Hydrogenation of δ-Spinasteryl Acetate.—One hundred milligrams of δ-spinasteryl acetate was dissolved in 10 cc. of glacial acetic acid and shaken for one hour in an atmosphere of hydrogen in the presence of 50 mg. of Adams catalyst. The product was recovered and recrystallized twice from 95% ethanol; yield 40 mg.; m. p. 111–112°; $[\alpha]^{24}$D 8.6° (44.5 mg., 2 cc. chloroform, l = 2 dm., α^{24}D 0.38°, *average* reading). This product when mixed with an authentic specimen of α-stigmastenyl acetate showed no depression in melting point.

Summary

1. From the unsaponifiable portion of Hardigan alfalfa seed oil we have isolated three isomeric sterols of formula $C_{29}H_{48}O\cdot\frac{1}{2}H_2O$: namely, α-spinasterol, β-spinasterol and a new sterol which was designated as δ-spinasterol.

2. Several derivatives of each of the sterols have been prepared and the physical constants and analysis observed.

3. Each of the three isomeric sterols can be reduced to α-stigmastenol.

Catalysts for Peroxide Decomposition[1]

BY M. BOBTELSKY AND A. E. SIMCHEN

Introduction.—In a previous paper[2] some facts were given relating to the catalytic decomposition of hydrogen peroxide in the presence of complex cobalt citrates acting as catalysts. One of them, pink in color, is stable and without catalytic activity; in the presence of hydrogen peroxide it is transformed into a green complex and simultaneously oxygen is evolved by the decomposition of the hydrogen peroxide. Gasometric experiments showed that the velocity of this evolution depends on the velocity with which the green complex is produced.

Nature of the Cobalt Citrate Complexes.—Our first concern was to ascertain the nature of the cobalt citrate complexes. This was accomplished by means of conductometric titrations of solutions of mono-, di- and tri-sodium citrates containing cobaltous ions.

These titrations were carried out with a Lautenschläger "Lyograph," in a cell of constant 0.52 with platinized and calcined platinum electrodes at 15 and 30°. The solutions of mono- and di-sodium citrates were prepared by mixing solutions of tri-sodium citrate and citric acid.

Figures 1 and 2 give some of our results. The breaks in curves 3 and 4 (Fig. 1) at 0.5 cc. of 1 M solution prove the presence of a compound with Co^{++}/Ci^{---} = 1. The small slope before the break indicates formation of undissociated molecules. Qualitative tests show that sodium hydroxide has no effect on the cobalt in these solutions. Figure 2 shows breaks in curves 8 and 9 at 1.5 cc. of 1 M NaH_2Ci and 0.75 cc. of 1 M Na_2HCi. These results prove that *only tertiary Ci^{---} ions take part in the formation of the complexes*.

The Catalytic Decomposition of Hydrogen Peroxide in Presence of Cobalto-citrate Complexes.—There are two phenomena to be elucidated: the transformation of the pink into the green complex and the catalytic decomposition of the hydrogen peroxide.

There are several possibilities as to the mechanism of the transformation of the pink complex. Hydrogen peroxide may not take part in an oxidation–reduction reaction, since experiments prove that cobalt is divalent in the green complex too (see below). Another possibility is that a peroxidized compound may be temporarily produced and then transposed into the green form.

The catalytic decomposition to hydrogen peroxide may also take place in several ways: hydrogen peroxide may add to the green complex forming an unstable addition compound; or oxygen atoms may add to the green complex and the resultant compound decomposes later, or the divalent cobalt may be oxidized to a higher valence and then immediately be reduced to Co^{++} with evolution of oxygen.

To test the various possibilities the quantities of two of the reactants, Co^{++}, Ci^{---} and hydrogen peroxide were kept constant and that of the third reactant was varied and the resultant changes in the system were measured by different

(1) An extensive revision of the original manuscript, chiefly concerned, however, with the presentation, was required and this was carried out under the Editor's direction. Under the disturbed international conditions now prevailing, it appeared impractical to obtain the authors' approval of this revision, and, to avoid delay, this revised version is therefore published on the Editor's responsibility.—THE EDITOR.

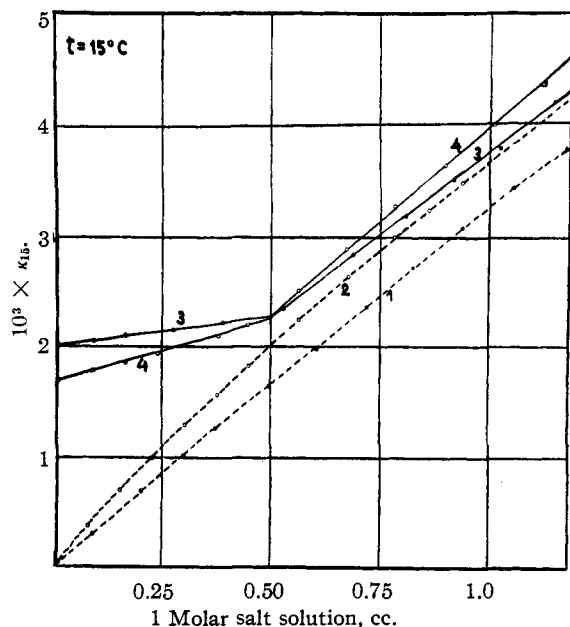(2) M. Bobtelsky and M. Rappoport, *Compt. rend.*, **205**, 234 (1937).

Fig. 1.—Conductometric titration curves, $t = 15°$: (1) 50 cc. of H_2O with $CoCl_2$ 1 m.; (2) 50 cc. of H_2O with Na_3Cl 1 m.; 50 cc. of Na_3Ci 0.01 m. with $CoCl_2$ 1 m.; (4) 50 cc. of $CoCl_2$ 0.01 m. with Na_3Ci 1 m.

Fig. 2.—Conductometric titration curves, $t = 30°$: (5) 50 cc. of H_2O with NaH_2Ci 1 m.; (6) 50 cc. of H_2O with Na_2HCi 1 m.; (7) 50 cc. of H_2O with Na_3Ci 1 m.; (8) 50 cc. of $CoCl_2$ 0.01 m. with NaH_2Ci 1 m.; (9) 50 cc. of $CoCl_2$ 0.01 m. with Na_2HCi 1 m.; (10) 50 cc. of $CoCl_2$ 0.01 m. with Na_3Ci 1 m.

methods. Optical measurements could not be made during an experiment because of the evolution of oxygen; they could, however, be carried out in solutions in which all of the hydrogen peroxide had decomposed.

(a) Preliminary Experiments.—The decomposition of hydrogen peroxide by the pink cobalto-citrate complex with simultaneous transformation of pink into green complex goes easily when the hydrogen peroxide is added to solutions containing more than 1 mole of tri-sodium citrate per mole of cobaltous chloride; in solutions with an excess of cobaltous ions the decomposition of hydrogen peroxide takes place very slowly.

Thus, e. g., 20 cc. of a solution 0.1 M in cobaltous chloride and 0.05 M in tri-sodium citrate became green ninety minutes after addition of 1.5 cc. of hydrogen peroxide. At greater dilutions light-brown precipitates were formed.

(b) Gasometric Experiments.—Experiments with variable quantities of citrate. The results plotted in Fig. 3 show that the velocity of decomposition of hydrogen peroxide tends to zero for the ratio $Na_3Ci/Co^{++} = 1$. General composition of the solutions used in obtaining Fig. 3: x cc. of 1 M cobaltous chloride + y cc. of 1 M tri-sodium citrate + $(9 - x - y)$ cc. of water and 1 cc. of 2 M hydrogen peroxide (added last). The results for $x = 0.50$ cc. are plotted in Fig. 3 (those of $x = 0.25$ cc. are similar).
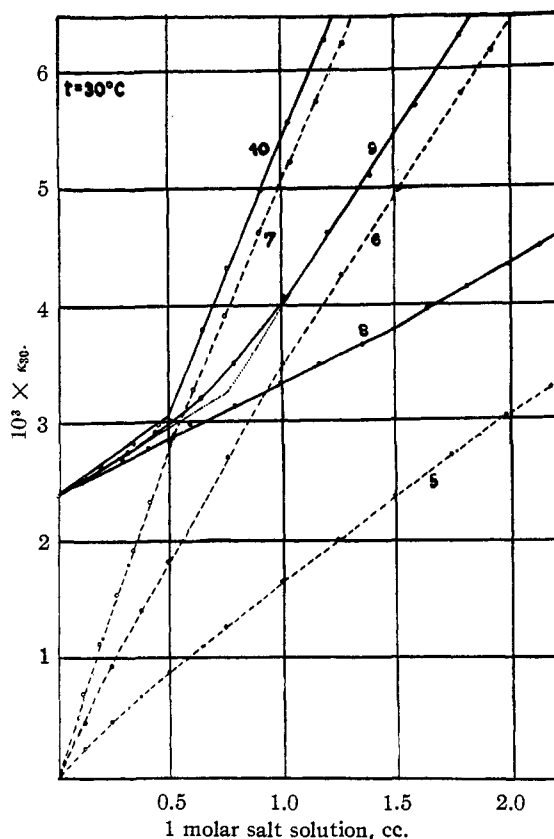
Experiments with Variable Quantities of Hydrogen Peroxide.—General composition of the solutions: 2 cc. of 0.2 M cobaltous chloride and 3 cc. of 0.2 M tri-sodium citrate + $(5 - x)$ cc. of water and x cc. of 1 M hydrogen peroxide (added last). The molar ratio $(H_2O_2)/(Co^{++})$ varied between 0.25 and 3.0. In every case 100% of the disposable oxygen of the hydrogen peroxide was evolved and the solution contained the green cobalto-citrate complex. Thus *no oxygen is used for the transformation of the pink into the green complex.* We may therefore conclude: (1) *in the final green solution the cobalt is only in the divalent state, and* (2) *citrate ion is not attacked during the reaction.*

The gasometric experiments were carried out with a specially constructed apparatus used in this Laboratory[3] permitting measurements up to 20 cc. with a precision of 0.02 cc. and enabling two experiments to be done simul-

(3) B. Kirson. Thesis. Jerusalem, 1938; M. Bobtelsky and L. Bobtelsky-Chaykin. *Compt. rend.*, **201**, 604 (1935).
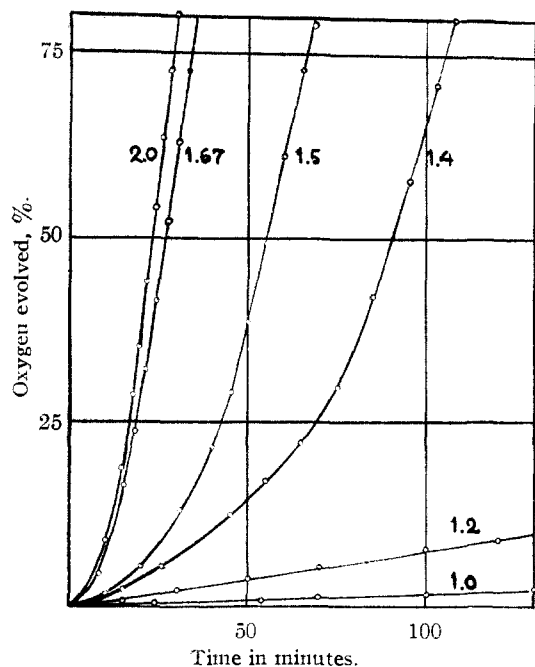
Fig. 3.—Oxygen evolved, % vs. time, at 15°, $[Co^{II}]$ = 0.05 m. The numbers on the curves indicate the ratio of ionic concns. $[Ci^{---}]/[Co^{++}]$.

taneously. The apparatus consists of two reaction vessels (glass flasks of 250-cc. volume) suspended on a rocking device seated in a water thermostat (±0.05°) and joined through rubber pressure tubes and three-way glass stopcocks to two micro-gas burets (seated in larger concentric glass tubes filled with water at room temperature). The reaction vessels are closed, after having introduced the reaction mixture, by means of rubber stoppers traversed by semi-capillary glass tubes (joined to the rubber tubes). In each rubber stopper a glass hook of about 5 cm. length is inserted on which a little glass bucket may be suspended containing the reactant to be added last. After having brought the reaction vessels to the thermostat temperature, the little glass bucket is thrown off the glass hook by sudden jarring; the mechanical rocking is then started and the evolution of gas recorded.

(c) **Conductometric Experiments.**—General composition of the solutions (30°): 1 cc. of 1 M cobaltous chloride + x cc. of 1 M tri-sodium citrate + y cc. of 1 M hydrogen peroxide (added last) + $(49 - x - y)$ cc. of water. All initial conductivity values of the mixtures with hydrogen peroxide were lower than the corresponding values for solutions containing water in place of the peroxide. The latter has a depressing action on conductivities of electrolytes.[4] From the different results obtained we show in Fig. 4 only one series with $x = 1.5$ cc. in which the concentration of peroxide was varied. In all cases the conductivity

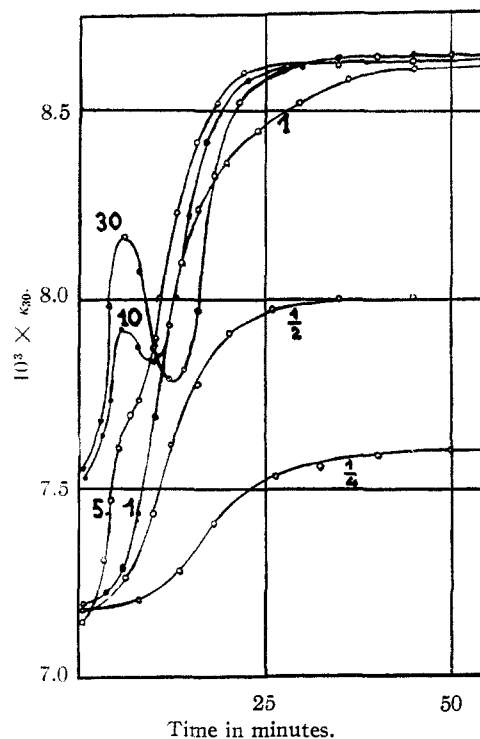(4) M. Bobtelsky and A. E. Simchen, THIS JOURNAL, **64**, 454 (1942).

Fig. 4.—Conductivity × 10^3 vs. time, at 30°—composition: 1 cc. of $CoCl_2$ 1 m. + 1.5 cc. of Na_3Ci 1 m. + (47.5 − x) cc. of H_2O + x cc. of H_2O_2 1 m. Numbers on curves represent cc. of H_2O_2.

increases during the reaction until a constant maximum value is attained in about forty minutes. The numbers on the curves of Fig. 4 show the molar ratio $(H_2O_2)/(Co^{++})$ which varies from 0.25–30. It is of interest that only when the ratio is ≧ 1 do we get a constant maximum of conductivity; as we shall see later we have in all these last cases 100% of the green complex. Thus the reaction is proven to be $1Co^{++}/1Ci^{---}/1H_2O_2$.

The appearance of relative maxima and minima of conductivity in the experiments made with greater quantities of hydrogen peroxide is the result of a specific influence of hydrogen peroxide on the conductivity of electrolytes as shown in another paper.[4] These maxima and minima are fairly reproducible and reappear after addition of hydrogen peroxide to the green cobalto-citrate complex. The lower branch of the curve, before the relative maximum is attained, does not reappear upon fresh additions of hydrogen peroxide; it corresponds to the transformation of the pink into the green complex. When carrying out gasometric and conductometric experiments of the same composition and at the same temperature (Fig. 5), it is seen that the relative maxima and

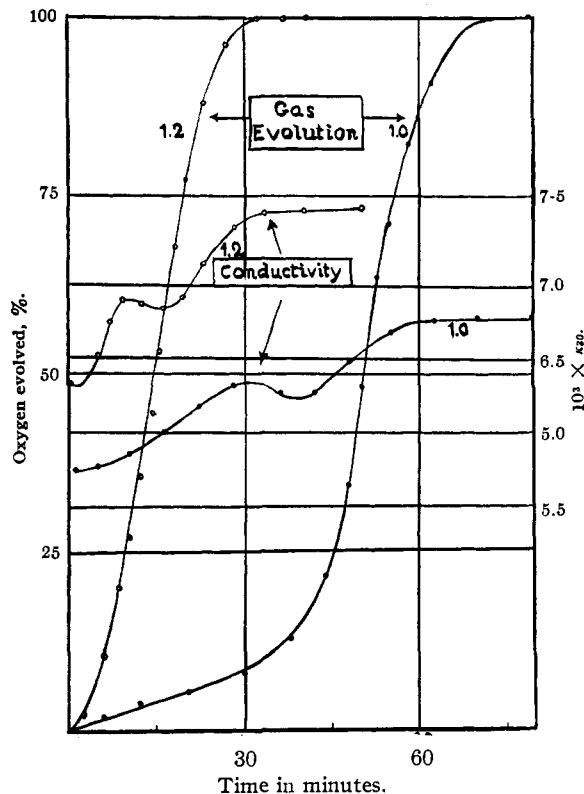minima of conductivity do not appear in the gaso-metric curve at all.

Fig. 5.—General composition: 1 cc. of CoCl₂ 1 m. + x cc. of Na₃Ci 1 m. + 10 cc. of H₂O₂ 1 m. + (39 − x) cc. of H₂O. Numbers on curves represent cc. of Na₃Ci 1 m.

(d) Optical Measurements.—Composition of the five solutions: 1 cc. of 1 M cobaltous chloride + 1.5 cc. of 1 M tri-sodium citrate + (47.5 − x) cc. of water + x cc. of 1 M hydrogen peroxide (added last). x = 0.33, 0.67, 1.0, 2.0 and 3.0 cc. After complete decomposition of hydrogen per-oxide the solutions are a mixture of the pink and the green complex. The measured percentages of green complex are plotted in Fig. 6. It is easily seen that here too the final value is obtained for $H_2O_2/Co^{++} = 1$.

The colorimetric measurements were made in a two-color colorimeter of the Duboscq type, of Hellige, using two solutions for comparison. Measurements were made at room temperature one hour after preparation in a layer 30 mm. thick. The solutions for comparison were (1) a green complex solution obtained in the above way with x = 6.0 cc. of 1 M peroxide (giving 100% green complex); (2) a pink complex solution without hydrogen peroxide (100% pink complex).

From the results of the conductometric as well as the colorimetric measurements the following conclusions may be drawn: the reaction between
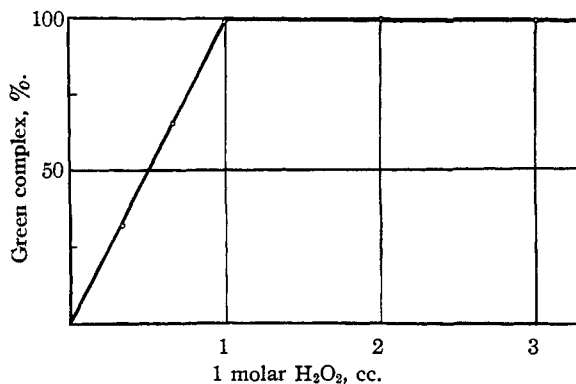

Fig. 6.—Green complex, %, vs. cc. of H₂O₂ 1 m.—composition: 1 cc. of CoCl₂ 1 m. + 1.5 cc. of Na₃Ci 1 m. + (47.5 − x) cc. of H₂O + x cc. of H₂O₂ 1 m.

hydrogen peroxide and the pink cobalto-citrate complex in the ratio $1Co^{++}/1Ci^{---}/1H_2O_2$ must go to completion almost immediately and there is no free hydrogen peroxide present during the slow transformation of the pink into the green complex.

(e) Influence of Concentrated Neutral Salts.—The influence of ammonium nitrate and chloride on the catalytic decomposition of hydrogen per-oxide by cobalto-citrate complexes has been studied by Bobtelsky and Rappoport.[2] We give in Fig. 7 results of some gasometric experiments made with and without ammonium nitrate (the chloride gives analogous results). At a concen-tration of 3 N the rate of oxygen evolution has a maximum and then diminishes with increasing concentration. The influence of electrolyte at lower concentration may be in the stabilization of the cobalto-citrate complex (similar to citrate ion concentration in excess). In the presence of highly concentrated electrolyte ($>3 N$) the green
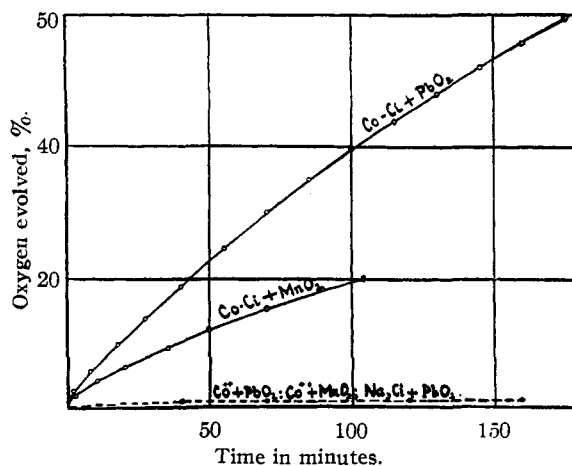

Fig. 7.

cobalto-citrate complex changes through a blue to a brick-red solution and this color remains stable for months.

Action of the Cobalto-citrate Complexes on the Solid Peroxides PbO₂ and MnO₂.—The catalytic decomposition of solid peroxides by the action of cobalto-citrate complexes was investigated by shaking the finely powdered peroxides at constant temperature (30°) with the pink and with the green complex and measuring the volume of oxygen evolved. A slow transformation of the pink complex into the green takes place with simultaneous evolution of oxygen. The last reactant added to the reaction mixture was either the cobaltous solution or the powdered lead dioxide. Composition of the reaction mixtures: with PbO₂: 4 cc. 1 M CoSO₄[5] + 12 cc. of 1 M Na₃Ci + 4 cc. H₂O + 0.5 g. PbO₂; with MnO₂: 4 cc. of 1 M CoSO₄ + 12 cc. of 1 M Na₃Ci + 4 cc. H₂O + 0.2 g. of MnO₂.

Figure 8 shows that more than half the peroxide oxygen is evolved from lead dioxide in two and one-half hours; lead dioxide is decomposed more quickly than manganese dioxide.
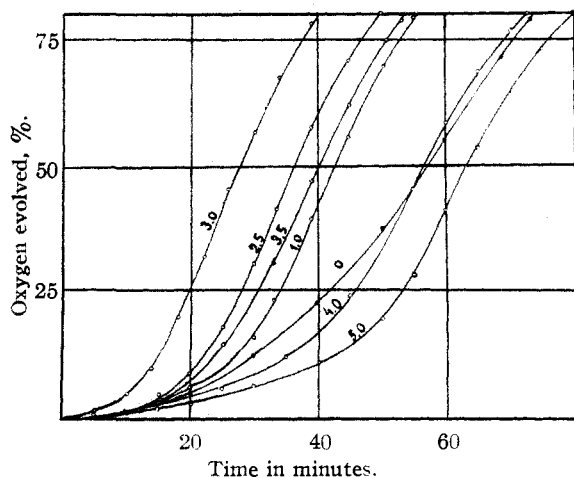

Fig. 8.—Influence of NH₄NO₃—composition: besides NH₄NO₃ the solutions contained per 20 cc.: 0.5 cc. of CoCl₂ 1 m. + 0.75 cc. of Na₃Ci 1 m. + 2 cc. of H₂O₂ 1 m. Numbers on the curves represent the final concentration of NH₄NO₃; $t = 15°$.

In the decomposition of solid peroxides it is probably not possible to speak of an addition of these substances to the pink complex; therefore, we probably have, during the formation of the green complex, *a transitory oxidation of the pink complex* followed by decomposition with evolution of oxygen. It may well be that a similar path

(5) Cobaltous chloride yields exactly the same values.

is followed during the reaction with hydrogen peroxide.

Shaking lead peroxide with a solution of the green complex formed by the action of excess hydrogen peroxide on a cobalto-citrate mixture showed that even after one and one-half hours no oxygen was evolved. *The green complex does not decompose these solid peroxides.*

The absorption spectrum of the green complex from the solid peroxides is identical with that of the green complex from hydrogen peroxide.

Comparison of Behavior of Cobalto-citrate and -tartrate Complexes.—(a) Qualitative experiments were made with Co⁺⁺- and di-sodium tartrate solutions. On mixing the two solutions a pink solution was obtained; its absorption spectrum was measured (Fig. 9) and compared to the absorption spectrum of the pink cobalto-citrate complex solution. Upon addition of hydrogen peroxide to the tartrate solution (e. g., 0.5 cc. of 1 M cobaltous chloride + 1 cc. of 1 M di-sodium tartrate + 25 cc. of water to which was added 4.5 cc. of 1 M hydrogen peroxide) a pink precipitate is formed. In the presence of still greater quantities of hydrogen peroxide the solution becomes brownish-green with precipitate and oxygen is evolved.[6]
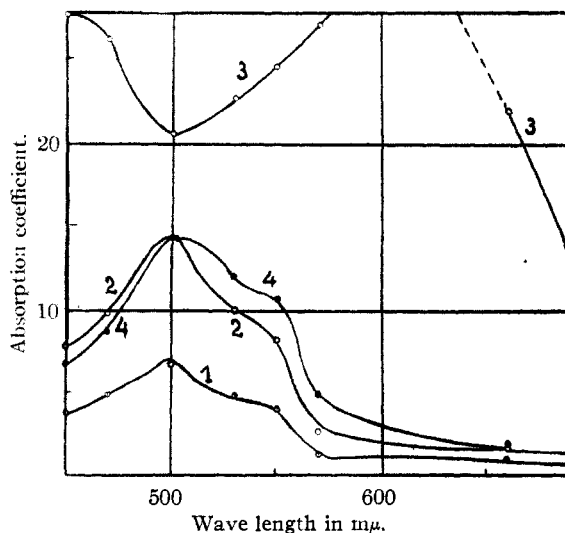

Fig. 9.—Light absorption curves: (1) CoCl₂; (2) pink cobalto-citric complex; (3) green cobalto-citric complex; (4) pink cobalto-tartaric complex.

(b) Conductometric titrations were carried out in solutions of 50 cc. of 0.01 M di-sodium tartrate

(6) Only a part of the disposable oxygen could be obtained, the tartrate having been attacked (unpublished results of M. Bobtelsky and L. Bobtelsky–Chaykin).

with 1 M cobaltous chloride and of 50 cc. of 0.01 M cobaltous chloride with 1 M di-sodium tartrate. In both cases breaks were obtained at exactly $Ta^{--}/Co^{++} = 1$ and $Ci^{---}/Co^{++} = 1$. At these points the Co^{++} ions as well as a part of the tartrate or citrate ions are bound with one another very strongly (sodium hydroxide gives no reaction with Co^{++}). From this fact the following computations can be carried out. The observed conductivities of 0.01 molar solutions were (30°): $CoCl_2$, $\kappa = 2.35 \times 10^{-3}$; Na_3Ci, $\kappa = 2.86 \times 10^{-3}$; Na_2Ta, $\kappa = 2.04 \times 10^{-3}$; and at 15°, $CoCl_2$ $\kappa = 1.70 \times 10^{-3}$; Na_3Ci, $\kappa = 2.0 \times 10^{-3}$. The ionic mobilities from a table are: $1/_3 Ci^{---}$, 60.3; $1/_2 Co^{++}$, 43; Cl^-, 65.4; Na^+, 43.5; $1/_2 Ta^{--}$, 55; acid Ta^-, 31. Table I is deduced from these values.

TABLE I

Ionic loss	$\kappa \times 10^3$ (15°) Calcd.	Found	$\kappa \times 10^3$ (30°) Calcd.	Found
$1/_2Co^{++} + 1/_3Ci^{---}$	2.98		4.16	
$1 Co^{++} + 1/_3 Ci^{---}$	2.64	2.30	3.70	3.10
$1 Co^{++} + 2/_3 Ci^{---}$	2.25		3.15	
$1/_2 Co^{++} + 1/_2 Ta^{--}$			3.36	
$1 Co^{++} + 1/_2 Ta^{--}$			2.89	
$1 Co^{++} + 1 Ta^{--}$			2.32	3.02
$1/_2 Co^{++} + HTa^-$			3.11	

It appears from the table that the last assumption is most probable in the case of citrate. There are several possibilities for the tartrate.

(c) Conductometric titrations of cobalto-tartrate complexes by sodium hydroxide and hydrochloric acid. The pink cobalto-citrate complex as well as the green complex was conductometrically titrated with 1 N sodium hydroxide and with 1 N hydrochloric acid (50 cc. complex solution contained 1 cc. of 1 M cobaltous chloride + 1.2 cc. of 1 M tri-sodium citrate). The titrations with hydrochloric acid did not give clear-cut phenomena; during this titration of the green complex solution, a slow transformation takes place of the green color into the color of cobaltous ions and the complex is destroyed (this is valid for the pink complex also).

The results of titrations with sodium hydroxide are plotted in Fig. 10. In the case of the pink complex there is a neat break at $NaOH/Co^{++} = 1$. In the case of the green complex there is probably a break at about $NaOH/Co^{++} = 2$.

The experiments described in this paper lead us to the conclusion that in the green complex, the cobalt is present in the *divalent* state. This green complex is an extremely active catalyst for the
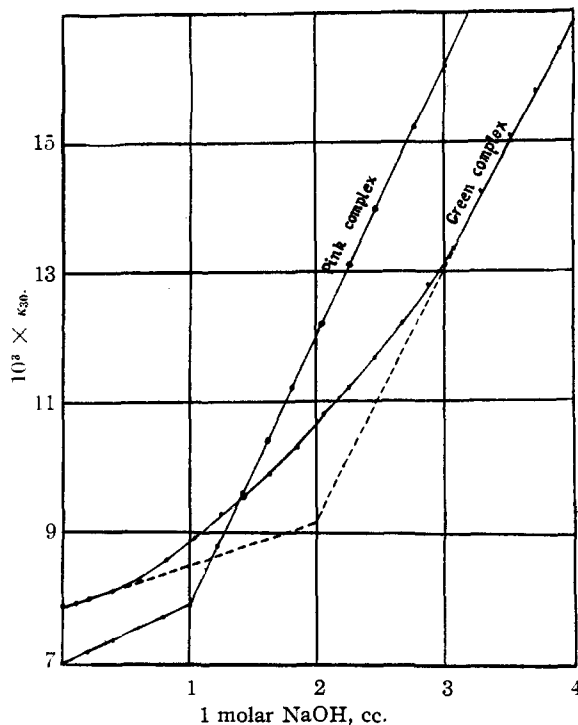

Fig. 10.—Conductometric titration curves with NaOH, at 30°: pink complex—1.0 cc. of $CoCl_2$ 1 m. + 1.2 cc. of Na_3Ci 1 m. + 47.8 cc. of H_2O titrated with NaOH 1 n; green complex: 1.0 cc. of $CoCl_2$ 1 m. + 1.2 cc. of Na_3Ci 1 m. + 42.8 cc. of H_2O + 5 cc. of H_2O_2 1 m., titrated one hour after preparation with NaOH 1 m.

decomposition of hydrogen peroxide. It is formed after a previous oxidation of the pink cobalto-citrate complex during which an intermediary peroxidized compound is produced and gradually transformed into the green complex, releasing the whole of the disposable oxygen at the same time. The green complex obtained in this complicated way is soluble in water and quickly catalyzes the decomposition of hydrogen peroxide (without itself being attacked) at concentrations as low as 10^{-6} mole g./l.

It is of interest to note that the ferric ion[7] shows in some respects a similar behavior, giving with tri-sodium citrate two[8] complexes, one of which is without catalytic activity while the second has a strong catalytic action.

The other citrate complexes of 2- or 3-valent cations (Cu^{++}, Mn^{++}, Ni^{++}, UO_2^{++}, Ce^{+++}, Pb^{++}, Al^{+++}, Mg^{++}, Ba^{++}, Cd^{++}, Zn^{++}) show scarcely any catalytic action upon the decomposition of hydrogen peroxide, they give generally one complex $Ci^{---}/Me^{++} = 1$; ferric ion on the

(7) M. Bobtelsky and B. Kirson. *Compt. rend.*, **208**, 1577 (1939).

(8) M. Bobtelsky and A. E. Simchen, *ibid.*, **208**, 1646 (1939).

other hand gives the complexes $(Fe_2Ci_3)^{---}$ (inactive) and $(Fe_3Ci_2)^{+++}$ (active). With cobalt, *both complexes, the green as well as the pink, contain divalent Co, in the ratio of $Ci^{---}/Co^{++} = 1$,* but they differ in their internal structure. The green cobalt-citrate complex proved to be the most sensitive catalyst of all the complex citrates studied by us for the decomposition of hydrogen peroxide.

The study of the structure of the citrate complexes compared with that of tartrate complexes will be the object of a special article. Di-sodium tartrate too yields with hydrogen peroxide a green complex which catalyzes the decomposition of the peroxide, but the tartrate is simultaneously attacked by the peroxide, gives a precipitate and is therefore unfit for study. The parallel study of Co^{++} and Fe^{+++}-citrate and -tartrate complexes gives a possibility for a deeper insight into the structure of these substances. It might be supposed that in the case of citrate (with only one oxy-group) complexes the hydrogen of the oxy-group is replaced by a metal valence and a stable compound is thus produced, while in the active form the metal may be found in another way through a secondary valence to the oxy-anion.

By comparison with cobalto-ammonia complexes which also catalyze the decomposition of hydrogen peroxide,[2] it seems probable that the structural difference between pink and green cobalto-citrate complexes is that in the case of the green complex the cobalt atom is linked to the citrate by a secondary valence, while the linking is much stronger in the case of the pink complex.

Summary

A mixture of Co^{++} and Ci^{---} ions (pink complex) with hydrogen peroxide in the ratio $1Co^{++}/1Ci^{---}/1H_2O_2$ immediately leads to a pink peroxidized compound (without change of color), which decomposes gradually with liberation of all the disposable oxygen into a green divalent cobalt citrate complex. This green complex can also be obtained by peroxidizing the pink cobalto-citrate complex with lead or manganese dioxide instead of hydrogen peroxide. The green cobalto-citrate complex thus obtained acts as an extremely active catalyst (the most active of all the complex citrates) for the decomposition of hydrogen peroxide, but it cannot decompose lead or manganese dioxides. During all these operations the citrates are not attacked at all while corresponding reactions with tartrates lead to attack of the tartrate ion.

The properties of the complexes were studied by gasometric, photometric and conductometric methods.

NOTES

The Catalytic Effect of Electrolytes on Solvolytic Reactions

BY L. F. AUDRIETH, L. D. SCOTT AND O. F. HILL

In a series of publications from this Laboratory[1] it has been demonstrated experimentally that ammonolytic and aminolytic reactions, involving the action of ammonia and amines upon esters, are catalyzed, respectively, by ammonium and amine salts presumably acting as acids in these solvents. In order to characterize still further the catalytic effects of various classes of substances upon solvolytic reactions in general, the influence of electrolytes (salts) upon the reactions (a) be-

tween *n*-butylamine and ethyl phenylacetate and (b) between liquid ammonia and ethyl benzoate were subjected to study. The experimental results presented below show (a) that additions of relatively small quantities of various neutral salts speed up effectively the conversion of the esters into the corresponding solvolytic products; (b) that the catalytic effect of equimolar concentrations of these salts is not nearly as marked as for the corresponding "onium" salts; and (c) that the findings heretofore considered as evidences for acid catalysis in basic solvents by the solvated proton may be but special cases of what might more properly be regarded as examples of electrolyte catalysis.

(1) See Glasoe, Scott and Audrieth, THIS JOURNAL, **63**, 2965 (1941), for earlier articles.