

to dryness and taken up with water. The solution was boiled and stirred with steam, while a solution of potassium cobalticyanide was run in slowly by means of a separatory funnel. The cobalticyanides were thrown down in the form of a white, granular precipitate. The liquid filtered easily, and the filtrate was precipitated by oxalic acid. The rare earth cobalticyanide was found to be insoluble in concentrated HCl or HNO₃. However, they were found to be easily attacked by sodium hydroxide. The oxalates that were finally obtained varied very considerably in their color. Fraction 1 was quite pink while Fraction 2 was nearly white. The latter showed only traces of erbium when examined by the spectroscope.

	1.	2.
Atomic weight.....	97.2	91.3
Weight of fraction.....	9.4 g.	4.9 g.

This great difference between two fractions appeared to be very promising and Fraction 1 was run again, and the new first fraction examined with regard to the equivalent. The result showed an atomic weight of about 107, and the oxide itself was of a pale rose color. Since the result was so very good, it was thought best to check it by running a larger quantity of oxide. This time four fractions were obtained by adding potassium cobalticyanide, while the fifth was formed by adding oxalic acid to the filtrate from Fraction 4.

	1.	2.	3.	4.	5.
Atomic weight.....	98.7	95.1	90.8	88.2	90.5
Weight of fraction.....	11.9 g.	11.3 g.	10.4 g.	4.1 g.	0.7 g.

Fraction 5 was interesting because of the high atomic weight. However, the spectroscope showed the presence of neodymium. This fraction, and also Fraction 4, showed an entire absence of erbium bands. The color of the oxides was white, while that of Fraction 1 had a decided pink tint.

This method for the preparation of pure yttrium is without doubt one of the most rapid that the writers have come across. The greatest difficulty consists in controlling the quantity of precipitate.

Further investigations are to be carried on, in the near future, with this very interesting reagent.

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THE DERIVATIVES OF PERCERIC OXIDE.

[SECOND PAPER.]¹

By C. C. MELLOCH.

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In a previous paper² the author discussed the preparation and properties of perceric potassium carbonate. Special attention was given to the

¹ This paper is based upon part of a thesis submitted to the Graduate Faculty of the University of Wisconsin for the degree of Doctor of Philosophy.

² THIS JOURNAL, 37, 2338 (1915).

manner in which the oxygen was combined. Two-thirds of the available oxygen was shown to be peroxide oxygen. The present paper is the result of a series of experiments conducted to investigate the possibility of preparing other perceric derivatives.

Perceric Sodium Carbonate.—Hitherto it has been impossible to prepare the sodium compound by a method analogous to that employed for the preparation of the potassium compound. However, by treatment of the perceric ammonium carbonate solution with solid sodium carbonate in excess and evaporating slowly *in vacuo*, a compound differing in many respects from the potassium compound can be obtained. The crystalline salt is prepared as follows: 26 g. of cerous ammonium nitrate are dissolved in 30 cc. of water and added slowly with stirring to 350 cc. of a saturated solution of ammonium carbonate, to which 10 cc. of 30% hydrogen peroxide have just previously been added. The whole is then agitated in a tall cylinder with a rapid stream of air, or carbon dioxide, until a maximum depth of color is obtained. Three hours' agitation is entirely sufficient. The dark red perceric ammonium carbonate solution thus prepared is then transferred, together with the undissolved portion of the precipitate, to a tall beaker. 200 g. of anhydrous sodium carbonate are then slowly added with constant stirring. The beaker is then placed in a vacuum desiccator containing sulfuric acid in the lower compartment and potassium hydroxide in small dishes in the upper compartment. The mixture is evaporated *in vacuo* at ordinary room temperature until most of the ammonia has been evolved and absorbed. When effervescence ceases in a good vacuum the operation is discontinued. The time required will not ordinarily exceed 48 hours. A pasty mass of sodium carbonate, sodium bicarbonate, sodium nitrate and the perceric sodium compound remains behind. The concentrated solution is filtered through a Büchner funnel and combined with the first extracts. The solid sodium carbonate, etc., is thoroughly mixed with a small portion of water. This solution is conveniently made in a porcelain mortar. The thick paste is then transferred to a Büchner funnel and the extract drawn off. The operations of extracting with a small portion of water and filtering are repeated until the solution obtained is no longer deeply colored. The various extracts are kept separate, or at least only those of approximately the same strength are combined. It is advantageous to start several preparations of the size indicated above and to combine them in the process of extraction. The various extracts are kept at about 5° for at least 48 hours. Usually a crop of crystals will have separated by this time. If the mother liquor be allowed to stand longer another crop will separate, especially if a crystal from the first crop is left in the beaker. The first crop is rarely contaminated with solid sodium carbonate, etc., but the last crop usually is. After pouring off the mother liquor it is well to remove

any large crusts of sodium carbonate, etc., that may be present. The crystals are then transferred to a Gooch crucible, or Büchner funnel with fine perforations, and washed with a coarse stream of pure ice water. A good supply of pure ice water, made by letting the wash bottle stand in an ice-salt mixture, should be at all times present in the wash bottle. Mere cold water will not suffice. A strong suction is employed. Neither filter paper nor asbestos are used, since it is necessary that the washing and drying be done rapidly. After the crystals have been washed, the strong suction is continued and the crystals stirred with a glass rod until they no longer adhere to each other or to the stirring rod. When dealing with small quantities it is best to hasten the drying by slipping a cylinder of hardened filter paper down the side walls of the Gooch crucible.

The crystals are sometimes as much as 1 cm. long and 2 to 3 mm. in diameter. The large crystals appear black and the small ones a very deep red. In thin layers the compound is transparent. It is only sparingly soluble in cold water, differing markedly in this respect from the potassium compound, the wash water from which is colored deep red, almost black, while the sodium salt colors the wash water yellow. The sodium compound effloresces in dry air more readily than the potassium compound. Sodium perceric carbonate must therefore be kept in a tightly stoppered bottle. A light brown, opaque compound is formed on efflorescence, which retains the external form of the original crystals. Contact with moisture above 0° causes hydrolysis. The crystals turn a dirty green color. With large quantities of water above 0° the crystals are completely decomposed and a gelatinous, orange-red precipitate is formed.

The compound was analyzed by the methods employed¹ for the analysis of the potassium compound. The results obtained were as follows:

TABLE I.

	I.	II.	III.	Av.	Ratio.		Theoret. comp.
					Det.	Probable.	
Ce.....	19.41%	19.40%	19.44%	19.42%	1.98	2	19.63%
Na ₂ O.....	17.70	17.70	17.71	17.70	4.08	4	17.36
CO ₂	18.41	18.54	...	18.48	6.01	6	18.47
O ²	3.46	3.47	...	3.47	3.10	3	3.36
O ³	3.60	3.63	...	3.59 ⁴	3.21	3	3.36
H ₂ O.....	37.42	37.26	...	37.34	29.62	30	37.82

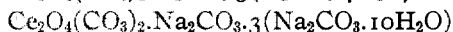
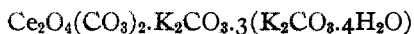
The formula for perceric sodium carbonate is therefore written Ce₂O₄(CO₂)_{2.4}Na₂CO₃·30H₂O. An interesting relation, though possibly without significance, is brought out by writing the formulas of the double potassium and sodium compounds as follows:

¹ THIS JOURNAL, 37, 2338 (1915).

² Available oxygen.

³ Unavailable oxygen not otherwise reported determined by difference.

⁴ This value is not an average but is obtained by difference.



Rubidium Perceric Carbonate.—The rubidium perceric carbonate solution was prepared by a method similar to that employed for the preparation of the potassium compound. Owing to the limited supply of material the following modification was adopted: 4 cc. of hydrogen peroxide were mixed with 135 cc. of rubidium carbonate solution which contained about 170 g. of rubidium carbonate. A solution of cerous ammonium nitrate, consisting of 10 g. of the salt dissolved in 15 cc. of water, was added gradually, with stirring. The whole was heated to 60° when almost all of the red-brown precipitate redissolved. The warm solution was chilled almost to 0° and carbon dioxide passed through until a large portion of the rubidium carbonate had been converted to the bicarbonate. The excess of the rubidium bicarbonate was then filtered off by means of a glass wool filter. The remainder of the insoluble material was then removed by filtration through a Büchner funnel provided with a hardened filter, or with a specially prepared asbestos felt. The resulting solution, though very deeply colored, was not sufficiently concentrated to yield crystals on cooling, so that evaporation *in vacuo* over sulfuric acid was required. After some time the solution became sufficiently concentrated to deposit crystals. These crystals were ruby-red in color and closely resembled those of the potassium compound, but have not yet been analyzed.

The rubidium perceric carbonate solution is, if anything, more readily prepared than the corresponding potassium solution and much less readily hydrolyzed. Oxygen is liberated when perceric rubidium carbonate solutions are left in contact with lead dioxide.

Perceric Ammonium Carbonate.—The isomorphism of many ammonium salts with the corresponding potassium salts suggests the possibility of preparing perceric ammonium carbonate. As a matter of fact a perceric ammonium carbonate solution may be prepared by a method analogous to that employed for the preparation of a perceric potassium carbonate solution. The essential difference is that the operation of heating to 60° is omitted. Solution is accomplished by agitation for about three hours with a current of air or of carbon dioxide. The details of the preparation have been given under the preparation of the sodium compound, for which purpose the perceric ammonium carbonate solution can be used to advantage. The last-mentioned solution is less stable than the corresponding solution of the potassium compound, is easily hydrolyzed and decomposes on standing with the formation of a yellow precipitate, presumably ceric carbonate. Although repeated attempts have been made to crystallize out the double ammonium compound by cooling the strong

solution and by slow evaporation *in vacuo* in the cold, such efforts have proven unsuccessful.

Other Perceric Double Carbonates.—The preparation of other perceric carbonates than those of the alkalis presents certain inherent difficulties. Indeed, it is almost certain that the main reason for the fact that double sodium perceric carbonate cannot be prepared by a method analogous to that used for the potassium compound is that the solubility of the sodium carbonate in water at ordinary temperatures is much less than that of potassium carbonate. Another factor possibly is the lesser solubility of the double sodium compound. In order that the double perceric carbonate of a metal may be easily prepared by the above method it seems that the carbonate of that metal must be very soluble. Also, the more electropositive the metal the more easily is the double compound prepared. The method used for the preparation of the sodium compound could probably be used for the preparation of the double perceric carbonates of other metals.

The Preparation of Other Perceric Compounds than the Carbonates.—

The substitution of various other acidic elements and radicals for the carbonate groups would seem to be easily accomplished, but, as previously stated, treatment with the mineral acids brings about complete decomposition of the perceric complex. The action of acetic, propionic and butyric acids is somewhat different. Here the solutions that result on neutralization are more or less colored. However, at least partial decomposition takes place, so that the problem cannot be solved in this way.

The possibility of using other readily soluble salts of weak acids instead of potassium carbonate was investigated and, of the salts that were tried, only potassium acetate and magnesium acetate yielded the desired results. The red coloration produced by treating alkaline acetate solutions of cerium with hydrogen peroxide was used by Hartley¹ as a qualitative test for the presence of cerium, but he seems not to have studied the solution quantitatively. The use of hydrogen peroxide and sodium or magnesium acetate as a means of separating cerium from a mixture of rare earths has been studied by Meyer and Koss.² The potassium perceric acetate solution used in the work described below was prepared as follows: 2.5 cc. of 30% hydrogen peroxide are mixed with 100 cc. of saturated potassium acetate solution contained in a small flask. 10 cc. of cerous ammonium nitrate solution, containing about 6.5 g. of the salt, are added slowly with constant stirring. The white precipitate which forms at first is presumably cerous acetate. This precipitate redissolves on rotating the flask and the solution changes from yellow to deep cherry-red

¹ *J. Chem. Soc.*, 41, 203 (1882); *Chem. News*, 45, 40 (1882); *Ber.*, 15, [1] 1439 (1882); *Jahrb. Fortschr. Chem.*, 35, 281 (1882).

² *Ber.*, 35, [1] 673 (1902).

in color. In a short time, in fact almost immediately on warming, a gelatinous red-brown precipitate forms which redissolves on standing, on heating to 60° , or on agitating with a current of air. By these means the excess of hydrogen peroxide is removed and a deep cherry-red solution is obtained identical in appearance with the red solution formed at the beginning, but more stable. It is probable that the excess of hydrogen peroxide is in part, at least, combined with the red-brown insoluble compound which forms, and that this intermediate compound is broken up on agitation, heating to 60° , etc. The red-brown precipitate¹ seems therefore to contain more oxygen than corresponds to the oxide CeO_3 . To obtain the solutions analyzed, the red-brown precipitate was redissolved by heating slowly to 60° and agitating until solution was complete. The red liquid was then cooled rapidly to room temperature.

The ratio of cerium to oxygen in this solution was determined by the following method: 0.7 g. of ferrous ammonium sulfate was placed in a dry titration flask and the air displaced by carbon dioxide. The ferrous sulfate was then dissolved in a minimum amount of cold boiled water. 50 cc. of saturated sodium pyrophosphate were added and the flask shaken until the precipitate which formed at first redissolved. 5 cc. of the perceric potassium acetate solution were mixed with 10 cc. of saturated potassium carbonate solution and added through a dropping funnel. 30 cc. of saturated potassium bicarbonate solution were used to wash the beaker, and were followed by a minimum amount of cold boiled water. The titration of the excess of Mohr's salt was made with potassium permanganate solution as described in a previous paper.²

When 5 cc. of the perceric acetate solution were measured out for the determination of available oxygen a similar portion was also measured out for the determination of the cerium. 5 cc. of concentrated nitric acid were added and the solution evaporated to dryness. In this way most of the acetic acid was removed. The residue was dissolved in water acidified with nitric acid and the cerium precipitated from the boiling solution by the addition of ammonium oxalate solution in slight excess. The cerous oxalate was filtered off, ignited and weighed as CeO_2 .

The ratio calculated from the results obtained from two different perceric potassium acetate solutions was:

Atoms of Ce : Atoms of O (available) : : (I) 2 : 2.66, (II) 2 : 2.67.

The instability of the perceric acetate solution accounts for the difference between these results and the theoretical ratio 2 : 3. An idea of the rate of decomposition is given by the following results obtained from the same solutions one hour later.

Atoms of Ce : Atoms of O (available) : : (I) 2 : 2.51, (II) 2 : 2.45.

¹ Cf. Job, *Ann. chim. phys.*, [7] 20, 261 (1900).

² *Loc. cit.*

The solution of perceric potassium acetate is hydrolyzed by water, liberates iodine from potassium iodide, yields a blood-red solution with potassium carbonate and a red-brown precipitate with hydrogen peroxide. Added to potassium acetate solution containing a little acetic acid, perceric potassium acetate solution is partially decomposed and oxygen is evolved. No success has thus far attended the attempts to crystallize out a double perceric acetate. However, the use of the solution in the preparation of other perceric compounds is quite possible.

The preparation of other perceric acetate solutions than those of the alkalis can probably be accomplished. At any rate, if an attempt be made to prepare perceric magnesium acetate solution by a method analogous to that used for perceric potassium acetate, a blood-red solution is obtained, especially on standing.

Summary.

Perceric sodium carbonate has been prepared for the first time and the rather unusual method of preparation given in detail. The formula is found to be $Ce_2O_4(CO_3)_{2.4}Na_2CO_3.30H_2O$. Although this compound closely resembles the double potassium perceric carbonate in its chemical properties it differs markedly from the latter in physical properties, such as color solubility.

Crystals of the rubidium perceric carbonate have been prepared, but not in sufficient quantity for detailed study. It was observed, however, that they resemble in appearance the corresponding potassium compound.

A method for the preparation of a perceric ammonium carbonate solution has been described and some of its properties studied, but the compound has not been isolated.

The solution prepared by the action of hydrogen peroxide on a cerous salt dissolved in potassium acetate solution has been shown to contain cerium in the perceric form and the important properties of this solution have been described.

The double perceric compounds thus far prepared show the following general characteristics: The metallic constituent other than cerium is a strong base and the acid radical is that of a weak acid. The simple salt which unites with the perceric complex is very soluble. In the cases in which analyses have been made the cerium is in a state of oxidation corresponding to the oxide CeO_3 . Half of the total oxygen combined directly with the cerium is available for wet oxidation under certain restricted conditions. Two-thirds of the total available oxygen is peroxide oxygen.

The facts with regard to perceric compounds are of unusual interest and suggest lines for further investigation. The separation of cerium from thorium has been studied by many chemists. No doubt, perceric compounds present certain possibilities for a new and better solution of this problem. Another problem worthy of investigation is the formation

of double peroxidized compounds of those rare earths which have been shown by Cleve and others to form peroxides. If a number of such compounds could be prepared they would no doubt exhibit a variety in their chemistry sufficient to insure a comparatively rapid and easy separation of at least some members of the rare earth group.

In conclusion, the author wishes to thank Professor Victor Lenher for helpful suggestions and for the interest which he has taken in the above work.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

SOME NEW RARE EARTH COMPOUNDS.

By A. J. GRANT AND C. JAMES.

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The methods of separation of the rare earths, although greatly improved during recent years, still leave much to be desired. This is especially true of the terbium, dysprosium, holmium portion. Accordingly it seemed advisable to continue the search for suitable compounds either for crystallization or precipitation. Some of the more interesting salts which were prepared, are described below:

Terbium Pyromucate, $\text{Tb}(\text{C}_4\text{H}_3\text{COO})_3 \cdot 5\text{H}_2\text{O}$.—This salt was obtained by neutralizing an aqueous solution of the acid, heated upon the water bath, with terbium hydroxide. In preparing salts of terbium derived from weak acids, it was found necessary to use terbium hydroxide, for the common oxide of terbium is a heavy, dark brown, sometimes almost black, substance very difficultly soluble in acids. When boiled with hydrochloric acid, it showed no signs of dissolving for a long time, but suddenly the whole went into solution.

The solution of the pyromucate was filtered, evaporated and allowed to crystallize. The compound formed radiating crystals, which were very soluble in water.

For analysis, some of the compound was weighed out and ignited to the dark oxide. This dark oxide was then calculated to the white oxide by using a conversion factor, which had previously been determined by a series of experiments in which the dark oxide had been converted to the normal type of oxide by heating in a current of hydrogen. The amount of Tb_2O_3 found indicated that five molecules of water were present. After heating for twelve hours at 94° in a drying oven, nine-tenths of the water was lost.

Terbium 1,2,4-Bromonitrobenzenesulfonate, $\text{Tb}(\text{C}_6\text{H}_3\text{Br} \cdot \text{NO}_2 \cdot \text{SO}_2\text{O})_3 \cdot 10\text{H}_2\text{O}$.—This salt was obtained in a similar manner to the pyromucate, with the exception that the solution was evaporated to dryness, the residue treated with alcohol and the remaining solid recrystallized from water.