of any of the three gases studied, nor to the rate of adsorption of carbon dioxide.

The rate of interaction of carbon monoxide with four representative catalysts at 20° and 76° has been investigated by measuring the decrease in pressure, and analyzing the gases after removal by evacuation at the end of a five-hour period. The rate of reoxidation by oxygen of the partly reduced materials was then determined in a similar manner.

Both the rate of interaction with carbon monoxide and the initial rate of reoxidation are greater for the mixtures than for the single oxides.

The behavior of copper oxide toward carbon monoxide differs greatly from that of manganese dioxide. In the latter case there is only one rate-determining step, the conversion to carbon dioxide is ultimately nearly complete, and the total adsorption coincides closely with that of carbon dioxide. In the case of copper oxide there are two rate-determining steps, the second of which is slower than the first. The result is that at 20° a large amount of carbon monoxide is held firmly by copper oxide, and the total adsorption is finally much greater than with carbon dioxide. The first step in this reaction and the single step in that with manganese dioxide are believed to be electronic rearrangements after rapid adsorption of small amounts of carbon monoxide.

In the reaction of the mixtures with carbon monoxide the component oxides appear to retain their characteristic properties, except that in each case the speed of the electronic rearrangement is increased.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF THE CRYSTALLIZATION OF SOME METAL LACTATES

BY F. C. KRAUSKOPF AND ALBERT S. CARTER

RECEIVED DECEMBER 28, 1925 PUBLISHED JUNE 5, 1926

Introduction

The preparation of barium lactate as a reagent for the preparation of ethyl lactate led to observation of the fact that this salt did not crystallize except in alkaline solutions. Very limited investigations seemed to indicate that neutral or slightly acid solutions would give a thick sirup, whereas, similar preparations of the salt containing a very marked excess of the base, barium hydroxide, would first form a sirupy mass and upon continued dehydration, would solidify with the formation of crystals of the salt. This peculiarity was considered of sufficient interest to justify further study.

Very little literature could be found on the salts of lactic acid, with the exception of those salts of the metals used in the purification of the acid and a few pharmaceuticals. Mention, however, was made of the sirupy formation and it was even suggested that this had, at one time, led to the impression that barium lactate was not a solid. Engelhardt and Maddrell[1] describe several salts of lactic acid giving some discussion of their preparation and in almost every case they mention the fact that the salts did not crystallize from solution, but it was necessary to dehydrate them as sirups with thick surface films. They also mentioned the preparation of acid salts in the presence of excess of acid. This latter result could not be duplicated, as will be discussed in this paper.

Hans Meyer[2] also mentions the formation of a thick, colorless sirup which was crystallized with difficulty in the formation of crystalline barium lactate.

Experimental Part

The Nature of the Semi-liquid Mass.—Preliminary experiments indicated that the solutions of prepared barium lactate would successfully crystallize only if heated for several days on a water-bath in the presence of an excess of the base, barium hydroxide. During this process of crystallization, the solution first became very thick and finally this viscous mass solidified into an aggregate of apparently rectangular needles. A neutral solution, under the same conditions did not solidify, but remained in the same semi-liquid state which was found to be characteristic of an acid solution of barium lactate. It was observed that the form could be varied from a solid, apparently amorphous mass in neutral solution, similar to brown glass, to a viscous liquid, the viscosity depending upon the variation of the acid concentration. Further, it was observed that the salt could be recrystallized from neutral solutions of the previously crystallized salt, but did not solidify when small amounts of acid were added to the solution.

Three methods were used in the preparation of barium lactate to obtain it in acid, neutral and basic solutions. These preparations were repeated from time to time throughout the experimental work for comparisons and to replenish the stocks of lactate. Each of the methods produced a characteristic form of the salt, and repeated runs of the same method gave lactates of the same physical nature.

Attempts were made to prepare barium lactate in acid solution by titrating concd. barium hydroxide solution with concd. acid to neutrality, and adding an excess of 1 cc. of the acid. Evaporation of this solution gave a very thick, viscous liquid which did not crystallize or solidify during heating on the water-bath for a month.

To prepare barium lactate in basic solution, pure commercial 90% lactic acid was diluted to about four times its original volume and treated with

[1] Engelhardt and Maddrell, *Ann.*, **63**, 83 (1847).

[2] Meyer, *Ber.*, **19**, 2454 (1880).

solid barium hydroxide, 30% in excess of the equivalent amount being added. This was slowly heated on the water-bath for several days, with the formation of a thick sirup. Upon continued heating, a week generally being necessary, this sirup solidified with the formation of crystal masses which were apparently rectangular needles. To remove the excess of barium hydroxide, these crystals were again dissolved and the solution was subjected to a stream of carbon dioxide as long as there was any precipitation of barium carbonate. After filtration and recrystallization, the remaining barium hydroxide was removed by continued washing with ethyl alcohol, in which the barium lactate was found to be insoluble. The crystallization of barium lactate after treatment with carbon dioxide was approximately as rapid as crystallization in the presence of excess of the base, and thus more rapid than in neutral solution.

Concurrent with the preparation of barium lactate in basic solution, the salt was made in neutral solution. Concd. lactic acid was titrated with concd. barium hydroxide solution (approximately 5.5%) to neutrality; since the end-point was not definite, 0.5 cc. of the base was added in excess and removed at the end of three hours by back titrating with sulfuric acid to precipitate the barium. (Phenolphthalein was used as the indicator throughout these operations.) After being filtered, this solution together with the sample being prepared in the excess of the base was placed on the water-bath and the two were evaporated under the same conditions. A sirup first resulted, similar in every respect to that obtained in the basic solution, but upon continued evaporation, no crystals were obtained. Under no conditions (acid, basic, or neutral solution) was it possible to cause crystallization by "seeding." The mass from neutral solution solidified into a glassy, yellow-brown, amorphous solid after being evaporated for 16 days.

The Influence of Anhydride.—The anhydride forms of lactic acid, particularly the "lactide" form, are relatively inactive, and it was thought that these forms might exert some influence upon the crystallization of the salts.

The lactide form is the most common anhydride, resulting upon distillation of the acid and is probably present in most samples of the acid. Samples of the acid used throughout this experimental work showed a much greater acidity when warmed on a water-bath for several days with an excess of the base and back titrated, than when titrated to apparent neutrality and allowed to stand for four hours in the cold before being back titrated. This not only seems to indicate the presence of lactide, but also that its hydrolysis is slow and demands a high concentration of alkali. This being the case, it may not only be present to some extent in acid solutions, but also in neutral solutions, as it has but slight acid properties. Kraft and Dyes[3] state that lactide and lactic acid anhydride are readily

---

[3] Kraft and Dyes, *Ber.*, **28**, 2591 (1895).

formed by heating lactic acid to 140° and even by continued standing in the cold in a desiccator.

It is possible that the presence of lactide in the solution hinders crystallization. It is not probable that any other of the anhydride forms of the acid would be effective, for, with the exception of the acid anhydride, they are not readily formed and the acid anhydride which is formed, is readily hydrolyzed. Such being the case, in acid or neutral solutions, which might contain lactide, no crystallization would occur, but in the presence of excess base, the lactide would be removed by hydrolysis.

With this idea in mind, we might expect: (1) immediate crystallization in the absence of the lactide; (a) salts would be recrystallized from solutions where there could be no lactide formed; (b) salts could be prepared from other salts by double decomposition where presence of lactide is avoided and crystallization accomplished; (2) the crystallization of the barium salt could be made impossible through the addition of lactide to a solution which would otherwise crystallize, that is, one free from lactide.

The following experimental work gives considerable evidence for the acceptance of this theory. Lactic acid was heated with a large excess of barium hydroxide for two days to hydrolyze the lactide which might be present. This solution was then treated with sulfuric acid to free the acid and precipitate the barium. After removal of the barium sulfate, titration of the dilute acid showed a rather sharp end-point and upon evaporation of the neutralized solution, a crystalline solid was obtained with the same ease as in the presence of excess of the base. By this method, the presence of lactide would be avoided unless it were formed during the small interval of time between the liberation of the acid with sulfuric acid and the time of neutralization with barium hydroxide in the formation of the salt. Hence, these results would seem to be in agreement with the idea suggested in (1) above.

Frequent recrystallizations were attempted and in each case where the conditions were such that the formation of lactide was avoided, they were successful. However, when a small amount of the acid liberated through the addition of a few drops of sulfuric acid was present, the crystallizing ability of the system was very markedly decreased, probably through the formation of lactide during evaporation. In connection with this, when a very small amount of sulfuric acid was added, thus forming a small amount of free lactic acid, and the solution was allowed to evaporate at room temperature to the sirupy stage, it was found possible to obtain crystals around the edge of the dish even in slightly acid solution. This would seem to indicate that it was not the acid which was the cause of the decrease in crystallizing ability of the salt, but the lactide, which would not be formed to a very great extent in the cold solution. Continuing this idea, it might be possible to convert this free acid into lactide, in the solution and thus inhibit the crystallization. To accomplish this, the evaporated, sirupy mass was heated at 120° until it became very viscous. Upon cooling, this solidified into a glassy, amorphous mass similar to those obtained in neutral solutions. The few crystals which had previously formed around the edge of the dish were absorbed by the mass during the heating and there was no evidence of crystallization. Attempts were made to obtain crystals from this by resolution and slow evaporation in the air, but it was impossible. It has, then, been possible to produce partial crystallization in a solution which is slightly acid, but which probably does not contain lactide, and upon conversion of this free acid to lactide, the crystallizing ability of the solution has been lost. These results are in perfect agreement with point 1 above.

Preliminary runs in the presence of excess of base seemed to indicate that the salts of the alkali metals with lactic acid would not readily crystallize. From the literature on the purification of lactic acid, it was known that zinc formed a crystalline lactate, hence zinc sulfate was chosen as a very suitable salt from the standpoint of its solubility for the preparation of a metal lactate by double decomposition with barium lactate and precipitation of barium sulfate. $Ba(CH_2CHOHCO_2)_2 + ZnSO_4 = Zn(CH_3CHOHCO_2)_2 + BaSO_4$. Zinc lactate was prepared in this manner and by comparing this with zinc lactate prepared in basic solution from zinc hydroxide and lactic acid, it was found that the crystallizing ability was as great, if not greater. This indicated that crystallization in neutral solutions was made possible through operations which avoided the presence of lactide.

A solution of barium lactate in water was divided into two samples of equal volume. These were evaporated to the thick, sirupy stage and to one of them was added some previously prepared lactide. The sample to which no lactide had been added crystallized upon evaporation on the water-bath, but the sample to which the lactide had been added, crystallized only in part. Since the solution was very thick and viscous when the lactide was added (beginning to show crystallization at the edges), it was possible to bring about crystallization within a half hour, as far as it would go. This, together with the slight solubility of the lactide, prevented it from diffusing through the entire mass, and thus its effect was only local. A second run was made in a similar manner, but this time the lactide was added before the evaporation had gone as far; following the addition, the solution was stirred at intervals during the crystallization. Thus the lactide was kept suspended throughout the entire mass and could not collect in drops. The stirring hastened the crystallization of the barium lactate containing no lactide, but there was no evidence of crystals in the sample containing the lactide.

It was thought that if the lactide could be mechanically removed from these solutions which had only partially crystallized and recrystallization of the product successfully accomplished, it would aid greatly in showing that the lactide was the effective factor. To carry this out, the drops of lactide were picked out of the mass as far as possible; the remainder was rapidly put in water solution and immediately filtered, thus removing the most of the undissolved lactide before it had sufficient time to enter the solution. Upon evaporation of this solution a fair crystallization was accomplished. The product did not form as fine white crystals as were previously obtained upon recrystallization of pure barium lactate, but it was sufficient to indicate that the lactide was of importance in the prevention of the crystallization.

In order to insure that the product was the same in the samples containing the lactide as in the original barium lactate, analyses of the various products were made. Two-g. samples dried at 120° for one hour were analyzed by first igniting them to barium nitrate with decomposition of the lactate by roasting with five cc. of concd. nitric acid. The product was boiled to dryness twice with five cc. of hydrochloric acid and then taken up in 150 cc. of water containing one cc. of hydrochloric acid. Barium sulfate was precipitated by bringing the solution to the boiling point and adding sulfuric acid solution. This precipitate was allowed to stand overnight, filtered through a quantitative filter paper, dried and ignited, at first carefully, and then at a cherry-red heat until white.

The following results are the averages of four analyses of each of the five different products, expressed in grams of barium per gram of sample.

a. Original barium lactate: 0.4363 g.

b. Product obtained by recrystallization of barium lactate: 0.4359 g.

c. Semi-liquid product obtained in the regions near to the drops of lactide in the first run (not agitated): 0.4334 g.

d. Amorphous mass produced in the run where the lactide had been thoroughly diffused (excess of lactide filtered out of sample): 0.4344 g.

e. Sample from recrystallized product in the solution where the lactide had been mechanically removed: 0.4350 g.

The calculated amount for barium lactate is 0.4354 g. of barium per gram of sample.

The results of these analyses indicate the same product in each case. The difference in the cases where lactide was present is surprisingly slight; hence, the solubility is sufficiently small to have very little effect upon the value of the barium content of the samples, yet it is sufficient to cause the recorded effects upon the crystallization. The efficacy, therefore, of the small amount dissolved must be great, if it is the factor controlling the crystallization.

The results of the work on these two points, as outlined above, together with the general observations, seem to indicate quite definitely that the lactide is the controlling member in a system from which the crystallization of barium lactate is being attempted.

This effect of lactide upon the crystallization forms an interesting comparison and may be closely related with work carried out in this Laboratory by Walton and Jenkins[4] upon the velocity of crystallization. Their results indicate similar inhibiting effects in consequence of the presence of foreign materials. It was also found by their results that the crystallization velocity of lactose anhydride was decreased through the secondary reaction forming the hydrate: lactose anhydride + H_2O = lactose hydrate.

Possibility of Complex or Basic Salts.—Before coming to the conclusion that the lactide was the important factor controlling the crystallization it was thought that perhaps some acid salt or complex was formed in acid and neutral solutions or basic salts in alkaline solution, which controlled the crystalline nature of the product. By analysis the nature of these products was shown to be the same and to correspond to the normal salt; hence, the possibility of complexes was excluded. The analysis gave 0.4306 g. (average) of barium per gram of sample from the amorphous salt and 0.4319 g. from the crystalline salt. The calculated value would be 0.4354 g. of barium per gram of sample.

Mechanics of the Effect and Influence upon Other Salts.—The sirupy masses and apparently amorphous substances prepared in the presence of lactide display a Tyndall effect with some polarization. This is also true to a less degree in the case of the sirup formed just before crystallization in the absence of lactide. This would indicate that the manner in which the lactide inhibits the crystallization of barium lactate is, perhaps, a colloidal phenomenon. Even in the absence of lactide, the barium lactate evidently tends to form a colloid which is precipitated upon standing during continued evaporation. It is probable that the lactide acts as a protective colloid, delaying the precipitation of the colloidal salt. Such protective action could be possible in the presence of such small amounts of the agent as seems to be the case in this work. Bechhold[5] shows that two drops of a 1% solution of gelatin will delay for twenty-four hours the precipitation of a suspension of mastic containing magnesium sulfate, which would have precipitated in 15 minutes in the absence of the small amount of gelatin. The stability of the colloidal barium lactate is increased by the protective action of the lactide and the lactate is not precipitated by evaporation. When an excess of the base is present, it is the influential factor in the conversion from the stable to the unstable form of colloid and also may act as the electrolyte causing its precipitation.

If the effect of lactide is that of a protective colloid, it might be expected that it would have a similar effect upon the other salts of lactic acid if they tended to form a sirup. Tests were made by preparing various salts through double decomposition of a sulfate with barium lactate,

---

[4] Jenkins, This Journal, **47**, 903 (1925).

[5] Bechhold, *Z. physik. Chem.*, **48**, 408 (1904).

or through direct treatment of the acid with an alkali. In each case, it seemed apparent that the lactide had the same effect as upon the barium salt, for in concurrent runs of the salts without lactide and solutions containing lactide, crystallization was accomplished with greater ease in its absence. In the course of this work, there was found a certain parallelism between the ability to crystallize and the basicity of the metal used in forming the salt. Thus it was found among the metals used that the zinc salt crystallized most readily; it crystallized even in the presence of lactide but, on the other extreme, the salt of cesium remained a liquid regardless of the amount of standing or desiccation applied to it. Intermediate between these two fell magnesium, calcium, strontium, barium, lithium, potassium and sodium, with decreasing rapidity of crystallization in the order named. Sodium and potassium, falling at the bottom of the list, gave no solid form, but a very thick sirup. Doubtless we have two factors to deal with here; (a) a decreasing tendency to form a solid phase under ordinary conditions, which would be a specific property of the salt, perhaps closely related to solubility and, hence, probably the more important; and (b) the effect of the lactide upon the formation of crystal nuclei or upon their growth. There is a possibility that the increasing basicity of the metal increases the efficiency of the colloidal protection or the tendency to form colloids, but this would probably be overshadowed by the specific tendency of each salt to form crystals.

Summary

It has been shown that from a solution of barium lactate containing an excess of barium hydroxide, normal barium lactate crystallizes in apparently rectangular needles. A neutral solution or one containing a small amount of free lactic acid will evaporate to a thick sirup and in certain cases to a glass-like solid with no tendency to formation of crystals. By analysis the barium content of the crystals and the amorphous, glass-like solid is shown to be the same, corresponding to the formula of normal barium lactate.

The production of definite crystalline forms is more difficult in the salts of the more positive metals; thus crystalline lactates of the alkali metals could not be obtained.

It has been shown that the lactide anhydride of lactic acid plays an important part in the crystallization of the metal salts of lactic acid. Salts which are easily crystallized in the absence of lactide are generally found to crystallize with difficulty or not at all when the anhydride is present. A possible explanation of the effect of the lactide is suggested.

MADISON, WISCONSIN