

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Oxygen-carrying Synthetic Chelate Compounds. III. Cycling Properties and Oxygen Production¹

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The previous papers of this series² have discussed the formation of stable peroxides by the reaction of gaseous oxygen and certain metallo-organic chelates. These peroxides, upon heating or evacuation, decompose reversibly to form the original reactants. This reversible peroxide formation and decomposition can be carried out many times, in the more favorable cases, without appreciable loss of oxygen-carrying capacity. However, upon continued cycling, one finds that the oxygen desorbed on each cycle very slowly decreases in amount, indicating a slow concurrent irreversible decomposition of the original chelate. The following study is concerned with the rate of, and the products formed by, this irreversible decomposition.

The loss of oxygen-carrying capacity of a chelate was studied by the alternate absorption and desorption of oxygen on a single sample of the chelate. The rate at which each of these two stages of the cycle proceeds depends upon the temperature and the partial pressure of the oxygen gas. The choice of these variables and the duration of each stage of the cycle was governed largely by two practical considerations. Firstly, we were concerned primarily with the balance of experimental conditions that would produce a maximum of pure desorbed oxygen in a given time with a minimum of irreversible decomposition. Secondly, the testing apparatus was designed to give results that could be duplicated on a much larger scale with commercially available apparatus.

Cycling studies, consisting of alternate oxygenation and deoxygenation with simultaneous measurement of oxygen capacity, were made on two active chelates, CoSaEn and 3F-CoSaEn. The chelate, CoSaEn, was first studied because it was the first example of successful use of such a chelate peroxide for oxygen production. Later the chelate 3F-CoSaEn was developed. Preliminary studies showed that it was less subject to irreversible oxidation than CoSaEn so it was also tested by continuous cycling.

Several factors undoubtedly contribute to the deterioration of a chelate. However, the most important appears to be an irreversible oxidation by molecular oxygen. A preliminary study by chemical analysis of the deteriorated CoSaEn was undertaken here and those data are also presented.

(1) Done under a contract (OEMsr-279) between the University of California and the National Defense Research Committee.

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(2) Papers I and II, *THIS JOURNAL*, **68**, 2254, 2257 (1946).

Experimental

Deterioration of CoSaEn.—The active form of CoSaEn can be prepared directly in water solution or can be formed by vacuum heating of a pyridinate. The material used in the particular run here reported was of the first type. It was prepared on a relatively large scale, had a lower initial capacity and a greater rate of irreversible decomposition than the active form prepared from the pyridinate on a laboratory scale. However, it was desirable to have the data as to cycling stability on the commercial product as this grade of material would have been used at that time in large scale units.

The tests were made in a double pass heat interchanger in which 860 g. of the pelleted chelate was contained in 30 one-half inch copper tubes twenty inches in length. The chelate, as received, would absorb only 83.5% of the theoretical oxygen. The theoretical absorption for this peroxide is 4.92% by weight of oxygen. The cycling tests were performed in the following way:

A stream of air (dew-point, -40°) at 90 lb./sq. in. gage pressure was passed through the tubes containing the pelleted chelate at a rate of 65 standard cu. ft./hr. Tap water was circulated around the tubes during this process to dissipate the heat of oxygenation. This first stage of the cycle continued for thirteen and one-third minutes and in this time a 2.5-fold excess of oxygen had passed through the pelleted chelate. The desorption stage of the cycle is effected by stopping the flow of high pressure air through the interchanger, release of the air pressure in the interchanger, and the passage of steam around the tubes containing the chelate. The steam is admitted at the top of the vertical interchanger and the oxygen desorbed by the chelate sweeps the remaining air ahead of it and out of the interchanger. This self-purging of the air remaining in the interchanger is sufficient to produce over 90% of the desorbed oxygen with a purity of 99%. If further purity is required the original air can be removed by evacuation before the steam is admitted to the interchanger. This desorption of oxygen is continued at atmospheric pressure for six and two-third minutes, thus completing the cycle.

The times chosen above do not permit complete oxygenation or deoxygenation to take place. The reactions are interrupted in this fashion because the completion of either the oxygenation or deoxygenation is effected very slowly. The unit, operating in this way, can produce more oxygen per unit time by more frequent cycling than could be produced by carrying the reactions to completion. This slowness experienced in the last 10–15% of the reaction is partially inherent in the chemical reaction and partially a problem of heat transfer in the cycling unit.

The unit operated with solenoid valves which were automatically controlled by an electrical timing unit.³

The experimental results are shown in Fig. 1. The upper dotted line represents the total initial reversible oxygen capacity in per cent. of the theoretical activity. This value of 83.5% was obtained by measuring the oxygen absorption of the original sample when it is allowed to come to equilibrium at these temperatures and pressures of air. The 16.5% of inactive material is made up of preparative impurities and CoSaEn in the inactive crystal form. The reversible desorption of oxygen under the cycling conditions is given by the points which are plotted against the number of cycles. This is a measure of the oxygen produced per cycle as outlined above and is somewhat less than the saturation value. It was measured di-

(3) This timing unit was constructed for us by the Arthur D. Little Co.

rectly in an integrating flowmeter. This oxygen production fell to approximately 50% of theoretical after 300 cycles and the test was discontinued. However, the saturation value was then measured again and is given by the short dotted line at 61% of theoretical as against the initial value of 83.5%.

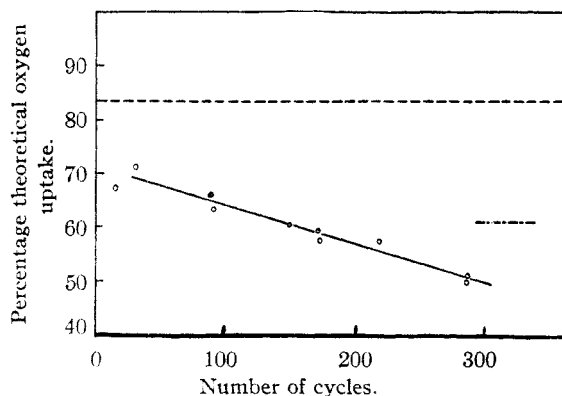


Fig. 1.—Deterioration of the parent compound: ---, initial saturation, 90 lb. air; —○—, 20 min. cycle, 13½ min. absorption; ----, final saturation.

Deterioration of 3F-CoSaEn.—This chelate can be prepared¹ as a hydrate, as a hydrated peroxide, as a piperidinate, and as a non-solvated form. All of these except the non-solvated form can be activated by vacuum heating. However, the various solvated crystals produce active chelate samples which have a somewhat different total capacity and rate of oxygenation. X-Ray studies indicate that all samples of the activated chelate possess the same crystal form. These differences in capacity presumably depend upon impurities or formation of some of the inactive 3F-CoSaEn during the activation process. The difference in rates of oxygenation² is probably caused by the differences in the shapes of the active crystals.

Preparation I.—The active material in this preparation was obtained in the following way. The red crystals of the hydrated 3F-chelate are moistened with ether in contact with air. A black peroxide is formed which upon vacuum heating loses weight corresponding to one molecule of water and one atom of oxygen per molecule of chelate. The resulting compound has a high rate of oxygenation and a capacity of 3.85% by weight (4.4% theoretical).

Preparation II.—This material is prepared by vacuum heating of the piperidinate. Each molecule of chelate loses one molecule of piperidine. The resulting compound has the highest rate of oxygenation of any of the active chelates.

The two preparations used had an initial capacity of 4.04 and 4.25% by weight.

The apparatus consists of a 0.5-inch copper tube heat interchanger containing approximately 10 g. of the pelleted chelate. Air flow, steam and water are controlled by solenoid valves. The cycle is again automatically regulated by the timing apparatus.³ The chelate is oxygenated with air at 20 lb./sq. in. gage pressure. Cooling, during this stage, is effected by circulating tap water through the interchanger. The desorption stage is carried out at 100° and one atmosphere pressure. The time cycle was determined by measuring the rate of absorption and desorption of the material in the interchanger under the experimental conditions stated above. In these initial rate capacity tests the oxygenation is carried out with pure oxygen at a pressure equal to its partial pressure in air at 20 lb./sq. in. gage. This was done because of the greater ease of measurement with these rather small samples of chelates. We had previously shown, before adopting this

procedure, that the rate would be directly comparable except that the oxygenation with air might be slightly faster because of the cooling effect of the continuous stream of air.

The time cycle chosen was three and one-half minutes for absorption and six minutes for desorption. The air flow rate was 0.68 standard cu. ft./lb./min. (a 3.3-fold excess). These times were used in testing both preparations for comparative purposes although this resulted in 82% of saturation oxygenation and 92% of complete deoxygenation in Preparation I as compared with 94 and 90%, respectively, for Preparation II.

The sample being studied was placed in the small interchanger and allowed to cycle continuously. It was again not convenient to measure the desorption volumes directly because of the small sample size. Instead the cycling was interrupted at intervals of 100–200 cycles and the rate of oxygenation and total capacity was measured with pure oxygen as previously described. However, immediately before this absorption measurement the interchanger was attached to a high vacuum line and pumped at 100° for one hour. This drying was done because we had hoped to follow the weight changes during the cycling. However, this vacuum heating could also reactivate any loss of capacity due to formation of the hydrated crystal form. Other tests lead us to believe that no appreciable hydration of this chelate would take place under testing conditions.

The data are given in Fig. 2. The per cent. of original activity is plotted against the number of cycles. It will be noted that the points now represent saturation values and not, as in the tests on CoSaEn, the absorption during the actual test. The rate of oxygenation remained constant throughout the tests so the actual absorption during cycling will be less than that indicated by approximately the percentages given above. Preparation I was cycled only with air with a dew-point of -50° but Preparation II was also tested with air with a dew-point of -10° . It is probable that the variations observed are not due to this variation in experimental conditions but rather the initial purity of the sample.

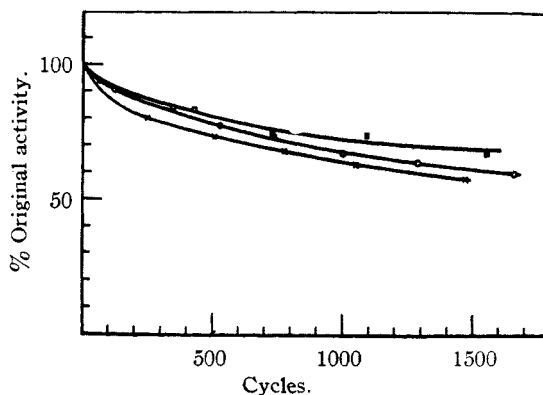


Fig. 2.—Deterioration of the 3-F compound: □, 3F active from piperidinate, air dewpoint -10° ; ○, 3F active from oxy-hydrate, air dew-point -50° ; ×, 3F active from piperidinate, air dew-point -50° .

Analysis of Deteriorated CoSaEn.—A sample of deteriorated material for chemical analysis was prepared by placing some active CoSaEn in an oven, exposed to the air, and maintained at a temperature of 110° . The reversible oxygen capacity, which was originally 4.83% by weight, was measured at weekly intervals and fell steadily. The final value, after six weeks at 110° , was 0.38% by weight. The sample was also weighed at weekly intervals and it was found to be continuously losing weight. The total weight loss over the six-week period amounted to 4.77%.

Elementary Analysis.—The deteriorated material was analyzed for carbon, hydrogen, nitrogen and cobalt as a

(4) See Ref. 2, paper I. The details of the preparative work will appear later in a paper with R. E. Bailes.

(5) See Ref. 2, paper I.

residue. The following values were obtained: C, 47.02, 47.04; H, 2.80, 2.86; N, 7.81, 7.92; Co, 18.79, 18.58 which is to be compared with the theoretical of C, 59.0; H, 4.31; N, 8.62; Co, 18.15. Approximate calculations indicate that, as an average, each CoSaEn has lost 4 atoms of C, 6 atoms of hydrogen, and a trace of nitrogen, and has picked up three atoms of oxygen.

Analysis of Cobalt Ion.—A chemical analysis for cobaltic cobalt was carried out in the following fashion. One gram of the deoxygenated deteriorated sample was dissolved in 50 cc. of glacial acetic acid. Excess saturated aqueous potassium iodide was added and the sample diluted to 100 cc. Then 10 cc. of 18 *N* sulfuric acid was added, the solution allowed to stand five minutes, and then titrated with $\text{S}_2\text{O}_8^{2-}$ using a starch indicator. The titers were equal to blanks run on undeteriorated material and indicated no cobaltic cobalt within the limit of error of the method (approximately $\pm 4\%$). A further check on the method was made by analysis of $\text{Co}^{III}(\text{OH})\text{SaEn}$. The results were of a comparable accuracy and were: experimental titer 23.8, 24.3; calculated, 21.9. The blank correction, which was not applied to above values, was approximately 1.5 cc. in good agreement with the data.

Analysis for Recoverable Salicylaldehyde.—A 0.300-g. sample of the deteriorated material was dissolved in 9 *N* sulfuric acid. The solution was steam distilled until the distillate no longer gave a purple color with ferric chloride. This required approximately 100 cc. of distillate. The condenser was rinsed with ethyl alcohol and sufficient alcohol added to the distillate to dissolve the salicylaldehyde. The *p*-nitrophenylhydrazine solution (0.8 g. of *p*-nitrophenylhydrazine, 10 cc. of ethyl alcohol, 2 cc. of glacial acetic acid, 1 cc. of concentrated hydrochloric acid, water to 25 cc.) is added to the aldehyde solution. The mixed solution is allowed to stand five minutes, and then warmed on a steam-bath ten minutes. Water is gradually added until no further precipitation of the hydrazone occurs. The heating is continued for five minutes and then the suspension is cooled in an ice-bath. The precipitate is filtered, washed with water, and dried to constant weight. 25% of the original aldehyde was found to be present. A blank run with undeteriorated CoSaEn yielded 100 \pm 2% of the original salicylaldehyde as the hydrazone; m. p. 225–226°.

Determination of Primary Aliphatic Amino Nitrogen.—A sample of the deteriorated CoSaEn was dissolved in the absence of air, in 5 cc. of 6 *N* hydrochloric acid. The reaction vessel was cooled in an ice-bath and 5 cc. of an ice-cold solution of sodium nitrite (1 g./cc.) was added. After one to two minutes, the reaction vessel was warmed, and the liberated gases swept with carbon dioxide into a gas burette containing alkaline permanganate. The alkaline permanganate solution absorbs the carbon dioxide and nitric oxide resulting from decomposition of the nitrous acid. The nitrogen gas, produced by reaction of a primary amine and nitrous acid, is measured directly. The following results were obtained. For undeteriorated CoSaEn, cc. N_2 found 21.3, 21.7; calcd. 21.5. For the deteriorated material, cc. N_2 found 8.6, 7.2; calcd. 21.5.

Spectroscopic Determination of Salicylic Acid.—Solutions of salicylic acid are found to have an absorption maxima at approximately 3070 Å. Solutions of the deteriorated CoSaEn were also found to have a maximum absorption peak at this wave length. However, the deteriorated material contained other unknown substances which gave a background absorption in this region and no quantitative estimates could be made as to the amount of salicylic acid in the deteriorated samples. The data are summarized in Table I.

TABLE I

Reversible oxygen-carrying capacity	7.8% of orig.
Recoverable aldehyde from deteriorate	25% of orig.
Primary amine in deteriorate	36% of orig.
Salicylic acid in deteriorate	Present
Cobaltic cobalt in deteriorate	Absent

Discussion

The deterioration of CoSaEn, as measured by its oxygen production in the given experimental cycle, appears to be almost proportional to the number of times it has been cycled. However, this linearity may well be fortuitous as a number of chemical and physical changes may be contributing to the deterioration. The curves for the 3F-derivative differ most markedly, aside from the compound's greatly increased stability to cycling, in the rather sharp initial drop in capacity and later in a marked departure from linearity.

The initial rapid loss of capacity, in the case of the 3F-chelate, suggests that at least one of the processes contributing to the deterioration is operating only during the first few hundred cycles. We are inclined to believe this is due to the presence of small amounts of impurities, which are coprecipitated during the preparation of the chelate, and are reacting chemically with the active chelate and destroying it. However, one is forced to assume, if this explanation is correct, that the inert material in the CoSaEn acts in a somewhat different manner. This assumption is not unreasonable when one considers the complexity of the process.

The 3F-CoSaEn, it will be noted, contains far less inert material than does the CoSaEn. It may be, therefore, that the small upward curvature observed later in the deterioration curve is the more normal type of behavior for a pure chelate. A plot of the same data for the 3F derivative on a logarithmic scale is fairly linear except for the initial region discussed above. One can readily derive such a law for the deterioration if one assumes the same fraction of the active chelate is lost by deterioration on each cycle. This assumption, however, could also hardly be correct over a large range of deteriorates except as a first approximation, since, as we shall see, many factors are contributing to the measured effects.

It was previously stated that irreversible oxidation was considered one of the principle causes for loss of capacity. It can be seen that this destructive oxidation may appear at one or several points in the process. The oxygen must initially diffuse through the unoxxygenated chelate to the phase boundary where the peroxide formation is taking place. There the peroxide is formed from the transition state molecule with concurrent motion of the crystal lattice. The peroxide is then exposed to oxygen until the desorption is initiated with reversal of the path of oxygen through the transition state and motion of the crystal lattice back to its initial positions. We have only one piece of data that helps evaluate the relative chance of destructive oxidation in the above steps. It is known that the oxygen capacity is lost very slowly, even at 100° in contact with one atmosphere of oxygen, if the chelate is stored in its unoxxygenated form. Apparently, either the peroxide or the transition state molecules undergo

most of the destructive oxidation. Loss of a constant fraction in either of these steps would explain the logarithmic plot.

Certain other processes are known to contribute to the deterioration. X-Ray examination of the deteriorates⁶ reveals that the deteriorated samples contain much amorphous material. In addition, in the case of CoSaEn, the powder patterns show lines due to the inactive CoSaEn. This crystal form is the thermodynamically stable one under the experimental conditions and the active form is slowly recrystallizing to this more stable crystal form.

The X-ray examination also showed another interesting effect. Powder patterns of the deteriorated peroxide, of CoSaEn, even after exposure to oxygen for many hours, showed lines due to the unoxygenated active crystal form. The presence of this active material and large amounts of amorphous material, under conditions where one would have expected all of the active material to be converted to the peroxide, seemed to indicate that regions of active material had become surrounded by an amorphous material that oxygen could not penetrate. This is presumably mainly caused by the destructive oxidation.

We were able, by sublimation, to grow a single active crystal of CoSaEn. This crystal, whose dimensions were 0.29 mm. \times 0.03 mm., was observed in a microscope stage during four cycles of absorption and desorption of oxygen. It was seen that considerable strains set in at each absorption of oxygen and the crystal had broken into many small fragments after the four cycles. It is possible that if such a process were continued, even though the strains and cracking were less pronounced with the very small crystals, the active material might eventually be broken into particles small enough to give amorphous scattering of the X-ray beam. In fact, if this process continued far enough, it might result in actual loss of oxygen-carrying capacity. This would be expected if certain regions of the crystal, as for example the surfaces, were unable to form peroxide molecules.

The analytical data are available only in the deteriorated CoSaEn. Further, it will be noted that the deterioration was carried out by oven heating at 110° and not by cycling. The oxygen equilibrium pressure at 110° is considerably above the oxygen pressure in air and any destructive oxidation must have resulted largely from the action of oxygen on the unoxygenated active crystals. It is possible that the chemical nature of the

deteriorated material, produced under these conditions, differs somewhat from that produced by cycling.

Two main conclusions can be drawn from the data in Table I: It can be seen that the oxygen capacity decreases far more rapidly than does the amount of recoverable aldehyde or primary amine. This is understandable in view of the results of the X-ray analysis. Secondly, the destructive oxidation does not appear to result in the formation of cobaltic cobalt. This conclusion can be deduced from the above facts only if, in the process of solution, any cobaltic cobalt present was not reduced by other products formed to the cobaltous valence state. However, a magnetic study of the deteriorated solid leads to the same conclusion. These measurements showed that the deteriorated samples had, at most, only a few per cent. of cobaltic cobalt.

Neither the point of attack by the oxygen nor the products formed by it can be deduced from these studies. However, the close proximity of the peroxide oxygen to the imine double bonds would lead one to suppose that the initial attack might be there. The actual isolation of these primary products is rendered difficult for several reasons. Further reaction, either with oxygen or chelate molecules, appears to take place. The badly deteriorated samples always contain colored poorly-soluble materials of high molecular weight. Secondly, the relatively high temperature and flow of gas in these experiments would lead to volatilization of any of the more volatile products.

The available data are unfortunately far too meager to draw conclusions on the cycling stability of the substituted chelates. The problem is not simply one of the effect of substitution at the three position on the reactivity of the isolated molecule. Such substitution must also change, at least slightly, the crystal structure itself. The reactivity of certain atoms of the chelate in such a condensed phase would probably change markedly with either electronic or steric interaction between adjacent molecules. It is, however, interesting that the introduction of the fluorine atom, a substitution which in general contributes to unreactivity, so markedly increases the cycling stability.

Summary

A study of the cycling properties of two oxygen-carrying synthetic chelate compounds has been made. The factors influencing the cycling properties and stability are discussed.

(6) The details of this will appear in a paper by E. W. Hughes.