Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. II. Compositions of Cobalt Soaps

By Hirotaro KAMBE*

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Cobalt soap is generally a neutral salt between a bivalent cobalt cation and two univalent fatty acid anions. For example, the composition of cobalt stearate is ideally expressed by $Co(C_{17}H_{35}COO)_2$.

Oudemans(1) and Caspari(2) have pointed out that cobalt laurate is monohydrate. Kaufmann and Lüssling(3) found that while, under some conditions, cobalt oleate was obtained as an acidic salt, $Co(C_{17}H_{35}COO)_2\cdot(C_{17}H_{35}COO)_2$, cobalt stearate was a neutral salt.

In the previous part of these studies(4), it was found that cobalt soaps obtained by metathesis in aqueous ethanol showed three different colors, that is, pink, blue and red.

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

1) A. C. Oudemans, *J. prakt. Chem.*, [1], **89**, 206 (1863).

2) C. E. Caspari, *Am. Chem. J.*, **27**, 310 (1902).

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

4) H. Kambe, This Bulletin, **34**, 1786 (1961).

In the present part they will be analyzed. As a result, it will be ascertained that different colors are principally due to the difference of hydration of the cobalt soap.

Experimental

Materials.—Cobalt soaps are cobalt stearates, described in the previous paper[4]. Several specimens of each typical color were chosen from among many samples.

Analyses.—*Free Fatty Acid.*—Free fatty acid was extracted from soaps by the use of acetone for 1 hr. with a Soxhlet extractor. The color of the soaps was not altered by extraction. Acetone was dehydrated by anhydrous potassium carbonate. A glass cylinder was inserted around a cylindrical filter paper in order to improve the circulation of the solvent[5]. The amount of free acid was determined by evaporating the solution. The residue was dissolved in ethanol, and the solution was titrated by a standard alkaline solution.

Combined Fatty Acid.—Cobalt soaps were decomposed by boiling with 0.1 N sulfuric acid. Isolated fatty acid and unreacted soap melted and floated in a mass on the surface of the solution. The decomposition was continued until the molten mass became wholly colorless.

Cobalt soap can be decomposed also by a 0.1 N alkaline solution. This method was not adequate here, however, because the solution foamed so much, that it was feared that unreacted soap might overflow the vessel.

The solution was cooled, and the seperated fatty acid was filtered off. The filtrate obtained in this process was used for determining the content of the cobalt. Fatty acid was dried on filter paper, dissolved in hot ethanol, and titrated by a standard alkaline solution.

Cobalt.—The amount of cobalt was determined by several methods. (i) Soaps were burnt to ashes, which were weighed as Co_3O_4. (ii) Cobalt was precipitated from the solution as a complex salt by α-nitroso-β-naphthol. (iii) Cobalt was deposited on a platinum electrode electrolytically. (iv) The cobalt solution was titrated by an EDTA solution.

Burning Method.—Cobalt soap was heated in a porcelain crucible by a Bunsen burner. Stearic acid was carbonized at first, and then the whole mass was ignited and completely oxidized by strong heating. The residue was weighed as Co_3O_4.

α-Nitroso-β-naphthol Method.—By adding an excess of hydrogen peroxide to the acidic solution of cobalt, cobalt ions were oxidized from bivalent to tervalent. The black cobaltic hydroxide precipitated from the solution by the addition of a sodium hydroxide solution. The precipitate was dissolved again by glacial acetic acid, and the dark brown solution obtained was diluted with some warm water and mixed with the solution of α-nitroso-β-naphthol in acetic acid. The reddish brown precipitate was filtered off, dried at 130°C, and weighed as $(C_{10}H_6ONO)_3Co$.

Electrodeposition Method.—Cobalt stearate (0.1 g.) was decomposed by 0.1 N sulfuric acid (20 ml.), and the separated fatty acid was filtered off. The filtrate was concentrated to 10 ml., ammonium sulfate (0.5 g.) was added, and the solution was made alkaline with 0.1 N ammonia solution (40 ml.), and sodium bisulfate (0.02 g.) was added. With platinum plates as electrodes, the golden solution was electrolyzed with a current 0.2 amp. and 3.5 V. at 60°C for 8 hr. The cobalt metal deposited on the cathode was weighed after drying in an air-oven at 110°C.

EDTA Titration.—Cobalt soap (30 mg.) was decomposed by 0.3 N hydrochloric acid (20 ml.). The fatty acid was solidified to a mass. The solution was diluted to 70 ml. by water, murexide (ammonium purpurate) was added as an indicator[6], and the solution was neutralized by 1 N ammonia solution in some excess. The yellow solution was titrated by 0.01 M EDTA (disodium ethylenediamine tetraacetate), until the color of the solution became pink. The concentration of EDTA solution was calibrated by a standard cuprous nitrate solution.

Water of Hydration.—Cobalt soaps had been dried in a vacuum at room temperature. Pink species gained a tinge of blue, but other soaps did not change their colors substantially in this process. Their colors did not change during storage in an ambient atmosphere.

Inorganic cobalt salts contain some water of hydration, some of which could not be removed in the vacuum. It is possible for cobalt soaps to have such a tightly combined water of hydration. The water content was determined (i) by a Karl-Fischer reagent and (ii) by weighing after heating in a vacuum.

Karl-Fischer Titration.—From among the several methods of this technique, the inverse dead-stop method with "magic eye" titrometer was carried out[7]. The titration vessel was equipped with a draining cock, as proposed by Campbell[8].

The standard methanol used was an extra pure reagent, made by Takeda Chemicals Co., the water content of which was about 0.5% by volume. The Karl-Fischer reagent was prepared as usual[9] and calibrated by sodium acetate trihydrate.

The cobalt soaps did not dissolve, but were well dispersed in mixtures of methanol and pyridine, which were basic solvents of the reagent. However, because the soap was powder, it was difficult to place it in titration vessel. This was the main origin of errors.

Dehydration in Vacuum at Heating.—The decrease of weights was measured by a quartz spring balance in an evacuated glass tube at 10^{-3} mmHg. An electric furnace was used to heat the soap up to 150°C. The sensitivity of the quartz balance was 7.54 cm./g., and its accuracy was 0.2 mg. in weight. A sample of 0.1 g. was usually taken for measurements.

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[5] K. J. Mysels, H. H. Pomeroy and G. H. Smith, *Anal. Chem.*, **20**, 878 (1948).

[6] H. Flaschka, *Mikrochemie*, **39**, 38 (1952).

[7] R. Kieselbach, *Anal. Chem.*, **21**, 1578 (1949).

[8] D. E. Campbell, ibid,. **25**, 203 (1953).

[9] J. Mitchell, Jr., and D. M. Smith, "Aquametry", Interscience Publishers, Inc., New York (1948).

Results and Discussion

Free Fatty Acid.—The amounts of free fatty acid in several samples of each species of cobalt stearate were measured. The average values are shown in Table I. The amount of free acid was relatively little. It was most in pink, but very little in red, soap. The following analyses were carried out with samples, the free acid of which had been completely extracted.

TABLE I. FREE FATTY ACID CONTENTS IN COBALT STEARATES

Pink	4.14 %
Blue	2.36 %
Red	0.70 %

Compositions.—Several analyses of each species of cobalt stearate were executed by various methods. These results are tabulated together in Table II. Although the values were scattered in some ranges, the average values of each method and their mean are shown.

Theoretical compositions calculated from several possible formulas of cobalt stearate are shown in Table III. In comparing Table II with Table III, it is certain that three forms of cobalt stearate are neither basic nor acidic salt.

The blue form corresponds to anhydrous neutral soap, for it shows no water content. The red form must be dihydrate, judging from the content of hydration water. The observed

TABLE II. OBSERVED COMPOSITIONS OF COBALT STEARATES

	Cobalt, %				Stearic acid, %	Hydration water, %		Total, %
	By burning to ashes	With α-nitroso-β-naphthol	By electro-deposition	By EDTA titration	By neutralization	By Karl-Fischer reagent	By heating in vacuum	
Pink	8.12	9.1	9.29		82.6		3.56	
	8.95	9.4	9.65		87.0		4.55	
	9.01	9.4	9.12		81.8		3.97	
		10.8	9.52		85.5		6.34	
		12.1	9.25		87.3		3.91	
		9.0					3.71	
							4.35	
							6.26	
							3.65	
	av. 8.65	av. 10.0	av. 9.38		av. 84.8		av. 4.36	
		mean 9.34			mean 84.8		mean 4.36	mean 98.50
Blue	8.94		9.35	9.32	88.0	−0.8	0.0	
	10.43		10.15	9.63	90.9	−0.5		
	9.91		10.15	9.59	92.5	1.4		
			10.33	9.34	91.5	0.26		
			10.78	9.51	88.1			
			9.78	9.58	89.1			
			10.12	9.48	92.4			
			10.54					
	av. 9.76		av. 10.14	av. 9.49	av. 90.4	av. 0.1		
		mean 9.80			mean 90.4	mean 0.0		mean 100.20
Red	7.88		9.04	9.04	84.5	3.46	5.43	
	9.65		9.11	9.21	86.0	4.40	5.67	
	8.24		9.36	9.11	86.9	1.28	5.41	
	8.57		9.18	9.01	78.6	5.48	5.72	
			9.26	9.01	87.6			
			9.71	9.02	87.6			
				9.04				
				9.06				
	av. 8.65		av. 9.34	av. 9.06	av. 85.1	av. 3.66	av. 5.56	
		mean 9.02			mean 85.1	mean 4.61		mean 98.73

TABLE III. CALCULATED COMPOSITIONS OF COBALT STEARATES

	Cobalt, %	Stearic acid, %	Water, %
Neutral salts, $(C_{17}H_{35}COO)_2Co$	9.42	90.58	—
Monohydrate, $(C_{17}H_{35}COO)_2Co \cdot H_2O$	9.15	88.05	2.80
Dihydrate, $(C_{17}H_{35}COO)_2Co \cdot 2H_2O$	8.90	85.64	5.46
Basic salt, $(C_{17}H_{35}COO)Co(OH)$	16.40	83.60	—
Acidic salt, $(C_{17}H_{35}COO)_2Co(C_{17}H_{35}COOH)$	6.47	93.53	—

contents of cobalt of these soaps were somewhat larger than the calculated values, for some of the combined fatty acid might be hydrolyzed and removed during the extraction by acetone.

The pink form shows a composition nearer to red dihydrate than to blue anhydrate. Experimental values are particularly scattered in this species. As the pink soap is an incipient product in metathesis, it may be natural that its composition is somewhat indefinite.

Mechanism of Color Change.—From these results, it has been ascertained that the difference of color is due to the degree of hydration of these soaps. In the previous paper[4)], it was found that under some conditions the pink soap thus formed soon turned blue and then red later in solution. This corresponds with the change of the amount of water of hydration, which first decreases and then increases again. This process seems very strange, but the following interpretation may be proposed.

The alkaline soap in aqueous ethanol takes the form of micelles, in which lyophilic ionic groups of soap molecules exist in the outer layer against solvent molecules. Ionic groups dissociate in different degrees, according to the solvent ratio in solution. When the cobalt ions are added, dissociated soap ions in the outer lyophilic layer react with cobalt ions immediately. Therefore, in the incipiently formed pink soap there remains the original micelle structure of alkaline soap, as will be discussed in the later part of these studies.

With the existence of sufficient alkali, cobalt soap turns gradually to red dihydrate, which is the most stable form in these solvents. When the alkali is insufficient, the dissociation of alkaline soap is greatly suppressed, and therefore the ionic reactions proceed limitedly. In these circumstances the yield of cobalt soap is little, and much free acid exists in the formed soap.

When the solvent ratio is higher than 1:1, the solvent becomes somewhat oleophilic and the formed pink soap turns blue, perhaps by an inversion of the micelle structure. In this case some of the lyophobic hydrocarbon chains appear outside. As the soap becomes less lyophilic in this system, blue crystals tend to rise to the surface of the solution.

In the following time, water molecules gradually penetrate into the interior of the micelles of blue soap and adhere to the hydrophilic cobalt ions as waters of hydration. As the penetration of water is difficult through such a thick layer of hydrocarbon chains, the change of color from blue to red generally occurs slowly.

Summary

Pink, blue and red cobalt stearates were analyzed and their compositions were determined. From these results, it has been confirmed that blue soap is anhydrate and red soap is dihydrate. The pink soap has a rather indefinite composition nearer to red soap. A mechanism of the color changes was proposed based on the inversion of the micelle structure under some circumstances.

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