Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. I. Preparation of Cobalt Soap by Metathesis

By Hirotaro KAMBE*

(Received February 24, 1961)

Heavy metal salts of higher fatty acids, usually called heavy metal soaps, can be made by a substitution reaction between fatty acid and the salt of weak inorganic acid such as acetate. In place of inorganic salts, oxide or hydroxide may be used. These reactions can be accelerated by fusing the reactants. This is the principle of the fusion method, which is commonly used as a means of preparation of heavy metal soaps.

Cobalt soap may be prepared by the fusion method. The melting of fatty acid with cobalt(II) acetate or cobalt(II) hydroxide is followed by the reactions:

$$Co(CH_3COO)_2+2RCOOH$$
$$=Co(RCOO)_2+2CH_3COOH$$

or $Co(OH)_2+2RCOOH=Co(RCOO)_2+2H_2O$

The cobalt soap made by the fusion method is not crystalline powder, but a glassy mass. Molten cobalt soap is easily oxidized and often becomes dark on prolonged heating in air. For these reasons we have concluded that the fusion method is not suited for preparing pure cobalt soap.

With water soluble salts of weak acid, fatty acid may react in solution. Kaufman and Lüssling¹⁾ reported that when they shook a solution of fatty acid in petroleum ether with an aqueous solution of cobalt(II) acetate, the upper petroleum ether layer became blue as the formed cobalt soap dissolved into petroleum ether. They obtained cobalt oleate by this method. But our preliminary experiment has shown that it is difficult to prepare cobalt stearate with this technique, for the stearate is less soluble in petroleum ether than the oleate. When we use ethyl alcohol instead of petroleum ether as the solvent, the reaction advances very smoothly in a homogeneous solution and crystalline cobalt stearate powder can be prepared. This may be another means of preparing cobalt soap, as is shown later.

Water soluble inorganic salts, either of weak acid or of strong acid, react instantaneously with alkaline soap. This type of reaction is called double decomposition or metathesis. Metathesis is most important in preparing metal soaps, and it is the basis of the so-called precipitation method. The soaps made by metathesis are generally crystalline powder.

In the case of cobalt soap, cobalt(II) chloride, nitrate, sulfate, and acetate may be used as inorganic salts in metathesis. Reactions between these and sodium or potassium soap would proceed readily in solution to form cobalt soaps. For example,

$$CoCl_2+2RCOONa=Co(RCOO)_2+2NaCl$$

Kahlenberg²⁾ has shown very long ago that metathetic formation of heavy metal soaps

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* Present address: Aeronautical Research Institute, the University of Tokyo, Meguro-ku, Tokyo.

1) H. P. Kaufmann and Th. Lüssling, *Fette und Seifen*, 55, 90 (1953).

2) L. Kahlenberg, *J. Phys. Chem.*, 6, 6 (1902).

could be carried out also in organic solvents. Koenig[3] prepared many metal soaps, including cobalt soap, by metathesis in warm water. The soap thus formed was dried in an air oven at 115~120°C for 10~12 hr., and the glassy solid obtained was then pulverized. Koenig observed a color change from pink to blue when cobalt soap was heated.

In Koenig's method an aqueous solution of sodium soap is used, and at the lower concentrations, alkaline soap may be hydrolyzed to free acid, which will contaminate the soap being formed. Whitmore and Lauro[4] proposed a method for preventing the hydrolysis of alkaline soap by the addition of ethanol to the solution.

Although Whitmore and Lauro did not prepare cobalt soap in this way, we have examined this method in detail and found that besides common pink hydrous cobalt soap, blue anhydrous and red hydrous soaps may be formed according to conditions. In this part of the study, metathetic preparation of cobalt soap was investigated, and particularly the effects of several factors on the color of the soap being formed were discussed.

Experimental

Materials.—*Fatty Acids.*—Stearic, palmitic, myristic, and lauric acid were fractionally distilled products, made by Nihon Yushi Co., and were recrystallized from absolute ethanol.

Solvents.—Ethanol and methanol were dehydrated and distilled over anhydrous calcium oxide. Acetone was dehydrated by potassium carbonate anhydrate.

Cobalt(II) Salts.—Cobalt chloride, $CoCl_2 \cdot 6H_2O$, nitrate, $Co(NO_3)_2 \cdot 6H_2O$, sulfate, $CoSO_4 \cdot 7H_2O$, and acetate, $Co(CH_3COO)_2 \cdot 4H_2O$ were chemically pure reagents and were recrystallized from water. These salts, except sulfate, are very deliquescent, and they were used with some water.

Metathesis.—The following standard procedure was adopted to control experimental factors.

(i) Fatty acid, mostly stearic acid, was dissolved in absolute ethanol by warming in a constant temperature water-bath at 60°C, and neutralized exactly by an alkaline solution, with phenolphthalein as indicator. The alkaline solution used was usually 0.15 N potassium hydroxide solution in water or in ethanol. If necessary, some amount of either solvent was added to the alkaline soap solution to control the ratio of the volume of solvent (ethanol in this case) to that of water in the system; this is called the solvent ratio hereafter. When this ratio is comparatively low, the alkaline soap solution becomes turbid by hydrolysis of the soap. In such cases the reaction products tend to contain free fatty acid, which may be extracted, however, by acetone, as is shown below.

(ii) An excess of cobalt salt, mostly cobalt chloride, was dissolved in the same water-bath in water, or, if necessary, in pure or aqueous ethanol. The solution of cobalt chloride in water is considerably acidic, and also the solution after metathesis becomes slightly acidic. It is natural for the soap made in this way to contain some free fatty acid. When cobalt acetate is used instead of chloride, the solution is not so acidic that free acid is not included in the soap, as was pointed out by Whitmore and Lauro[4].

(iii) After both solutions were warmed to 60°C, a cobalt salt solution was stirred into the alkaline soap solution little by little. As cobalt soap is almost insoluble in the solution, it precipitated immediately. The reaction must be carried out always below 60°C, because above this temperature the reaction products become somewhat bluish.

The color of soap in the solution was observed directly after the reaction and also after having been left in the solution for some time with or without stirring. The alkaline soap solution, which had at first shown a pink color due to phenolphthalein, became blue after the addition of a little of the cobalt salt solution because cobalt ion shows a blue color in ethanol. When the whole salt solution was added, the color of the solution faded generally, and pink soap precipitated.

(iv) The precipitates were filtered off by suction, washed by absolute ethanol to remove free fatty acid, and dried overnight in a vacuum desiccator over calcium chloride anhydrate at room temperature. The color of the soap was preserved during drying in this way. The dried soaps were pulverized by an agate mortar. Free fatty acid was extracted with acetone over anhydrous potassium carbonate in a Soxhlet extractor.

Results and Discussion

As a preliminary experiment, the colors of cobalt soaps formed at various solvent ratios, based on volume, were observed in the solution without stirring.

In pure ethanol, the yield of cobalt soap was very little. As metathesis is an ionic reaction, it is natural that the reaction is suppressed in a solvent, in which degrees of ionization of reactants are low. A solution of cobalt chloride in pure ethanol is blue, and metathesis in this solvent proceeded in a blue solution. But the reaction product was not pure blue; it seemed dark blue at first, and became pale violet after being left in the solution.

In pure water, the product was pink, but when dried, it gained a tinge of blue. If the solvent ratio was lower than 1 : 1, the color of the formed soap was pink as in pure water. When the ratio exceeded 1 : 1, although the formed soap was also pink at the beginning, often small blue particles grew overnight within pink precipitates. Sometimes the whole soap turned blue in a short time, less than an

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[3] A. E. Koenig, *J. Am. Chem. Soc.*, **36**, 951 (1914).

[4] W. F. Whitmore and M. Lauro, *Ind. Eng. Chem.*, **22**, 646 (1930).

hour. These color changes were most rapid at a solvent ratio somewhat higher than 1 : 1.

Effect of Stirring.—As stated above, sometimes blue soap grew in addition to pink soap in the solution when it was left without stirring. First, we examined the effect of stirring on this color change.

In a standard procedure with the solvent ratio 5 : 1, pink soap turned blue without stirring, even if very slowly, but the color changed in 1 hr. with stirring. If some blue soap powder, prepared previously, was added to the solution, the color change was completed in 15 min.

When the solution was kept at 60°C after reaction, the color did not change even after 1 hr., but if it was taken out from the waterbath and cooled by stirring, the color began to change immediately and turned perfectly blue in 25 min.

From these facts, it is concluded that the blue soap has grown from pink soap. The addition of some blue soap advances the color change remarkably, for added soap powder forms nuclei for color change. At 60°C spontaneous occurrences of nuclei are suppressed, and the color change is not observed. Below 60°C nuclei of blue soap would appear, but they grow so slowly without stirring, that the color change proceeds locally and heterogeneously, and as a result small blue particles appear within pink precipitates. Therefore, to change color completely, cooling the solution by stirring is absolutely necessary.

The bubbling of air into the solution did not alter the speed of color change. Closing the vessel and stirring by a magnetic stirrer also did not influence the effect. It is evident that oxidation is not a cause of color change.

Effect of Solvent Ratio.—Next we examined again the effect of the solvent ratio on the color change, but with stirring.

Stearic acid (2 g.) was dissolved in ethanol and/or water (250 ml.) and neutralized by 0.15 N potassium hydroxide in ethanol or water (about 50 ml.). The solution was mixed at 60°C with cobalt chloride in ethanol and/or water (50 ml.), with various solvent ratios, and cooled by stirring. The time needed to turn blue was observed. The results are shown in Table I.

In series I, with larger solvent ratios, the colors of the products seemed violet or pale blue from an early stage. They did not readily turn blue and contained some white powder of potassium soap. Below the ratio 6 : 1, pink soap was formed at the beginning and changed blue soon, as stated before.

In series II, which contained more water than series I, the speed of the color change became larger with the lower solvent ratio. Sometimes blue soap turned violet soon and became red overnight. The red cobalt stearates formed in these systems are completely different in appearance from pink soaps formed directly after the reaction. When dried, they can be pulverized very easily, in contrast to plastic pink soaps.

TABLE I. EFFECT OF THE SOLVENT RATIO ON THE COLOR OF COBALT SOAPS

System	No.	Solvent ratio based on volume	Color of product
Series I	1	(pure ethanol)	Bluish precipit. in blue soln., mixed with white K soap.
	2	30 : 1	Pale violet, turned blue in 2.5 hr., mixed with K soap.
	3	15 : 1	Violet, turned blue in 60 min., mixed with K soap.
	4	9 : 1	Reddish, turned blue in 60 min.
	5	6 : 1	Pink, turned blue in 60 min.
Series II	6	5 : 1	Pink, turned blue in 30 min.
	7	4 : 1	Pink, turned blue in 15 min., violet in 60 min., red overnight.
	8	3.3 : 1	Pink, turned blue in 15 min., violet in 40 min., red overnight.
	9	2.8 : 1	Pink, turned blue in 30 min.
	10	2.3 : 1	Pink, turned blue in 25 min.
Series III	11	2 : 1	Pink, turned blue in 10 min., red overnight.
	12	1.5 : 1	Pink, turned blue in 5 min., red overnight.
	13	1.3 : 1	Pink, turned blue in 10 min., red overnight.
Series IV	14	1 : 1	Pink, turned red overnight.
	15	1 : 1.5	Pink, turned red overnight.
	16	1 : 2	Pink, turned red overnight.
	17	1 : 3	Red, without change.
	18	1 : 5	Red, without change.

In series III, with the greater water content, the speed of the color change became very rapid, and at the solvent ratio of about 1.5 : 1, it was at a maximum. The products turned completely red overnight.

The last series, where the solvent ratio is lower than 1 : 1, was very different from the preceding series. In this series soaps did not change blue, however long stirred, but became red gradually. The systems which contained the most little amount of ethanol were red rather than pink from the outset. It was hard to dry them in vacuum, for they contained a large amount of water.

Together with the other results obtained, the following facts were confirmed:

(i) The color of the product is determined by the solvent ratio after mixing. The addition of either solvent to the solution after reaction did not affect the color.

(ii) If the resultant solvent ratio is the same, the compositions of the reactant solutions are indifferent to the color of the product.

(iii) The extent of excess of cobalt chloride over stearic acid and the order of mixing solutions did not significantly affect the color of the soap formed.

(iv) The speed of the color change from blue to red depends on the solvent ratio and the time of stirring. Blue soap always turned red if it was left in solution for long a time.

Effect of Degree of Neutralization.—In these experiments, the solution of stearic acid was exactly neutralized by an alkaline solution. Next we examined the effect of the degree of neutralization on the color change of cobalt soap.

At the solvent ratio 1 : 2, when exactly neutralized, the cobalt soap did not change blue, though it later became red. If the amount of added alkaline solution was varied between 60 and 140% of the equivalent, different effects were observed. When the system was insufficiently neutralized, the products became red sooner and contained much free fatty acid. When the added alkali was more deficient, the color change became slower. However, when an excess of alkali was added to the system, the product became violet. When there is a large excess of alkali, the reaction would not readily proceed because, as will be discussed in the next part, the cobalt soap may be decomposed to free acid by the presence of much alkali.

At the solvent ratio 2 : 1, when exactly neutralized, the formed pink soap soon became blue with stirring and later turned red in the solution. But when alkali was added in excess, a color change from pink to blue was not observed and the soap turned red at last. On the contrary, when alkali was insufficient, the speed of becoming blue was more rapid. When the degree of neutralization was lower, the color change became quicker, although the yield was smaller.

As well as adding insufficient alkali to the fatty acid solution, the addition of hydrochloric acid to the cobalt chloride solution had the same effect on color change. But after the forming of the pink soap, the addition of hydrochloric acid was not effective.

From these results it is concluded that the solution must be acidic at mixing for realizing the color change.

Effect of Using Other Solvents than Ethanol.—Throughout the preceding experiments, the solvent was a mixture of ethanol and water. Next we used acetone and methanol in place of ethanol. Any solvent which dissolves fatty acid may be used, but when the solvent does not mix with water, as the petroleum ether used by Kaufmann and Lüssling(1), the procedure becomes somewhat difficult. With methanol or acetone, metathesis could be carried out as with ethanol. In particular, when the solvent ratio was lower than 1 : 1, only pink soaps were formed. With these solvents, even if the solvent ratio was higher than 1 : 1, the blue soap could not be obtained. But when acetone was used, the formed soap became red quickly.

Effect of Using Other Cobalt Salts than Chloride.—Instead of cobalt chloride we tried to use other cobalt salts. Cobalt nitrate and sulfate may be used in the same way as chloride. But cobalt acetate showed somewhat different effects.

Cobalt acetate may react directly with stearic acid in aqueous ethanol. In this substitution reaction, when the solvent ratio is 2 : 1, the color changed blue and subsequently turned red. But at the ratio 1 : 2, the color did not change at all.

The color change was suppressed markedly by the addition of alkali. If the fatty acid was exactly neutralized, that is, in metathesis, the formed pink soap did not change blue in any solvent ratio.

At the solvent ratio 2 : 1, pink soap made by metathesis turned blue in 60 min. with cobalt chloride, in 30 min. with cobalt nitrate, in 20 min. with cobalt sulfate, and never with cobalt acetate.

In a substitution reaction with cobalt acetate, the addition of alkali suppressed markedly the color change to blue. The substitution reaction could be carried out between cobalt acetate and stearic acid with acetone in place of ethanol.

However, when acetone was used, with the solvent ratio 2 : 1, pink soap turned blue, even if very slowly, but perfectly blue soap was not obtained.

Effect of Using Other Fatty Acids than Stearic Acid.—Other cobalt soaps may be prepared by metathesis in the same way as stearate. In place of stearic acid, palmitic, myristic, and lauric acid were used.

These reactions proceeded just the same way as with stearate. The color changes were also observed, but the speed of color change from pink to blue becomes slower, as the chain length of fatty acid decreases. The laurate could not turn blue under the same conditions.

The time for turning blue with the solvent ratio is tabulated in Table II. These reactions were obtained by stirring the solutions at 45°C for 1 hr. and later leaving them in the solution without stirring. The solutions were slightly acidic.

TABLE II. TIME FOR TURNING BLUE OF PINK COBALT SOAPS

Solvent ratio	4 : 1	1.5 : 1	1 : 1.5	1 : 4
Cobalt stearate	15 min.	10 min.	—	—
Cobalt palmitate	2 days	1∼2 hr.	—	—
Cobalt myristate	4∼5 days	1 day	—	—
Cobalt laurate	—	—	—	—

— Did not become blue.

Summary

As a method of preparation of cobalt soap, metathesis between alkaline soap and cobalt salt was investigated.

Cobalt stearate, palmitate and myristate were obtained in pink, blue and red forms according to conditions. Cobalt laurate in blue form was not observed.

Metathetic products were always pink at the beginning. If the system has a solvent ratio (solvent to water) higher than 1 : 1, and the solution after mixing is acidic, the color of soap will turn blue with stirring. It will change red later when left in the solution. The blue form could not be obtained with acetone or methanol as a solvent.

The speed of the color change became considerably slower with fatty acid of a shorter chain length.

In substitution reaction between stearic acid and cobalt acetate with a solvent ratio higher than 1 : 1, the same color changes were observed. But in this system the addition of some alkali suppressed markedly the color change, and at an exactly neutralized metathetic reaction the soap did not turn blue. Even in this case, when acetone was used instead of ethanol, the color change was observed, but the speed was very slow.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi for his advice throughout this work and to Messrs. Itaru Mita, Hirokazu Watanabe and Hiroshi Kayano for their assistance in experiments.

Institute for Science and Technology
The University of Tokyo
Meguro-ku, Tokyo