

Studies in Precipitation from Homogeneous Solution by Cation Release at Constant pH

Part I. Oxidation of EDTA Solution by Hydrogen Peroxide*

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Precipitation from homogeneous solution by cation release at constant pH may be achieved by the controlled release of cations from their EDTA complexes by oxidation with hydrogen peroxide. A study has been made of the effects of variations in concentration of hydrogen peroxide and pH of solution on the rate of oxidation of EDTA solution. The presence of certain precipitates has been found to be detrimental, causing rapid break-down of the hydrogen peroxide, thus rendering the method ineffective. This may be overcome by the addition of phosphate ions and the precipitation of metal phosphates.

THE object of precipitation from homogeneous solution is to bring about precipitation at a slow, controllable rate from an initially unsaturated solution, resulting in the formation of larger, more perfect crystals, with fewer errors owing to adsorption and co-precipitation. This is achieved by generating the necessary ions by chemical reaction in the solution. The technique has been widely applied to the precipitation of many compounds; much of the earlier work has been collected and described by Gordon, Salutsky and Willard.¹

The methods employed may be broadly classified as pH increase, anion release, cation release and synthesis of the precipitant *in situ*. Methods of pH increase and anion release have been studied by earlier workers,¹ and methods involving the synthesis of the precipitant are restricted to use with certain organic reagents.^{2,3,4} Comparatively few instances have been reported of the use of cation release, in which the cation to be precipitated is first held in solution as a complex and subsequently released by the slow, controlled destruction of the complex in the presence of a suitable anion.

Cation release may be brought about either by changing the pH of the solution to a value at which the complex is no longer stable or by chemical attack of the complex at constant pH. The former has been used for precipitating barium sulphate⁵ and silver chloride^{6,7} and the latter has been described by MacNevin and Dunton⁸ for precipitating hydrated iron oxide and by Gordon, Salutsky and Willard for precipitating hydrous thorium oxide. MacNevin and Dunton obtained dense precipitates of hydrated iron oxide by oxidising an EDTA - iron complex with hydrogen peroxide, but Gordon reported that the precipitates of hydrous thorium oxide obtained by oxidising an EDTA - thorium complex were unsatisfactory from the analytical viewpoint.

MacNevin and Dunton's paper was short and contained few details of experimental work. Thus, although the rate of oxidation of EDTA solution by hydrogen peroxide was studied at various pH values, the effects of variations in pH were not reported. The rate of oxidation of EDTA was said to be slower in the presence of ferric iron and was accompanied by the evolution of oxygen.

It was considered that a more thorough investigation of the method of cation release by oxidation of metal complexes at constant pH would allow the value of the technique to be more fully assessed. The use of EDTA as the complexing agent was of particular interest, since it forms water-soluble complexes with many cations and since the conditions of complex formation and factors influencing complex stability have been widely investigated. Hydrogen peroxide was a suitable oxidising agent, since the products of its break-down—water and oxygen—were not likely to interfere in any precipitation reaction.

To obtain a fuller understanding of the reactions involved it was first necessary to investigate the break-down of EDTA in solution by hydrogen peroxide. This paper describes

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experiments carried out to determine the effects of variations in pH and in concentration of hydrogen peroxide and the effect of the presence of precipitate particles.

EXPERIMENTAL

REAGENTS—

EDTA—Disodium ethylenediaminetetra-acetate dihydrate.

Hydrogen peroxide, 100-volume—Analytical-reagent grade.

All other reagents were of analytical grade.

APPARATUS—

All volumetric glassware was calibrated before use. During precipitation from homogeneous solution it was essential to use unscratched beakers to avoid losses owing to adherence of the precipitates to the walls of the vessels. All pH measurements were made to the nearest 0.05 unit of pH with a Pye meter having a glass electrode and a calomel reference cell.

METHOD

1. Variations in pH and concentration of hydrogen peroxide

Reaction solutions consisted of 2 g of EDTA, different amounts of 100-volume hydrogen peroxide and water to a total volume of 300 ml. The pH of each solution was adjusted to the required value by the addition of nitric acid or ammonia solution.

Reactions were carried out in a flask fitted with a reflux condenser and a thermometer to measure the solution temperature. During the reaction the flask was placed in a boiling-water bath to maintain a reaction temperature of 98° to 100° C.

EDTA and the necessary amount of water were placed in the flask, and were brought up to the required temperature; the hydrogen peroxide was then added. Timing of the reaction began when the solution temperature again reached 98° to 100° C. Samples of reaction solution were withdrawn at intervals and cooled, and the amounts of EDTA remaining in solution were determined by titrating with standard bismuth solution, pyrocatechol violet being used as indicator. The effects of variations in pH and concentration of hydrogen peroxide were studied; a blank determination was carried out in the absence of hydrogen peroxide. The results were expressed graphically by plotting the logarithm of the concentration of EDTA remaining in solution against time; straight-line graphs were obtained from which values for K , a constant for the rate of reaction under the conditions of the experiments, were calculated. The variation of K with changes in concentration of hydrogen peroxide and pH is shown in Figs. 1 and 2.

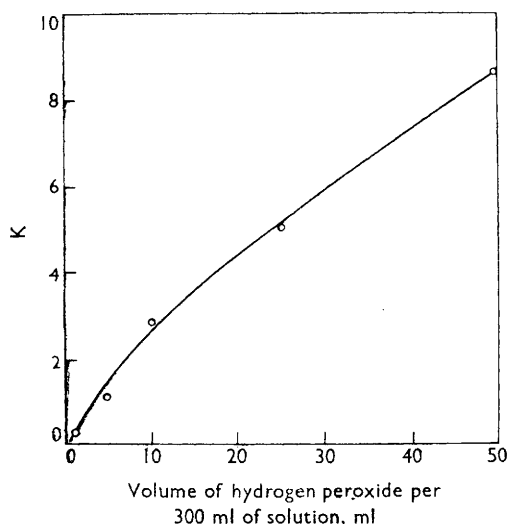


Fig. 1. Effect of variation in hydrogen peroxide concentration

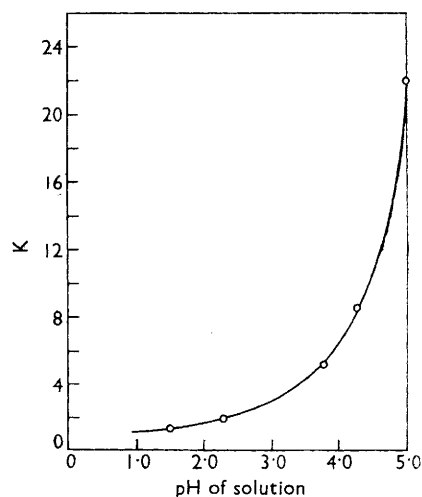


Fig. 2. Effect of variation in pH

2. The effect of precipitate particles

(a) HYDRATED OXIDES—

Experiments were carried out to determine the effect on the break-down of hydrogen peroxide solution of particles of precipitated hydrated oxides; precipitates of iron and bismuth were used.

Preparation of precipitates—Hydrated iron oxide was precipitated from homogeneous solution by MacNevin and Dunton's method. Hydrated bismuth oxide was prepared by boiling a solution containing bismuth - EDTA complex (500 mg of bismuth) with 50 ml of hydrogen peroxide at pH 4.0. The precipitates were collected in sintered porcelain filter crucibles, washed with water and dried at 105° to 110° C.

Reaction with hydrogen peroxide—Reactions were carried out under reflux with gentle boiling. Reaction solutions were prepared by diluting 25 ml of hydrogen peroxide to 500 ml with water and adjusting the pH values to 4.5 with nitric acid or ammonia solution. The solutions were gently boiled, and a sample was removed from each to determine the initial concentration of hydrogen peroxide. The required weights of precipitate were then added, and boiling was continued; samples were withdrawn at intervals, and the amounts of hydrogen peroxide remaining in solution were determined by titrating with standard potassium permanganate solution. A blank determination was carried out in the absence of precipitate particles. The results were expressed graphically by plotting the percentage of hydrogen peroxide remaining in solution against reaction time; from the graphs, the times for 90 per cent. break-down of hydrogen peroxide were calculated, as shown in Table I.

TABLE I
TIME FOR 90 per cent. BREAKDOWN OF HYDROGEN PEROXIDE

Cation present	Weight of precipitate, mg	Time for 90 per cent. breakdown, seconds
Blank.. .. .	—	2470
Bismuth	7.0	1400
	28.0	750
	100.0	280
Iron	14.0	1820
	32.0	1330

(b) BISMUTH PHOSPHATE—

The experiments were repeated in solutions containing bismuth phosphate precipitate at various pH values. A study was also made of the reaction in solutions containing phosphate ions at various pH values in the absence of precipitate, and the effect of variation in concentration of phosphate at one pH value was investigated.

Preparation of bismuth phosphate—Bismuth phosphate was precipitated by boiling a solution containing EDTA - bismuth complex (500 mg of bismuth) and 10 ml of phosphoric acid with 25 ml of hydrogen peroxide at pH 1.0. The precipitate was filtered, washed, and dried at 105° to 110° C.

TABLE II
DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE
OF BISMUTH PHOSPHATE PRECIPITATE

pH of solution	Weight of precipitate, mg	Break-down after 3000 seconds, %
1.5	100	3.5
1.5	Nil	67.0
4.5	100	5.0
4.5	Nil	63.5

The results were expressed graphically by plotting the percentage of hydrogen peroxide remaining in solution against reaction time, and the percentage break-down of hydrogen peroxide after 3000 seconds was calculated from the graphs. These results are shown in Tables II, III and IV.

TABLE III
DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE
OF PHOSPHATE ION

pH of solution	Phosphoric acid present, ml	Break-down after 3000 seconds, %
1.2	5.0	5.0
1.2	Nil	> 90.0
4.5	5.0	30.0
4.5	Nil	> 95.0
6.2	5.0	65.0
6.2	Nil	n.d.

TABLE IV
VARIATION IN CONCENTRATION OF PHOSPHORIC ACID
AT CONSTANT pH

Phosphoric acid present, ml	Break-down after 3000 seconds, %
Nil	45.0
0.25	25.0
0.50	23.0
1.00	23.0
2.50	20.0
5.00	3.0

DISCUSSION OF EXPERIMENTAL WORK

OXIDATION OF EDTA SOLUTION—

No attempt was made to derive true specific reaction constants for the reactions, since these were not necessary for this investigation and because insufficient was known about the mechanism of the reaction. The values of K shown in Figs. 1 and 2 provide a convenient method of expressing the rate of reaction, but apply only to the experimental conditions prevailing at the time.

Certain of the results obtained served to confirm the expected behaviour; the investigations were necessary, however, to provide a clearer understanding of subsequent experiments. Thus, the rate of oxidation of EDTA at constant pH was found to increase with increase in concentration of hydrogen peroxide. This agrees with the findings of MacNevin and Dunton, who reported that the rate of oxidation of an iron - EDTA complex could be increased by increasing the amount of hydrogen peroxide used.

The variation in the rate of oxidation of EDTA with change in pH is interesting; it can be seen from Fig. 2 that the rate is little changed over the pH range 1 to 4, but increases rapidly at higher pH values. This fact was found to have an important bearing on the ease of precipitation of certain metals; it will be referred to again at a later stage. During these oxidation reactions there were no signs of vigorous effervescence; some bubbles appeared to originate at imperfections in the wall of the flask, but these only served to prevent the solution from bumping during boiling.

EFFECT OF PRECIPITATE PARTICLES—

The addition of hydrated oxide precipitates caused an increase in the rate of break-down of hydrogen peroxide (see Table I), bismuth being more effective than iron; this was subsequently found to have a serious detrimental effect. In the precipitation of hydrated bismuth oxide, for example, all the peroxide present was destroyed by the first-formed precipitate particles, and further oxidation of the bismuth - EDTA complex ceased.

To study the precipitation of various metals it was necessary to find a method of overcoming the effect of the precipitate on the hydrogen peroxide. Phosphate ions were known to exert a stabilising action on hydrogen peroxide,⁹ and consequently the effects of phosphate ion and phosphate precipitate were investigated. The results shown in Tables II, III and IV confirm the stabilising action of phosphate ions and indicate that bismuth phosphate precipitate is not only inert, but also has a slight stabilising power. In the absence of precipitate,

the stabilising action of phosphate ions was found to be more effective in acid solution, whereas at constant pH the effect increased with increasing phosphate concentration.

Thus, by carrying out the reactions in the presence of phosphate ions it should be possible to avoid undue decomposition of the hydrogen peroxide by the precipitate particles, and so to study the effects of complex stability and concentration of reagents on the ease of precipitation of metals. The method was then applied to the precipitation of a number of metals, as phosphates, to determine the effect of change of cation. This work is described in Part II.

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