Gas Absorption by Cobalt Soaps

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Cobalt soaps are of wide industrial application as oxidizing calalysts in organic reactions, such as dryers of paints. It has been known that if the cobalt soaps of unsaturated acids, such as cobalt resinate, are left standing in the air, they change color from red to dark brown and sometimes ignite spontaneously. The mechanism of these characteristic oxidizing actions of cobalt soaps is not, however, known well. Ingle[1] has indeed presented a theory based on the oxidation of a substance by the oxygen carried by cobalt soaps, but direct evidence for this theory has not been offered. In this report the absorptive properties of cobalt oleate and stearate for a few gases are studied. Especially the absorption of oxygen by cobalt oleate is investigated from various points of view.

Experimental

Materials.—Cobalt soaps were prepared by metathesis from alkali soaps and cobaltous salts in ethanol-water solutions at about 50°C. It had previously been established that the composition of cobalt soaps depends perceptibly on the conditions of the preparation[2]. In this experiment the conditions were kept as constant as possible in order to obtain samples of a definite composition. The details are as follows.

Cobalt Oleate.—Oleic acid (15 g.) was dissolved in 95% ethanol (185 ml.) and neutralized by 1 N sodium hydroxide, using phenolphthalein as an indicator. This was diluted dy hot water (400 ml.) (solution A). Cobaltous nitrate (7.6 g.) was dissolved in water (230 ml.) (solution B). Both solutions were warmed at 50°C. Solution B was added to solution A drop by drop. The precipitated cobalt oleate was filtered and washed with ethanol and water. To avoid oxidation, all procedures were carried out in a stream of nitrogen gas. The sample was dried in vacuo at room temperatures and kept by sealing it in a glass bottle. Pink powder.

Found: Co, 12.70; C, 63.56; H, 10.13. Calcd. for $Co_3(C_{18}H_{33}O_2)_4(OH)_2\cdot 2H_2O$: Co, 12.88; C, 63.00; H, 10.13%.

Cobalt Stearate.—Stearic acid (2 g.) was dissolved in 95% ethanol (100 ml.) and neutralized with 1 N

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[1] H. Ingle, *J. Soc. Chem. Ind.*, **36**, 319 (1917).

[2] Y. Koga and R. Matuura, *Mem. Faculty Sci., Kyushu Univ.*, **C4**, 1 (1961).

sodium hydroxide as above. This mixture was then diluted with hot water (100 ml.) (solution A′). A solution of cobaltous chloride (1.2 g.) in water (50 ml.) (solution B′) was added drop by drop at 50°C to solution A′. The precipitate was treated as in the case of cobalt oleate. Blue powder.

Found: Co, 10.26; C, 69.01; H, 11.59. Calcd. for $Co(C_{18}H_{35}O_2)_2$: Co, 9.42; C, 69.02; H, 11.28%.

Oleic acid was obtained from camellia oil by treating it with potassium hydroxide, lead acetate and lithium hydroxide and finally by distilling it at 228.5°C/13 mmHg. M. p. 12.6°C. Stearic acid was recrystallized from commercial samples. M. p. 68.8∼69.3°C. Cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$, and chloride, $CoCl_2 \cdot 6H_2O$, were purified by recrystallization. As gases, oxygen, nitrogen and hydrogen were used. They were purified by the usual method.

Procedure.—The gas absorption was measured by using a Warburg manometer at 22∼23°C under atmospheric pressure. The weight change accompanying the gas absorption was also measured. X-Ray diffraction patterns and ultraviolet and infrared absorption spectra of oxygenated cobalt oleate were investigated, too. The X-ray patterns were obtained by the Debye-Scherrer method. A Shimadzu QB-50 spectrophotometer was used for the ultraviolet absorption spectra, while for the infrared studies a Hitachi EPI-2 infrared spectrometer was used.

Results and Discussion

Gas Absorption by Cobalt Oleate.—In Fig. 1 the volume of gases (STP) absorbed by one gram of cobalt oleate is plotted against the time required. It is clear that oxygen is absorbed noticeably, while the absorption of nitrogen and hydrogen is very small. For the first hundred minutes the absorption of oxygen by cobalt oleate is almost linear against time, and it was found that a few months are required to reach the absorption equilibrium. At the end of the linear part of the absorption rate curve, the composition of the sample corresponds to $Co_3(C_{18}H_{33}O_2)_4(OH)_2 \cdot 2H_2O \cdot 6O$. After the complete oxygenation of cobalt oleate, the composition was found to be $Co_3(C_{18}H_{33}O_2)_4 \cdot (OH)_2 \cdot 2H_2O \cdot 16O$. The color was changed from pink (original sample) to dark brown (completely oxygenated sample), and the solubility in organic solvents decreased considerably as a result of the absorption of oxygen. When cobalt oleate was in contact with dry air, the results were almost the same in quantity as in the case of oxygen absorption.

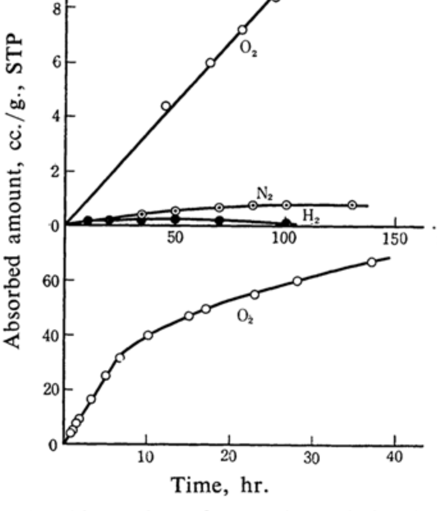

Fig. 1. Absorption of gases by cobalt oleate. 23°C, 1 atm.

The Absorption of Oxygen by Cobalt Stearate and by the Mixture of Cobalt Stearate and Oleic Acid.—From Fig. 2 it is evident that the absorptive power of cobalt stearate for oxygen is negligible compared with that of cobalt oleate. However, the mixture of cobalt stearate and oleic acid absorbs oxygen fairly well compared with the absorption of oxygen by oleic acid alone. It may be said that cobalt stearate, although a poor oxygen absorber by itself, is a rather good catalyzer for the oxygenation of oleic acid. At any rate, the absorptive capacity of cobalt oleate for oxygen is by far the most remarkable. Probably the origin of absorption exists both in cobalt atoms and in double bonds, which will be examined below.

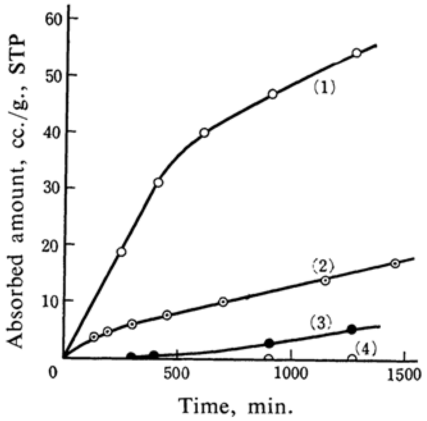

Fig. 2. Absorption of oxygen by (1) cobalt oleate, (2) cobalt stearate+oleic acid (1 : 70), (3) oleic acid, and (4) cobalt stearate.

Ultraviolet Spectroscopic Investigation of Oxygen Absorption by Cobalt Oleate.—A thin film of cobalt oleate was prepared on the surface of the quartz cell from its benzene solution, and the cell was placed in contact with dry air. The ultraviolet spectra of this film were taken at various intervals of time. The results are shown in Fig. 3. It is shown that the absorption at 350 $\mathrm{m}\mu$ increases. It is evident that this increase reveals the absorption of oxygen by cobalt oleate. The relation of the absorption intensity at 350 $\mathrm{m}\mu$ to time is represented in Fig. 4. The intensity becomes almost constant after about three days in contact with air. No doubt, the absorption at 350 $\mathrm{m}\mu$ is not due to the oxydation of the double bond of oleate, since there is no absorption near 350 $\mathrm{m}\mu$ in either the spectrum of oxygenated oleic acid as well or in that of non-oxygenated oleic acid. On the basis of various experimental results by many workers3), it is concluded that the absorption at 350 $\mathrm{m}\mu$ corresponds to the second absorption band, i. e., the absorption of shorter wavelength usually appearing in the spectrum of cobalt coordination compounds. In the process of oxygen absorption by cobalt oleate, therefore, it may be concluded that, at least in the initial stage, oxygen is coordinated to the cobalt atom.

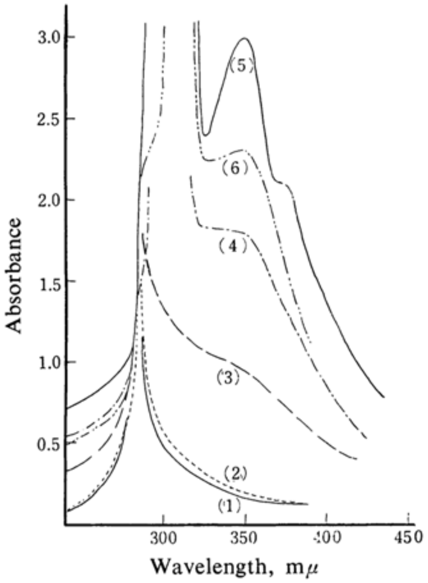

Fig. 3. Ultraviolet absorption spectra of oxygenated cobalt oleate. Oxygenation time: (1) 0, (2) 15, (3) 27, (4) 36, (5) 75 and (6) 175 hr.

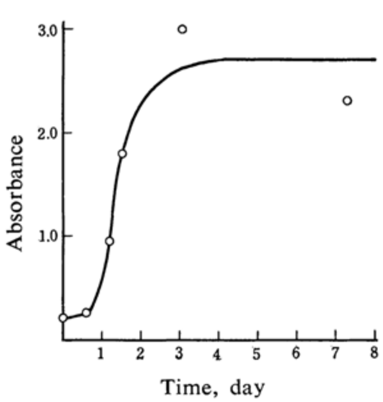

Fig. 4. Absorbance at 350 $\mathrm{m}\mu$ against time of oxygenation.

The Infrared Spectra of Oxygenated Cobalt Oleate.—Infrared spectra of the original cobalt oleate and of a few oxygenated cobalt oleates, differing in their degree of oxygenation, were taken by the potassium bromide disk method. In Fig. 5 the infrared absorption spectrum of non-oxygenated cobalt oleate is shown together with a reference spectrum of oleic acid. The essential differences between these spectra are the disappearance of the bands of 2670, 1715 and 935 cm^{-1} and the appearance of the 1565 cm^{-1} band in the spectrum of cobalt oleate. The three bands, 2670, 1715 and 935 cm^{-1}, are ascribed respectively to the stretching vibration of hydroxyl, the stretching vibration of carbonyl and the out-of-plane deformation mode of hydroxyl, all in the carboxyl group of oleic acid. It is known that the bands at 2670 and 935 cm^{-1} vanish on the esterification of the acid. The band at 1565 cm^{-1} is ascribed to the characteristic frequency of carbonyl in the ionized carboxyl group, appearing as a shift of the 1715 cm^{-1} absorption of carbonyl in the unionized carboxyl group. The ionic structure of cobalt oleate is thus clearly indicated. The band at 3031 cm^{-1} is ascribed to the stretching vibration of the $=\mathrm{CH}-$ group in unsaturated hydrocarbons.

The infrared absorption spectra of oxygenated cobalt oleates are shown in Fig. 6. The three samples used were different in their oxygenating time, that is, 4 hr., 24 hr. and 150 days. The noticeable effect of the oxygen absorption is the appearance of bands near 1720 and 1178 cm^{-1}, which bands increase in intensity as the oxygenation proceeds, and of a band at 971 cm^{-1}, which again decreases its intensity and

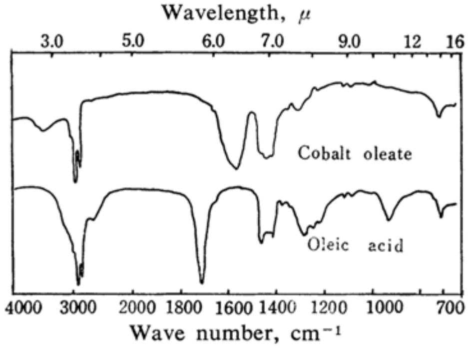

Fig. 5. Infrared absorption spectra of cobalt oleate and oleic acid.

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3) E. g., R. Tsuchida, This Bulletin, 13, 388, 436 (1938); M. Linhard and M. Weigel, *Z. physik. Chem.*, *N. F.*, 20 (1955).

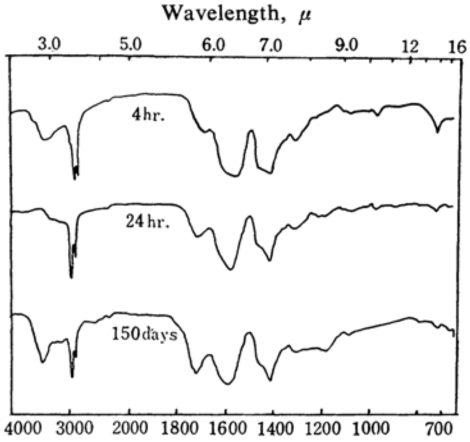
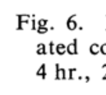


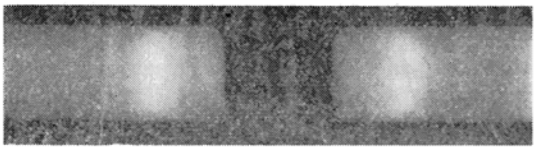
Fig. 6. Infrared absorption spectra of oxygenated cobalt oleates, for the oxygenating time, 4 hr., 24 hr. and 150 days.

finally disappears as a result of the strong oxygenation of cobalt oleate. A band at 3020 cm^{-1} of the original sample also vanishes when the sample is oxygenated strongly. The band at 1720 $^{-1}$ is ascribed to the stretching vibration of carbonyl in the carboxyl group of the acid, as has already been mentioned. The band at 971 cm^{-1} is originally the CH out-of-plane deformation vibration of the $-CH=CH-$ group (trans) which is observed in the spectrum of elaidic acid, a geometrical isomer of oleic acid (cis). Swern et al.[4-5] have reported that the cis-trans isomerization of methyl oleate arises from the oxygenation of oleyl group and that the trans-type hydroperoxide is produced. It is reasonable to ascribe the absorption at 1178 cm^{-1} to the stretching vibration of the

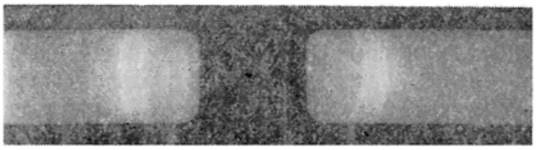


$$\begin{array}{cc} \mathrm{H} & \mathrm{H} \\ -\mathrm{C}- & \mathrm{C}- \\ | & | \\ \mathrm{O}- & \mathrm{O} \end{array}$$

group of hydroperoxide produced by the oxygenation of cobalt oleate. The decrease in intensity of a band at 3020 cm^{-1} with oxygenation shows that the double bond structure is destroyed as the oxygenation proceeds. All these results would indicate that, in the oxygenating process of cobalt oleate, the oxygenation of the double bond takes place and that a hydroperoxide structure is formed, together with acid produced by the destruction of the double bond. It is probable that oxygen attacks double bonds as well, as it is coordinated to the cobalt atom, as is shown by the ultraviolet spectroscopy of the oxygenating process.



Non-oxygenated cobalt oleate



Oxygenated cobalt oleate
(about three-month contact with dry air)

Fig. 7. The X-ray diffraction patterns of cobalt oleate.

The X-Ray Diffraction Pattern of Oxygenated Cobalt Oleate.—As shown in Fig. 7, the X-ray diffraction pattern of non-oxygenated cobalt oleate consists of a " halo ". This indicates that non-oxygenated cobalt oleate is an amorphous solid. When the sample is completely oxygenated (after about three months contact with air), it is seen that the crystallization is effected to some degree. We have proposed[6] a polymeric structure, loosely bonded through OH groups, for cobalt oleate, which gives rise to an amorphous pattern in an X-ray spectrum. The crystallization by oxygenation may results from the coordination of oxygen to cobalt and the formation of an oxidized product, which gives the rigid crystalline structure to the original cobalt oleate. However, the point must be investigated further.

The Probable Mechanism of the Catalytic Action of Cobalt Soaps.—It may be concluded from the experimental results obtained in the present study that oxygen is coordinated to the cobalt atom and attacks the double bond in the case of cobalt oleate. Cobalt stearate alone does not absorb oxygen, but in the presence of oleic acid considerable absorption of oxygen takes place. This suggests that the oxygen absorption by cobalt soaps takes place when the oxygen acceptor is present at the same time. Oxygen will be coordinated to the cobalt atom and activated, resulting in the oxidation of the unsaturated compounds existing with the soap. This is similar to Ingle's theory[1] on the mechanism of the drying action of metal soaps, but the present study gives a more direct explanation for the mechanism, based on various experimental facts.

Summary

The gas absorption by cobalt oleate and stearate has been studied. It was found that cobalt oleate absorbs oxygen very remarkably,

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[4] D. Swern et al., *J. Am. Chem. Soc.*, **75**, 3135 (1953).

[5] H. B. Knight, C. R. Eddy and D. Swern, *J. Am. Oil Chemists' Soc.*, **28**, 188 (1951).

[6] H. Funakoshi, *Bull. Fukuoka Gakugei Univ.*, Part III, **11**, 93 (1961).

but nitrogen and hydrogen, very little. Cobalt stearate absorbs oxygen negligibly, but in the presence of oleic acid the absorption becomes considerable. From the studies of ultraviolet and infrared spectra and X-ray analysis of the oxygen absorption by cobalt oleate, it was found that oxygen is coordinated by the cobalt atom and destroys the double bond structure. The probable mechanism of the catalytic action of cobalt soaps has also been presented.

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