

the purest alcohol of any of the methods used here. It should be pointed out, however, that non-absorbing impurities, such as water, are not detected by absorption measurements. The electrical conductivity may be used to detect the presence of small amounts of water, and a comparison of the conductivities of the different samples indicated that aluminum amalgam is fully as efficient a drying agent as calcium oxide. Metallic calcium, used as a drying agent, failed to give any better results than calcium oxide, either for light absorption or conductivity.

The iodine-zinc method of purification (curve B) does not give quite as good results as the other methods.

It is of interest that the absorption measurements of Bielecki and Henri (column I) which are the lowest hitherto reported, agree almost exactly with our alcohol F, while our samples D, G and H show a lower absorption in this threshold region.

In short wave lengths, however, where alcohol itself absorbs strongly, one would expect the difference between the various samples to be slight.

Summarizing, light absorption measurements indicate that the standard practice of drying ethyl alcohol over calcium oxide should be carried out in an oxygen-free atmosphere. The highest degree of purity, as measured by the absorption spectrum, is obtained by the use of aluminum amalgam for drying.

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SOME FACTORS AFFECTING THE CATALYTIC ACTIVITY OF COBALT OLEATE IN THE AUTOXIDATION OF PENTENE-2¹

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(A) Introduction

In a paper published some months ago,² the authors noted the catalytic activity of certain substances on the autoxidation of cracked gasolines. It was ascertained at that time that hydrogen chloride, for example, was a strong autoxidizing catalyst, whereas acetic acid was almost without effect. These reactions, as well as numerous other indications, prompted the authors^{2,3} to propose a new theory of autoxidation based on the acidic

¹ Presented before the Petroleum Division of the American Chemical Society at Cincinnati, Ohio, September 9-13, 1930.

² Wagner and Hyman, 10th Annual Meeting, A. P. I. Report, 3rd section, pages 118-123.

³ Hyman and Wagner, *J. Inst. Pet. Tech.*, **15**, 645 (1929).

character of the autoxidation catalysts, as well as on the possibility of oxonium compound formation in the cases where peracids were felt to act as catalysts.

Among the compounds showing a decided catalytic activity was reported a mixture of cobalt and nickel acetate crystals, despite their apparent insolubility in gasoline. In work reported in a recent paper,⁴ the authors have made use of this fact, using cobalt oleate as a catalyst in the autoxidation of the pentenes. Cobalt oleate (provided it is not removed too completely from its original solvent) is readily soluble in hydrocarbons.

Since the time that certain compounds were discovered to have a positive catalytic effect on the formation of pseudo-gum in cracked gasoline, the authors have felt that "promoted" autoxidation (*i. e.*, autoxidation which has been promoted by a foreign substance purposely added) could be brought under the same viewpoint as the "unpromoted" autoxidation. It is believed that the material to be presented in this paper tends to justify such an opinion.

The cobalt soaps have for years been used as "driers" in paints and varnishes and, according to various authorities,⁵ are the most active of all the soaps in this respect. Kissling⁶ recognized the action of the drying of an oil film to be in part, at least, an oxidation, and Fahrion⁷ was quick to apply Engler and Weissberg's extension of the original Engler-Bach theory of autoxidation⁸ to this problem. According to Fahrion's interpretation, the metals may act as carriers of atmospheric oxygen, transferring this oxygen either between two "acceptors"—olefin bonds of a drying oil—or else allowing half the oxygen to combine with water to form hydrogen peroxide. The manner in which such transfer was to take place was left moot, although Fahrion believed that the metal-oxygen combination was in the form of a metallic peroxide or hydro-peroxide. The theory, regarding the action of driers, which appears to have gained the most popularity is that of Ingle.⁹

Ingle's theory is an alteration and extension of Fahrion's theory, the most striking point of which is the postulation that only those metals act as siccatives (in the form of their soaps) which possess multiple valence states, and only then when the salts corresponding to the lower valence state are more stable than those corresponding to the higher state. In

⁴ Hyman and Wagner, *THIS JOURNAL*, **52**, 4345 (1930).

⁵ Fokin, *Seif.-Zig.*, **34**, 821 (1907); Eibner and Pallauf, *Chem. Umschau*, **32**, 97 (1925); Mackey and Ingle, *J. Soc. Chem. Ind.*, **36**, 317 (1917).

⁶ Kissling, *Z. angew. Chem.*, **4**, 395 (1891).

⁷ Fahrion, *Chem.-Zig.*, 1196 (1904).

⁸ Engler and Weissberg, "Kritische Studien ueber die Vorgaenge der Autoxydation," Braunschweig, 1904.

⁹ (a) Mackey and Ingle, *J. Soc. Chem. Ind.*, **35**, 454 (1916); (b) **36**, 317 (1917); (c) Ingle, *ibid.*, p. 319.

order to distinguish between the drying activities of the various metals possessing multiple valence states, Ingle further postulated that the more valence states a metal could assume, the more active it would be as a drier.¹⁰

That Ingle's scheme cannot express the action of driers completely is obvious, as its author admitted.^{9b} For example, cobalt, having but two valence states is more active (in its soaps) as a drier, than is vanadium, with at least four. Furthermore, soaps of aluminum, calcium, sodium and silver act as driers to some extent, despite the fact that these metals possess but one valence state. The authors believe, with Ingle,⁹ that their use of metal catalysts with unsaturated hydrocarbons parallels to quite an extent the use of such catalysts with the vegetable oils. In fact, metal catalysis in atmospheric oxidation does not seem to be limited to these fields at all, but appears to play a very important role in other branches of chemistry as well, as for example, in physiological chemistry.¹¹

As a matter of fact, in the petroleum industry, metal catalysis in autoxidation is undoubtedly present. As a very minor but immediate example, the use of a copper dish for gum determination leads to inordinately high gum values, which can be accounted for only by assuming a catalytic activity of the copper, *i. e.*, the copper compounds formed by interaction of the acids present in the oxidized gasoline with the copper dish.

(B) Preliminary Preparations

It is now common knowledge that aldehydes such as benzaldehyde and acetaldehyde, when exposed to sunlight in the presence of oxygen, are converted partially at least into peroxides. In the absence of light a somewhat similar but much slower reaction takes place.

If, however, acetaldehyde is dissolved in alcohol to which a crystal of cobalt acetate and a few drops of acetic acid have previously been added, and if such a solution is permitted to stand under oxygen in the dark, the peroxide formation is even more rapid than in sunlight. During the reaction, the light pink solution is changed to olive-green. This reaction suggests that one of the reasons for the autoxidation of acid-free aldehydes in the dark may lie in the presence of traces of metallic salts as impurities.

It was decided to prepare a sample of cobalt oleate, free from solvent. This was tried both by methods of fusion and precipitation. The former method, however, never made a product free from fatty acid, and therefore the latter method was used throughout the work. The general method of preparation was, first, to make the potassium soap by allowing U. S. P. oleic acid, diluted with alcohol, to react with a 10% excess of potassium hydroxide dissolved in a large portion of distilled water. To this solution,

¹⁰ Fokin⁵ also assumed this latter generalization.

¹¹ O. Warburg, *Ber.*, **58**, 1001 (1925).

after being filtered, was added either a slight excess or a slight insufficiency of c. p. $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, also previously dissolved in considerable distilled water, and filtered. The precipitate of the cobalt soap formed immediately upon mixing. It was taken up in as little ether as possible, centrifuged, the ether extract filtered, and alcohol added until an ether-soap layer formed. A cobalt oleate solution, such as the layer just mentioned represents, is a deep purple, very heavy solution which hardens immediately on contact with air. The hardening is not due to oxidation, apparently, but rather to evaporation of the ether. If the ether-soap solution is evaporated *in vacuo*¹² a solid substance is formed, which, however, is not the pure soap but a combination of soap, alcohol and ether. If this material is heated on the water-bath in vacuum until the odor of alcohol is gone, a purple colored rubbery substance is formed which appears to be the cobalt oleate itself. The fact that it shows a cobalt content of 10.2–10.3% (the cobalt soap being ignited to the oxide, which is then reduced to metallic cobalt by hydrogen, and weighed as such), whereas theoretically cobalt oleate should contain but 9.48% of the metal, indicates that the U. S. P. oleic acid contains acids of molecular weights lower than that of pure oleic acid.¹³ However, for the purposes of this work, it was necessary only to avoid the presence of free fatty acid, and therefore no attempt was made to purify the oleic acid further.

For the preparation of the cobalt oleate used in the main experiments, it was found advantageous to use chloroform instead of ether as a solvent, chiefly because of the very low solubility of water in the former. It was also found unnecessary to wash the chloroform extract with alcohol; thus, the chloroform solution was evaporated *in vacuo* in a water-bath heated to 60°, and the danger of decomposing the soap, consequently, considerably reduced. Such soap also shows a cobalt content of 10.2–10.3%. In the work herein reported the cobalt oleate was never freed from the original chloroform solvent but, rather, more chloroform was added to the solution.

(C) Experimental

If cobalt oleate catalyzes the autoxidation of the olefin bond, it should be an autocatalyst of itself, that is, it should hasten its own oxidation. Indeed, the induction period in this particular autoxidation should disappear entirely, for it is impossible to imagine a negative catalyst present in so large an amount as to prevent completely, even for a very short while,

¹² A simple and satisfactory arrangement for vacuum evaporation consists of a heavy-walled lipless Pyrex dye beaker, a funnel whose rim fits the inner part of the rim of the beaker, and a ring of thin sheet rubber, used as a gasket. The suction pump hose is connected to the stem of the funnel. Care must be taken to prevent excessive foaming of the soap solution.

¹³ Of course, there is always the possibility of the formation of a mixed soap, namely, cobalt aceto-oleate, in fairly constant proportions.

the autoxidation of so fairly pure a soap solution as the cobalt oleate solution prepared by us. Cobalt oleate, however, is not oxidized immediately, if exposed to oxygen in the dark. In fact, the oxidation does not become noticeable until a lapse of twelve to fifteen hours. The oxidation of cobalt compounds in organic media is readily visible by the color change. The original purple color changes first to brown, and then rapidly to an olive green. The experiment previously alluded to was carried out by allowing several drops of a chloroform solution of cobalt oleate to drop onto a piece of quantitative filter paper. The chloroform was evaporated by blowing with compressed oxygen, and the paper then placed in a four-ounce oil bottle, which was filled with oxygen and kept in the dark. The results obtained indicate quite clearly that some compound other than cobalt oleate is the real catalyst in the reaction. This compound seems to form slowly in the soap, induced perhaps through traces of impurities; for once oxidation has begun, it appears to proceed very rapidly. It usually appears to begin at the fringes of the spot of cobalt oleate. A drop of distilled water in the bottle seems to delay oxidation slightly; a trace of acetic acid appears to hasten the oxidation considerably; on the other hand, a drop of aqueous ammonia retards the oxidation for several days. The authors believe these exploratory experiments to be of considerable importance, for while the present-day tendency might be to interpret these results solely in the light of surface activity and hydrogen-ion concentration, the authors feel that a simpler and more fundamental viewpoint lies in assuming, on the one hand, the interaction of fatty acid and the cobalt oleate, at least minutely, to produce a complex acid possessing catalytic powers, while the ammonia, on the other hand, would tend to bind these acids, or even form amine-cobalt complexes so as to prevent the formation of complex acids.¹⁴ The experiments previously spoken of were continued by determining the rate of autoxidation of pentene-2 in the presence of cobalt oleate alone, as well as in the presence of stearic acid and triethylamine. Pentene-2 was prepared from *sec.*-amyl alcohol and sulfuric acid.¹⁵ It is the simplest of the amylenes to prepare with a fair degree of purity and has been shown by the authors⁴ to be oxidized by molecular oxygen with comparative ease. The manner of carrying out the experiments and the mode of titration used was the same as that used by the authors in the paper just referred to.

The results in Table I substantiate the results obtained by noting the action of acetic acid and ammonia on drops of cobalt oleate solution taken up by filter paper (see page 3022). A very interesting point to note in Table I, however, is the initial "induction period," during which time oxida-

¹⁴ Mackey and Ingle⁵ suggested that partial valences of the soap ions might play a part in the catalytic action of metal driers.

¹⁵ Norris and Joubert, *THIS JOURNAL*, **49**, 873 (1927).

TABLE I
 RESULTS OF EXPERIMENTS

Material	Cc. of 0.01 N		Na ₂ S ₂ O ₃	used after		
	4 hrs.	21 hrs.		89 hrs.	117 hrs.	165 hrs.
1 Pentene-2, blank	0.00	0.00	0.00	0.00
2 No. 1 + 2 drops 14.4% soln. of Co(oleate) ₂ in CHCl ₃	.00	0.00	..	0.00	3.60	8.90
3 No. 2 + 2 drops 10% soln. of stearic acid in pentene-2	.00	1.30	3.20	5.40
4 No. 2 + 2 drops 10% soln. of N(C ₂ H ₅) ₃ in pentene-2	.00	0.00	0.00	0.00

tion does not appear to take place (see the first column of Table I). If the idea of complex acid formation is adhered to, it is at once apparent that the tremendous catalyzing influence of cobalt soaps cannot depend on the action of a complex cobaltous acid in such quantities as might be found by simply mixing a cobaltous soap with a fatty acid. The remaining possibility is the activating influence of a complex cobaltic acid.

The fact that normal cobaltic salts are quite unstable excepting in strongly acid solution makes the preparation of cobaltic soaps by precipitation a rather difficult task. Fusion methods were felt by the authors to be unsatisfactory for this work, because of the possibility of formation of decomposition products which might mask the character of the results. It was therefore decided to oxidize a chloroform solution of cobaltous oleate, in the presence of oleic acid, using hydrogen peroxide of 10% strength as the oxidizing agent. The calculated amount of oleic acid was used, and 50% more hydrogen peroxide than the theoretical equation would require. The resulting product, which is of an olive-green color, was washed repeatedly with water, to remove the excess hydrogen peroxide, then heated for a half hour on the water-bath, any excess oleic acid removed by repeated extraction with ethyl alcohol, and the remaining ethyl alcohol and chloroform evaporated *in vacuo* as previously described. A cobalt determination gave the very surprising result of 13.4% cobalt in the new product, whereas the cobaltous material showed only 10.3% cobalt. The cobaltic material made without the addition of the oleic acid showed a similar analysis.

The most plausible explanation for the above-mentioned analysis lies in the assumption that the cobaltic compound formed from the oxidation of cobaltous oleate immediately splits off oleic acid, a certain amount of which is removed by alcohol extraction. A simple analogous experiment may be conducted as follows.

Dissolve a few crystals of cobalt acetate in a little 95% alcohol. Add a few drops of 10% hydrogen peroxide. The purple solution becomes olive-green so rapidly that the intermediate brown state is scarcely perceptible. If a little of this clear solution is poured on a piece of fine filter paper, the

color distributes itself evenly over the entire blot. As the alcohol evaporates, the odor of acetic acid may be noticed. After standing overnight, the solution will have turned brown, and if a few drops are poured onto a piece of filter paper, the brown color will not spread with the liquid. This indicates that the (apparently) basic cobaltic acetate has hydrolyzed completely to form colloidal cobaltic hydroxide. It is logical to assume that a similar series of changes takes place with the oxidized cobaltous oleate. The complete hydrolysis, however, seems to take place very slowly, if at all. If a piece of cobalt oleate is exposed to the air for several days, the surface becomes sticky. If the surface is washed with alcohol, and the alcohol evaporated, a pale yellow film, evidently of oleic acid, remains behind.

In this way, then, the oxidation of a cobalt soap may produce its own fatty acid. Numerous series of tests similar to that recorded in Table I have been made, using a chloroform solution of the green cobaltic oleate compound as a catalyst. A representative run appears in Table II. Because of the fact that only those values at the beginning of the runs are of immediate interest, only these have been noted. As the runs continued, the values for the various titrations merge into one another.

TABLE II
DATA OF A REPRESENTATIVE RUN

Material	Cc. of 0.01 <i>N</i> Na_2SO_3 used after		
	4 hrs.	28 hrs.	78 hrs.
1 Pentene-2, blank	0.00	0.00	0.00
2 No. 1 + 2 drops 8.2% soln. of Co^{+++} compound in CHCl_3 + 4 drops pure CHCl_3	0.80 ^a	5.20	10.00
3 No. 1 + 2 drops Co^{+++} soln. + 4 drops 10% stearic acid soln. in CHCl_3	0.90	5.55	11.95
4 No. 1 + 2 drops Co^{+++} soln. + 4 drops normal soln. NH_3 in CHCl_3	0.00 ^b	0.00	7.10

^a No. 2, titrated at the beginning of the test, showed practically no iodine liberation.

^b Two drops of *N* ammonia solution added to sample after portion for first titration had been removed, to allow for ammonia lost by evaporation. No ammonia added thereafter for the remainder of the run. The amount of ammonia used at the beginning in series No. 4 was approximately double that needed to form a compound $(\text{Co}(\text{NH}_3)_6)\text{X}_3$.

The results of the experiments recorded in Table II attract attention in more than one respect. The most striking feature is the lack of an induction period in series 2 and 3.

Again, the influence of acidic and basic substances is apparent, quite in accordance with the authors' viewpoint. The fact that the plain cobaltic solution shows a high initial catalytic influence the authors would ascribe to the formation of a fairly stable complex cobaltic acid during the preparatory oxidation. The powerful inhibiting effect of ammonia leads the authors to the conclusion that so long as a strong free base is present, cobaltic soaps will not function as catalysts. As a concluding remark

relevant to these experiments, therefore, it appears probable that when a cobalt soap acts as a catalyst, the *oxidized* soap is the active principle; furthermore, the most apparent explanation for the nature of this active principle is to assume the formation of a complex cobaltic acid.

(D) Theory

Provided one may then assume the active principle of a cobalt soap to be a complex cobaltic acid, and provided, furthermore, that one may generalize the case of cobalt soaps to driers in general, a logical picture of "promoted autoxidation" may be gained, somewhat as follows.

If the metals, present in their soaps, have several valence states, and if the metals were present originally in their lowest valence states, then the peroxides formed by autoxidation may raise the metals to higher valences. For example, Co^{++} will be raised to Co^{+++} , Mn^{++} will be raised to Mn^{++++} or higher and Pb^{++} will be raised to Pb^{++++} , which will be the normal valence states for these metals so long as any peroxides are present. If, therefore, complex acids are to be formed, the nuclear atoms will be Co^{+++} , Mn^{++++} and Pb^{++++} . Now, although Mn^{++++} and Pb^{++++} have not received much investigation regarding their complex-forming tendency, Co^{+++} is known as the ion possessing the greatest tendency in this respect. Cr^{+++} , which also possesses a high complex-forming tendency, is oxidized by peroxides to a higher valence state. Pt^{++++} , another complex-forming ion, acts as a rather good drier in the form of its soaps.

In 1899, Abegg and Bodländer¹⁶ made the important observation that, in general, metallic cations form complexes more readily, the weaker their electro-affinities. This is equivalent in the case at hand to saying that the greater the oxidation potential exerted when a metallic ion existing in the presence of peroxides is reduced to its next lower valence state, the greater will be the tendency of that ion to form complexes. The very incomplete data on this subject¹⁷ indicate clearly that the active siccative ions possess high potentials, the cobaltic ion heading the list. Thus, a bridge may be formed between the tendency toward complex formation and the drying powers of metallic soaps. It can hardly be doubted, however, that the stabilities of the individual acids (formed under the conditions of the autoxidation) play an important role in determining the activity of the soap in question.

As to the acidity of such complex acids, they all¹⁸ belong to the class known as true acids, that is, compounds showing acidic tendencies even in so-called non-ionizing media, as distinct from the pseudo-acids,¹⁹ to which category the plain fatty acids belong.

¹⁶ Abegg and Bodländer, *Z. anorg. allgem. Chem.*, **20**, 471 (1899).

¹⁷ See "International Critical Tables," 1st ed., Vol. VI, pp. 332-333.

¹⁸ Hantzsch, *Z. Elektrochem.*, **29**, 231 (1923).

¹⁹ Ref. 18, p. 227.

Conductivity experiments made some time ago in their laboratory by the authors has shown that vapor-phase gasoline which had undergone oxidation possessed to a very appreciable degree the ability to conduct the electric current. Hence, it is apparent that ions actually are present in such *a. medium*. This information has been of value to the authors in explaining the results of their investigation on the autoxidation of the amylenes,⁴ assuming that the atmospheric oxidation of amylenes also produces ions, or maintains ionization.

(E) Summary

1. Cobalt soaps of oleic acid have been prepared, and their catalytic effects studied.
2. It has been shown that the cobaltic soap is responsible for the great catalytic activity of cobalt soaps in promoting autoxidation.
3. It has further been shown that bases exert a negative whereas fatty acids exert a positive catalytic effect on autoxidation in the presence of a cobalt soap.
4. The activity of cobalt soaps has been explained on the assumption of the formation of a complex cobaltic acid.

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SALTS OF THE AMMONO-ENOLIC MODIFICATION OF QUINALDINE¹

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Introduction

Since the group —CH=N— is related to ammonia as —CH=O is related to water,² it follows that the heterocyclic nitrogen compounds, pyridine, quinoline, isoquinoline and quinoxaline are aldehyde-acetals of an ammonia system. The aldehydic properties of pyridine, quinoline and isoquinoline are not marked, because of the stability of the six-membered ring they contain. Nevertheless, Mr. McAllister and the author have shown that all three of these compounds react with the Grignard reagent in ether at 150° .³ Ziegler and his co-workers have quite recently

¹ Presented at the Berkeley, California, meeting of the National Academy of Sciences, September, 1930, and at the Eugene, Oregon, meeting of the A. A. S., June, 1930. Abstract in *Science*, **72**, 402 (1930).

² This is not strictly true, since nitrogen is trivalent, while oxygen is divalent. The third valence of the nitrogen in the —CH=N— group may be attached to an alkyl or aryl radical, giving all of the ammono aldehydes the dual character of aldehyde-acetals [Strain, *THIS JOURNAL*, **49**, 1559 (1927)].

³ Bergstrom and McAllister, *ibid.*, **52**, 2845 (1930).