}:$ below) for our purpose may be simplified to $H:\ddot{S}:R:\ddot{O}:H$.   The hydrogen of the carboxyl group ionizes more readily than that of the thiol group so that on dissolving iron in the thioglycolic acid the salt formed would have the structure $H:\ddot{S}:R:\ddot{O}:Fe:\ddot{O}:R:\ddot{S}:H$ or, since it is at least to a certain extent

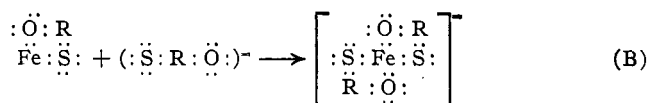complex, (A) $H:\ddot{S}:\ddot{Fe}:\ddot{S}:H$. (with $:\ddot{O}:R$ above and $R:\ddot{O}:$ below) This corresponds to the complex I, but the electronic formula A shows no difference between primary and secondary bonds.   In this condition the thiol group must be un-ionized; otherwise there is no reason why on making more alkaline the complex II should precipitate.   The formation of II is perfectly comprehensible, however, if in the first step of the ionization of A, a dibasic complex acid, the resulting more negative character of one of the sulfur atoms makes possible a closer linkage of the iron and this sulfur atom.   The preference of the iron for this closer link with the sulfur rather than its link with the oxygen is the cause of what has been called the shift of the main valence bond from oxygen to sulfur in the change of I to II.   This can be represented thus

$$H:\ddot{S}:\ddot{Fe}:\ddot{S}:H \text{ (with } :\ddot{O}:R \text{ above, } R:\ddot{O}: \text{ below)} + (OH)^- \longrightarrow \ddot{Fe}:\ddot{S} \text{ (with } :\ddot{O}:R \text{ above)} + (H:\ddot{S}:R:\ddot{O}:)^- + H_2O$$

Now on further making alkaline the reaction

$$(H:\ddot{S}:R:\ddot{O}:)^- + (OH)^- \longrightarrow (:\ddot{S}:R:\ddot{O}:)^- + H_2O$$
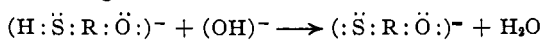
is favored and again the iron can exert its preference for the link with sulfur

$$\ddot{Fe}:\ddot{S}: \text{ (with } :\ddot{O}:R \text{ above)} + (:\ddot{S}:R:\ddot{O}:)^- \longrightarrow \left[:\ddot{S}:\ddot{Fe}:\ddot{S}: \text{ (with } :\ddot{O}:R \text{ above, } R:\ddot{O}: \text{ below)} \right]^- \qquad (B)$$

But although the electronic formula B looks like A after complete ionization, it must be understood that a great change has taken place in the way the electron pairs between the sulfur atoms and the iron are held. Physically this is reflected in the great development of color on changing from A to B which could not be explained merely as a result of ionization.

    This brings out a defect of both the valence method of representing the

structure of these complexes as exemplified in I, II and III, which emphasizes the difference in the kind of bond, and the electronic method shown in A and B in which there is no difference at all. Actually the difference might be represented roughly by showing the electron pair between iron and sulfur displaced at various distances between these elements as the electronegative character of sulfur changes by ionization. It would seem likely that as the sulfur becomes more negative the electron pair would be pulled further toward the iron. It is only in some such sense as this that the distinction between primary and secondary valence bonds is to be understood in this paper.

This apparent preference of iron to link as closely as possible with sulfur is hindered when the sulfur is already covalently linked with hydrogen, but here the hydrogen is easily removable by ionization. If instead of hydrogen a benzyl group be substituted which is not displaced as the hydrogen, then the formation of more deeply colored complexes is completely hindered. The only compound that could be isolated with the S-benzylcysteine is a pink salt of the composition $Co(OOCCHNH_2CH_2SCH_2C_6H_5)_2$. The formation of the yellow or green complexes like those represented by III does not occur at all.

But if the hydrogen of the carboxyl group be replaced by an alkyl group as in thioglycolic ester then the formation of the yellow and green complexes does occur and in these the main valence links must be between metal and sulfur as

$$C_2H_5R \overset{S}{\underset{}{\diagup}} \rangle Me \langle \overset{S}{\underset{}{\diagdown}} RC_2H_5$$

IV
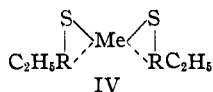
These complexes of both iron and cobalt have been isolated. This is the real reason why the complex A has been identified with I where the main valence link is with the carboxyl group as in the S-benzylcysteine compound with cobalt and B has been identified with III where the main valence link is with sulfur as in IV.

The conditions in solution under which complexes of type III are formed are the same as those in which iron acts as a catalyst for the oxidation of thiol acids in the presence of air. If solutions containing III be prepared under hydrogen with careful exclusion of all oxygen, they can be kept indefinitely. But as soon as they are exposed to the air the color changes, for example, in the case of iron and thioglycolic acid from a red-orange to a much more intense dark red and almost immediately ferric hydroxide begins to precipitate while the color gradually fades. It is at this point that, in attempting to follow the chemistry of these changes made so difficult by the lability of the oxidized iron complexes, the corresponding cobalt complexes are studied instead. Cobalt complexes of the structure II and III have been described previously. The cobalto bis cysteinate of

structure III is an intense blue-green.   On exposure to the air it is oxidized like the iron complex and turns to an olive-brown but this olive-brown cobalt complex, unlike the corresponding intensely red oxidized iron complex, is stable.

Let us now consider the structure of these oxidized cobalt complexes which from their close connection with the unstable iron complexes may be expected to give us some information on the structure of these catalytically important compounds.

Kendall and Holst[4] studied the oxidation of cobalto-bis-cysteinate to cobalti-bis-cysteinate and came to the conclusion that there is an intermediate formation of a cobalti-tris-cysteinate according to the scheme

$$3Co^{II}(Cy)_2 \longrightarrow 2Co^{III}(Cy)_3 + Co^{++} \longrightarrow 2Co^{III}(Cy)_2 + Cystine \qquad (1)$$
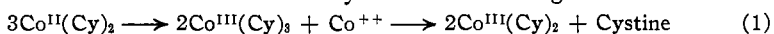
The maximum theoretical yield of cobalti-bis-cysteinate calculated on the basis of the cysteine hydrochloride used would then be 67% of the yield to be expected from a simple direct oxidation of the character

$$3Co^{II}(Cy)_2 \longrightarrow 3Co^{III}(Cy)_2 \qquad (2)$$
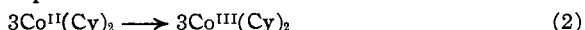
Since actual practical yields of 75 to 80% calculated on the basis of (2) have been obtained with both cysteine and thioglycolic acid, the more complicated reaction (1) is not only unnecessary but impossible.

The oxidation of the cobalto-bis-cysteinate according to (2) can be imagined in three ways, giving rise to VA, VB and VC.   Now on changing acidity the complex nucleus of VA being a monovalent anion can give rise to only a single potassium salt besides the corresponding free acid; that of VB being a divalent acid ion can form only two potassium salts, the free acid and a hydrochloride of the coördinated hydroxo group, while VC having a tetrabasic acid ion could give rise to at least three different potassium salts as well as the free acid and no chloride is possible.
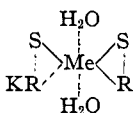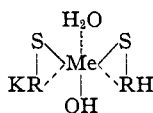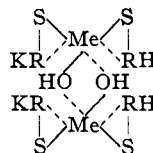
VA   VB   VC

Working with both cysteine and thioglycolic acid, three salts have been obtained, a primary, a secondary and a quaternary, as well as the free acid. Although this complete series has not been prepared for either the cysteine or thioglycolic acid complexes, this is only a question of difficulty of obtaining them in crystalline form as their behavior on changing P_H is identical, this identity of the complex nucleus being further borne out by the close similarity of their absorption spectra.   The impossibility of obtaining a chloride even in strongly acid solutions of the cobalti-
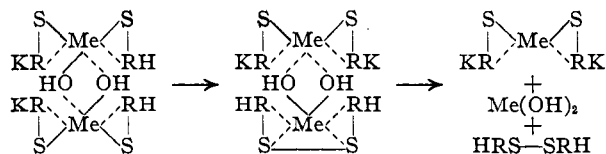
4 Kendall and Holst, *J. Biol. Chem.*, **91**, 435 (1931).

bis-thioglycolate contributes to discredit VB. The existence of a hydrochloride of the corresponding cysteine complex has been previously shown to be due to the amino groups present.

This chemical evidence then definitely favors the formula VC to represent the structure of the cobalti-bis-thiol acid complexes. The free acid behaves as a fairly strong acid, not being precipitable by acetic acid but requiring hydrochloric acid. On the other hand, the secondary potassium salt is the form isolated at PH 9 to 10. This would mean that the pKa values of the last two of the acid hydrogen atoms must be quite high. In a dilute aqueous solution any one of these forms of VC would be expected to be in equilibrium with several of the others. This might account for the impossibility experienced previously of determining the molecular weight of VC by cryoscopic methods.

As a result of this work the most probable course of the catalytic process seems to be first the formation of the ferrous complex III. This is oxidized by oxygen, giving the ferric complex VC as the second step. The third step consists in a reduction of this ferric complex with a splitting off of the oxidized disulfide acid. This might be due to the generally less stable nature of ferric complexes and the tendency of these to pass into ferrous complexes. A theoretical reason for the greater stability of the ferrous complexes is suggested by Sidgwick's[5] considerations on the electron configurations of metal atoms in complexes. This theory also accounts for the great stability of cobaltic complexes. The theory is, however, open to so many objections and exceptions that although it fits the present case quite well, it cannot be taken too seriously and is mentioned merely as the only available suggestion as to why the ferric complexes undergo the third step completing the catalytic process while the cobaltic complexes stop at the second step and consequently cannot form part of a catalytic cycle.

Only one possible way of representing this third step need be mentioned.

$$
\begin{array}{ccc}
\text{S} \diagdown \text{Me} \diagup \text{S} & \text{S} \diagdown \text{Me} \diagup \text{S} & \text{S} \diagdown \text{Me} \diagup \text{S} \\
\text{KR} \diagup \quad \diagdown \text{RH} & \text{KR} \diagup \quad \diagdown \text{RK} & \text{KR} \diagup \quad \diagdown \text{RK} \\
\text{HO} \quad \text{OH} & \text{HO} \quad \text{OH} & + \\
\text{KR} \diagdown \quad \diagup \text{RH} & \text{HR} \diagdown \quad \diagup \text{RH} & \text{Me(OH)}_2 \\
\text{S} \diagup \text{Me} \diagdown \text{S} & \text{S} \diagup \text{Me} \diagdown \text{S} & + \\
& & \text{HRS—SRH}
\end{array}
$$

One of the iron atoms pulls in an electron from each of the sulfur atoms with which it is combined and passes one on to the other iron atom giving, after breaking up the naturally unstable intermediate, a molecule of ferrous bis-thiol acid, one of disulfide acid and one of ferrous hydroxide, which combines with thiol acid again, completing the catalytic cycle.

For the preparation of any of the iron complexes it is necessary to carry out the whole procedure in the absence of air. This is accomplished by use of the apparatus,

⁵ Sidgwick, *J. Chem. Soc.*, **123**, 725 (1923); also Mann, *ibid.*, 651 (1929).

a diagram of which has already been published,[6] and to which reference will be made in what follows. The test-tube A is omitted; in B is placed either a freshly prepared solution of ferrous chloride or better still a pure grade of iron powder with hydrochloric acid; the flask C contains the cysteine or thioglycolic acid solution and the flask I contains the alkali necessary, which can be added drop by drop. Otherwise the manipulation is as previously described and need not be repeated here.

The complexes of type II are prepared as follows. After complete removal of air the ferrous chloride solution in B, containing about 20 to 25 millimoles of iron, is tipped into C containing from 25 to 50 millimoles of thiol acid. Potassium hydroxide solution is forced back into C from I drop by drop until a permanent light yellow color develops. In the case of thioglycolic acid precipitation of the complex is almost immediate and alkali may be added, while shaking the whole, until this reaches a maximum, but in the case of cysteine the precipitation is slower and it is best to proceed more cautiously. In either case the precipitated compound is light yellow and by warming slightly with a beaker of hot water crystallization is rapid. Filtration and washing are as previously described. The P_H at which this precipitation occurs is probably about 5 as filtrates tested were acid to litmus and alkaline to congo red. After drying over sulfuric acid at less than 1 mm. pressure, these analytical results were obtained.

Anal. Calcd. for $Fe(OOCCHS)\cdot1.5H_2O$. Fe, 32.35; S, 18.50. Found for different preparations: Fe, 32.89, 32.98; S, 18.81, 19.10. Calcd. for $Fe(OOCCHNH_2CHS)\cdot$-$1.5H_2O$: Fe, 27.70; N, 6.93; S, 15.84. Found: Fe, 27.89; N, 6.44; S, 16.42.

These complexes after drying are perfectly stable in air. They undergo no apparent change when suspended in water, in which they are quite insoluble. Addition of dilute alkali causes no change but if a little thio acid be added simultaneously in the absence of air, then the deep red color of the complexes III is produced.

The complexes of type III at first seemed much more difficult to prepare. This is due to the great solubility of these complexes, together with their great sensitiveness to oxidation by oxygen so that rigid exclusion of air is essential until the crystalline product is separated from solution and washed.

The potassium salt of this complex has been prepared by a long complicated process involving a preparation of ferrous hydroxide, a thorough washing of this material followed by addition of thioglycolic acid and potassium hydroxide and evaporation of the resulting solution to small volume, an addition of air-free alcohol and a cooling on ice for some twelve hours. The resulting yellow rectangular platelets are filtered and washed with alcohol. This entire set of operations is carried out in closed vessels through which a continuous stream of purified hydrogen is passed. After drying *in vacuo* over sulfuric acid the analysis agreed reasonably, considering the impossibility of any purification procedures, with $Fe(SCH_2COOK)_2\cdot2H_2O$.

Anal. Calcd.: Fe, 16.87; S, 19.27; K, 23.50. Found, for independent preparations: Fe, 19.42, 16.25; S, 19.26, 20.00; K, 25.14, 25.87.

The sodium salt of this complex can be prepared more easily. In the test-tube B of the special flask set-up are placed 5.5 g. of $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 15 cc. of water and in the main flask 3 cc. of thioglycolic acid and 5 cc. of water. After complete removal of air sodium hydroxide is slowly added from the flask I. At first the yellow precipitate of the complex II appears but this soon redissolves, giving the usual deep red solution from which, after adding 9 to 10 cc. of 7.3 *M* sodium hydroxide, there slowly crystallizes a yellow substance. It is best to shake steadily while this is in progress as the crystals tend to stick to the sides of the flask. This product is filtered, washed with air-free water and alcohol as usual. Dried *in vacuo* its analysis corresponds with $Fe(SCH_2COONa)_2\cdot2H_2O$. The results of two preparations are given.

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[6] THIS JOURNAL, **53**, 3858 (1931).

Anal. Calcd.: Fe, 17.60; S, 20.11; Na, 14.46. Found: Fe, 18.46, 17.26; S, 20.45, 20.20; Na, 15.26, 15.86.

Freshly prepared and before exposure to the air the crystals are yellow and dissolve readily in air-free water, giving a raspberry-red solution which on exposure to air turns to a much deeper red. The dry crystals themselves on exposure to air turn from yellow to yellow-green and finally to an orange-red. Using a Warburg micro-respiration apparatus, they were found to absorb oxygen slowly from the air. That this is not merely a case of adsorption of gas due to drying the crystals at less than 1 mm. pressure is shown by the fact that in an atmosphere of hydrogen no gas is taken up at all. In a number of experiments, making the transfer from the desiccator to the Warburg vessel as quickly as possible, which with weighing and allowing the vessel to come to temperature equilibrium in the bath occupied ten to fifteen minutes, 20 to 25 millimoles of the complex absorbed 5 to 10 millimoles of oxygen in three to four hours. About the same oxygen consumption was measured by dissolving the crystals in borate buffer. In either case an orange-red crystalline product was obtained. This product is insoluble in water, borate buffer and dilute acetic acid and when washed and dried shows an iron content of 53.0%, which with the absence of other elements makes it appear as ferric hydroxide. If dissolved in dilute hydrochloric acid and reprecipitated with alkali, the usual form of ferric hydroxide appears.

The cobalt salt of S-benzylcysteine is easily prepared by dissolving 4 g. of benzyl-cysteine made as described by Suter[7] in 200 cc. of hot water containing 15 g. of secondary sodium phosphate and slowly adding a mixture of 4 cc. of 1 M $CoCl_2$ and 25 cc. of saturated Na_2HPO_4, digesting the mixture for an hour at boiling temperature until no more cobaltous phosphate remains, filtering and washing with boiling water; 2 g. of pink crystals consisting of flat plates is obtained.

Anal. Calcd. for $Co(OOCCHNH_2CH_2SCH_2C_6H_5)_2 \cdot H_2O$: Co, 11.87; S, 12.87; N, 5.63. Found: Co, 11.69; S, 13.67; N, 5.50.

The ferrous complexes of the ethyl ester of thioglycolic acid were prepared in a manner similar to that described for complexes of type VI. For example, 7 g. of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and 25 cc. of water are placed in test-tube B, 3.7 cc. of thio-glycolic ester in flask C and after deaeration the iron is tipped into the flask C. From I 3.5 M potassium hydroxide is added dropwise. On the first addition of alkali a yellow precipitate forms which rapidly crystallizes but there are dark red or brown spots present which disappear for the most part on warming the mixture with a beaker of water. The yellow crystals are filtered, washed and transferred to a desiccator. It is much more difficult to get reasonable analytical data on this complex because as soon as the desiccator is opened there appears to be a rapid combination with oxygen and the dry crystalline product gets quite hot, fumes are given off and in some cases the substance even glows. This action lasts only a minute or two, after which there appears to be no further change. Analytical data on the three best preparations are as follows.

Anal. Calcd. for $Fe(SCH_2COOC_2H_5)_2$: Fe, 19.05; S, 21.77. Found: Fe, 18.74, 19.58; S, 22.07, 20.60. Calcd. for $Fe(SCH_2COOC_2H_5) \cdot 2H_2O$: Fe, 16.97; S, 19.39. Found: Fe, 17.19; S, 19.57.

The same procedure was followed to prepare the corresponding cobalt complex, which separates as thin leaflets of a gold-green color with a metallic sheen. This compound after washing and drying appears to be stable in air.

Anal. Calcd. for $[Co(SCH_2COOC_2H_5)_2]_2HSCH_2COOC_2H_5$: Co, 16.52; S, 22.39. Found: Co, 16.86, 17.45: S, 23.01, 23.03.

7 Suter, *Z. physiol. Chem.*, **20**, 562 (1895).

This complex dissolves in chloroform to give a deep red solution. If this complex is refluxed with chloroform for a while, filtered and treated with an equal volume of alcohol, a gelatinous precipitate is formed which may be redissolved on gentle warming. On slow cooling a granular deposit of very tiny black crystals forms. The same substance is also formed by mixing a solution of 2.5 cc. of thioglycolic ester in 10 cc. of alcohol with one of 2.5 g. of $CoCl_2.6H_2O$ in 30 cc. of alcohol and bubbling air through the mixture for an hour. After standing for a day a fine granular deposit settles out which is washed most conveniently with alcohol by centrifuging, yielding 1 g. of product after drying. Either method of preparation gives the compound $Co(SCH_2COOC_2H_5)_3$.

Anal. Calcd.: Co, 14.18; S, 23.08. Found: Co, 14.60, 13.90; S, 23.27, 22.99.

Cobalt complexes with nuclei of type VC have already been described, the only one which is new being a tetrapotassium salt of the cysteine complex. The simplest method of preparation is to start with the corresponding free acid, 5 g. of which is dissolved in 15 cc. of 3.7 M potassium hydroxide; then 25 cc. more of this potassium hydroxide solution is added, followed by 50 cc. of alcohol, stirring vigorously during this addition. After standing for an hour the mixture becomes almost solid with masses of very fine hair-like crystals which are filtered off and washed with a little cold water and then with alcohol.

Anal. Calcd. for $[Co(SCH_2CHNH_2COOK)_2OH]_2$: Co, 15.05; S, 16.34; K, 19.89. Found: Co, 14.97; S, 16.47; K, 20.11.

Attempts to prepare the corresponding salt of the thioglycolate complexes resulted only in the separation of uncrystallizable liquids. The barium salts prepared at these high alkalinities were different from those made at a P_H range of 8 to 10 but likewise resisted attempts to crystallize and so were unsuitable for analysis.

Thanks are due to Mr. Bitterlich of this Laboratory for all analytical work done in connection with this paper.

Summary

By working in the absence of oxygen a number of complexes of divalent iron with cysteine, thioglycolic acid and ethyl thioglycolate have been prepared and their structures discussed in some detail. The role of these complexes in the catalytic oxidation of thiol acids in the presence of iron salts is pointed out and on this basis as well as that of some previous work a theory of the mechanism of this catalysis is presented.

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