

XXXI.—*On the Peroxides of the Radicals of the Organic Acids.*

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(Abstracted by the Author from the Philosophical Transactions 1864, p. 407.)

In a former communication* I announced to the Royal Society the discovery of a new group of chemical substances, the peroxides of the radicals of the organic acids—bodies which, in the systems of the combinations of these radicals, occupy the same relative position as is held by the peroxides of hydrogen, barium, or manganese in the systems of the combinations of those elements.

The investigation of these peroxides is attended with peculiar difficulties. It is by no means easy to prepare in any considerable quantity the anhydrous acids and chlorides themselves, which is only the first step in the preparation of the peroxides. The greater number of these substances are also excessively unstable; they are decomposed in the very reactions by which they are produced, and the quantity actually obtained is very far from corresponding to that which is indicated by theory. There can be little hope of a complete and successful investigation of the decompositions of these bodies, until methods are discovered by which the substances themselves can be more readily procured. I have for these reasons not yet been able to submit their transformations to the profound study which the subject merits, and which will doubtless be some day followed by a rich harvest of discovery.

One exception should be made to the above remarks, the peroxide of benzoyl. This beautiful substance can be procured with comparative facility, and I hope to pursue the investigation of its metamorphoses. It appeared to me, however, of primary importance to establish the perfect generality of the fundamental reaction by which these bodies are prepared. This I have effected by forming several members of the group: and I have also, in one instance, at least, succeeded in ascertaining the constitution of the peroxide of a bibasic acid, a member of a new class of chemical substances, fundamentally different (as the chemist would perhaps anticipate) from the peroxides of the monobasic acids, and characterised by well-marked reactions.

* Proceedings of the Royal Society, vol. ix, p. 361.

The peroxide of barium, in respect to the definite and universal character of its reactions, may be placed by the side of the alkalies themselves. Every anhydrous organic acid with which I have made the experiment, without any exception, has been found to be converted by its agency into an organic peroxide. It is a new instrument of chemical research, admirable for the power and the simplicity of its action, and which will certainly find, in the future of chemistry, many applications besides those which are here recorded. Its preparation is a matter of importance.

Preparation of Peroxide of Barium.

The peroxide of barium, as prepared by leading oxygen over heated baryta, is useless for the purposes of the following experiments, for the reason that the oxidation of the baryta is never complete, and that the peroxide is mixed with large quantities of the oxide of barium. However, the first step towards the preparation of a pure peroxide is the preparation of a crude material.

When oxygen gas is passed over fragments of baryta heated in a porcelain tube, the absorption of the gas proceeds at first with great rapidity; and if the heat be properly regulated, not a trace of oxygen will pass through the apparatus. It is, nevertheless, extremely difficult to prepare in this manner a peroxide which shall contain more than about 6 parts of oxygen to 100 of baryta, however long the action of the oxygen be continued, the theoretical amount of oxygen required for the formation of the peroxide being 10.46 parts of oxygen to 100 of baryta. By far the simplest and most practical process for the oxidation of baryta is that devised by Liebig, which consists in exposing to a gentle heat an intimate mixture of powdered baryta and chlorate of potassium. The mixture is thrown by degrees into a crucible heated to low redness; an ignition is perceived when the chlorate of potassium melts. The fused mass is powdered and exhausted with water, which leaves an insoluble residue, containing large quantities of peroxide of barium.

On determining the amount of oxygen combined with the baryta in this experiment, I found that the peroxide did not contain above half the theoretical amount of oxygen. Experiments, of which the details are here omitted,* leave no doubt that, in this

* For these see the original memoir.

reaction, the baryta is oxidised to the condition, not of peroxide, but of sesquioxide of barium.

When lime or strontia was substituted for baryta in the preceding experiment, not a trace of peroxide of hydrogen could be detected in the resulting solution.

To prepare pure peroxide of barium, the crude peroxide, as prepared by either of the above processes, is finely pulverized and rubbed with water in a mortar, so as entirely to convert it into hydrate. It is then mixed gradually with a very dilute solution of hydrochloric acid, care being taken to keep the solution constantly acid. This solution is filtered, and rendered alkaline with a slight excess of baryta-water. The addition of the latter effects the precipitation of the alumina and iron. The alkaline solution, which immediately begins to decompose, is rapidly filtered through linen filters, and to the clear filtrate is added an excess of baryta-water. The hydrated peroxide of barium is precipitated in brilliant plates, which are insoluble in water, and may be washed by decantation. In order to ascertain whether the whole of the peroxide is precipitated, a small portion of the solution may be filtered, rendered acid, and tested with a dilute solution of bichromate of potassium.

The washed precipitate is to be collected on a filter, pressed out between blotting-paper, and dried under the air-pump, by which means the whole of the water of crystallization may be driven off. The dry peroxide appears in the form of a fine white powder, resembling magnesia. I have analysed this substance, and found it to consist of anhydrous peroxide of barium, Ba_2O_2 , the only impurity being a trace of carbonate. It is in this condition a perfectly stable substance.

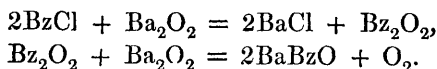
The absolute amount of peroxide of barium contained in the different preparations employed in the following experiments, was ascertained either by a direct determination of the oxygen evolved by the action of platinum-black and a dilute acid, or by means of a standard solution of permanganate of potassium, according to the method which I have given in a former paper.

Peroxide of Benzoyl, $\text{C}_{14}\text{H}_{10}\text{O}_4$.

The peroxide of benzoyl is prepared by the action either of the chloride of benzoyl, or of the benzoic anhydride on hydrated peroxide of barium. When the following precautions are taken, the reaction is perfectly definite.

Equivalent quantities are to be weighed out of chloride of benzoyl and pure peroxide of barium. The peroxide of barium is converted into hydrate, and pressed between blotting-paper, to remove any great excess of water; it is then added by degrees to the chloride of benzoyl in a small mortar, and the two substances well mixed by means of a pestle. The mixture is allowed to remain for some hours; and the resulting substance having been mixed with water is thrown on a filter, and washed until the chloride of barium is removed. It is then treated with a weak solution of carbonate of sodium, so as to render the solution decidedly alkaline. After thus removing the benzoic acid, of which a certain portion is always formed in the reaction, the substance is pressed out between blotting-paper, and dried under the air-pump. When perfectly dry, it is to be dissolved in bisulphide of carbon at a temperature not exceeding 35°C , and three or four times crystallized from that fluid. Of several slightly different methods of preparation, this gave by far the most satisfactory results.

If, in the preparation of this substance, the peroxide of barium be taken in excess, that is, more than one equivalent of that peroxide Ba_2O_2 , to two of chloride of benzoyl, 2BzCl , the amount of peroxide of benzoyl formed is reduced; and if a great excess of peroxide of barium be employed, as for example one equivalent of that substance, Ba_2O_2 , to one equivalent of chloride of benzoyl, BzCl , oxygen gas is evolved, and hardly a trace of peroxide will be formed. This arises from the circumstance that the reaction by which the peroxide of benzoyl is formed is immediately succeeded by a second reaction in which that substance is destroyed, according to the equations—



I have ascertained by direct experiment that the peroxide of barium, when mixed in water with the peroxide of benzoyl, is decomposed, with evolution of oxygen gas.

This affords a striking example of a class of decompositions which I recently brought before the Society,—in which one equivalent of the peroxide of barium acts as an agent of oxidation, while a second equivalent acts as a reducing agent, destroying the substance formed in the first reaction.

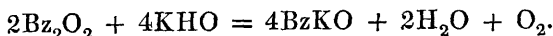
The peroxide of benzoyl thus prepared is in splendid crystals.

From large quantities of solution I have occasionally obtained these crystals as much as three-fourths of an inch in diameter. They are referable to the right prismatic system, and their form, as crystallised from ether, has been examined by Professor W. H. Miller, of Cambridge.* It is difficult to ascertain with absolute accuracy the melting-point of this substance. The point of decomposition lies close upon the melting-point; and it is only in very small quantities that it can be melted without being decomposed. My experiments, however, place the melting-point at 103.5°C . At 15°C . 100 parts of bisulphide of carbon dissolve 2.53 parts of the peroxide of benzoyl. It is also soluble in ether and benzol.

This substance gave on analysis the following results:—

	I.	II.	The numbers required by theory are	
Carbon.....	69.31	69.31	$\text{C}_{14} = 168$	69.42
Hydrogen.....	4.23	4.18	$\text{H}_{10} = 10$	4.13
Oxygen.....	26.46	26.51	$\text{O}_4 = 64$	26.45
	<hr/> 100.00	<hr/> 100.00	<hr/> 242	<hr/> 100.00

When the peroxide of benzoyl is boiled with a solution of hydrate of potassium, oxygen gas is evolved and benzoate of potassium is formed—



If the peroxide of benzoyl be heated, it is decomposed with a slight explosion. By mixing the finely powdered peroxide with sand, the action may be moderated; under these circumstances carbonic acid is evolved. The decomposition commences at about 85°C . I have estimated the loss of weight which the substance undergoes in this decomposition: in two experiments 100 parts of peroxide lost 18.6 and 18.18 parts; in three other experiments somewhat lower numbers were obtained, 17.78, 16.56, and 16.7 per cent. The theoretical loss, if one equivalent of carbonic anhydride, CO_2 , were evolved from one equivalent of the peroxide, $\text{C}_{14}\text{H}_{10}\text{O}_4$, would be 18.18 per cent. The substance formed by the removal of one equivalent of carbonic anhydride from the peroxide of benzoyl, $\text{C}_{13}\text{H}_{10}\text{O}_2$, would be isomeric with the benzoate of phenyl.

* See Proceedings of the Royal Society, January 15, 1862.

I have not, however, yet succeeded in so moderating the action as to form only one substance. During the decomposition a small quantity of benzoic acid sublimes, and on exhausting the sand with ether, filtering, and evaporating the ethereal solution, a soft glutinous residue is obtained, of which a portion dissolves on prolonged boiling in water. Benzoic acid passes over with the vapour of the water, and ultimately a hard and perfectly transparent resin remains, which is soluble in potash, and in all respects resembles a natural resin. I hope again to recur to this substance.

If peroxide of benzoyl be treated with a large excess of concentrated nitric acid, it is dissolved by the acid. When this solution is poured into water, a slightly yellow flocculent substance separates, which, dried under the air-pump, is soluble in bisulphide of carbon.

3 grms. of peroxide of benzoyl were thrown into about 3 fluid-ounces of fuming nitric acid, specific gravity 1.505. There was no perceptible increase of temperature or evolution of gas. The peroxide was rapidly dissolved, the mixture became deeper in colour, and after some time the vessel was filled with fumes of hyponitric acid. After standing about twenty-four hours, the solution in nitric acid was mixed with ten times its bulk of water. The precipitate formed was collected on a filter and washed free from acid. It was then dried under the air-pump, and dissolved in bisulphide of carbon. On the cooling of the bisulphide, a slightly yellow flocculent body separated. This was again dried under the air-pump and analysed.

The formula of the substance derived from the peroxide of benzoyl by the substitution of two atoms of peroxide of nitrogen, NO_2 , for two atoms of hydrogen, H, is $\text{C}_{14}\text{H}_8(\text{NO}_2)_2\text{O}_4 = \text{C}_{14}\text{H}_8\text{N}_2\text{O}_8$, and requires—

	Found.		Required.
Carbon.....	50.60	$\text{C}_{14} = 168$	50.60
Hydrogen	2.58	$\text{H}_8 = 8$	2.41
Nitrogen	8.49	$\text{N}_2 = 28$	8.43
Oxygen.....	35.33	$\text{O}_8 = 128$	38.56
	<hr/> 100.00	<hr/> 332	<hr/> 100.00

This body, when heated, decomposes with a slight explosion, leaving a resinous matter similar in appearance to that formed by the decomposition of the peroxide of benzoyl.

Peroxide of Cumenyl.

The peroxide of barium is decomposed by the chloride of cumenyl precisely as by the chloride of benzoyl. The resulting substance crystallizes from ether in long and beautiful needles; when heated it explodes, leaving a resinous residue.

I have only once prepared this substance, and did not succeed in procuring it in a state of absolute purity.

Analysis gave—

Carbon	73·24
Hydrogen	7·00
Oxygen	19·76
	<hr/>
	100·00

The formula $C_{20}H_{22}O_4$ requires—

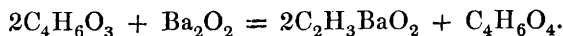
$C_{20} =$	240	74·23
$H_{22} =$	22	6·75
$O_4 =$	64	19·02
	<hr/>	<hr/>
	326	100·00

Peroxide of Acetyl.

In the preparation of the peroxides of the acetic series, the use of the anhydrous acid has great advantages over the use of the corresponding chloride. By the action of the anhydride of the acid on peroxide of barium, I have succeeded in preparing three of these peroxides, the peroxides of acetyl, butyl, and valeryl.

The peroxide of acetyl is prepared by dissolving anhydrous acetic acid in pure ether, and adding gradually to this solution an equivalent quantity of peroxide of barium.

The decomposition takes place according to the equation—



The reaction is attended with an elevation of temperature which causes the ether to boil; the temperature is not to be allowed to reach this point. After standing for some time, the solution is filtered from the gelatinous residue, which does not contain a trace of peroxide of barium, and the ether is distilled off at a very low temperature, great care being taken not to allow the temperature to rise towards the end of the operation. The residue, washed first

with water and then with a very weak solution of carbonate of sodium, appears as a thick and viscid fluid, which solidifies to a mass of minute crystals, when the tube containing it is placed in ice. I have in this manner experimented on as much as 20 grms. of anhydrous acetic acid, dissolved in about four times its bulk of pure ether. The addition of the equivalent quantity of peroxide of barium occupied two hours. From these 20 grms. of anhydrous acetic acid, only as much peroxide of acetyl was procured as to be sufficient for the two following determinations. The analysis was thus affected :—

An undetermined quantity of the peroxide of acetyl was placed in a little water at the bottom of a small flask, with a bulb attached to it, somewhat similar to those occasionally used for the estimation of carbonic acid. The bulb was filled with baryta-water, a small tube containing platinum-black introduced into the apparatus, and the whole was weighed. The peroxide was now decomposed by allowing the baryta-water to flow into the flask from the bulb. Acetate of barium and peroxide of barium are formed. The peroxide of barium was decomposed by bringing the platinum-black contained in the small tube in contact with it. After the completion of the reaction, the apparatus was again weighed, and thus the loss of oxygen was determined.

A current of carbonic acid was now passed through the solution, which was boiled and filtered, and the barium estimated as sulphate. The sulphate of barium thus formed is the measure of the acetate produced by the decomposition of the peroxide of acetyl.

Experiment I. The weight of the apparatus before and after the experiment gave a loss of oxygen of 0.1225 gm.

The solution precipitated by sulphuric acid gave 1.776 gm. of sulphate of barium.

Experiment II. The loss of oxygen estimated as before was 0.137 gm.

The solution precipitated by sulphuric acid gave 1.944 gm. of sulphate.

In Experiment I, 100 parts of sulphate being formed, 6.89 parts of oxygen were evolved.

In Experiment II, 100 parts of sulphate were obtained and 7.04 of oxygen evolved.

Theory requires that for every 100 parts of sulphate of barium formed, 6.86 parts of oxygen should be evolved.

When a small drop of the peroxide of acetyl is heated in a

watch-glass, it is decomposed with an explosive violence, only to be paralled by the decomposition of chloride of nitrogen. Hence the greatest care is necessary in its preparation, especially during the distillation of the ether in which it is dissolved. I had frequently effected this operation without accident; but on one occasion my assistant was engaged in distilling off the ether from a rather considerable quantity of the substance, which was contained in a flask placed in warm water on a small copper water-bath; the temperature was probably allowed to rise too high, and towards the close of the operation a violent explosion took place with a report as of a cannon. A large hole was made in the copper water-bath, through which the hand might be passed, the copper being folded back upon the sides of the bath. The explosion, though of excessive violence, was local, and nothing in the laboratory in which the explosion took place was injured.*

The peroxide of acetyl is readily decomposed under the influence of sunlight. A measured quantity of the substance was kept unaltered in bulk for above eighteen hours in the dark, but when placed in water in the bright sunlight, the same substance rapidly disappeared.

This peroxide is a most powerful agent of oxidation; like chlorine it rapidly bleaches indigo; it separates iodine from hydriodic acid and from iodide of potassium; it converts a solution of ferrocyanide of potassium into ferricyanide; and immediately oxidises the hydrated protoxide of manganese.

These properties it has in common with the peroxide of hydrogen; but it is readily distinguished from that substance by not producing the peculiar effects of reduction by which the peroxide of hydrogen is characterised. It does not reduce an acid

* Since the first publication of this paper, I have had an accident in the preparation of the peroxide of acetyl, which shows the excessive care required in dealing with it. I had in my hand a small thin glass tube, containing perhaps 40 drops of the peroxide, which had just been removed from the solution in which it had been procured. I was engaged in projecting into it some very small pieces of chloride of calcium. Five or six pieces had been thrown in, when, on the addition of the next piece, the substance exploded with terrific violence, driving the glass in minute fragments into my hands. The concussion of the air produced bruises on the eyes and face, and several small fragments of the glass tube were deeply embedded in the hands and face. If I had been operating with two or three times the quantity of the peroxide, the accident would, undoubtedly, have been of a most serious nature. I may observe that I had never before seen the substance explode without the application of considerable heat, and that I had repeatedly dried the peroxide of butyl in a similar manner with chloride of calcium, without effecting its decomposition.

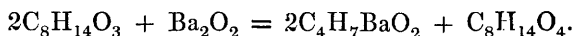
solution of chromic or permanganic acids. The addition of baryta-water to the peroxide of acetyl suspended in water, causes an immediate precipitate of crystals of the hydrated peroxide of barium.

We can have no more convincing proof, if such proof were needed, than that furnished by this experiment, that the difference of properties which oxygen manifests in its different combinations is due, not, as has been imagined, to the existence of certain distinct varieties of that element, but to the circumstance that the combining properties of oxygen, as of other elements, vary with the nature of the chemical substances with which it is combined or associated.

Peroxide of Butyl.

The butylic peroxide is readily prepared by mixing hydrated peroxide of barium with anhydrous butyric acid. Experiments made with the view of preparing this substance by the action, in ether, of the dry peroxide of barium on anhydrous acid, were unsuccessful.

The result of this reaction is given in the equation



The experiment may be advantageously conducted as follows :—

The anhydrous acid is placed in a small mortar, and an equivalent quantity of hydrated peroxide of barium, from which any great excess of water has been removed, is gradually added to it, the whole being well mixed after each addition of the peroxide. An excess of peroxide of barium is to be carefully avoided, as it again decomposes the peroxide of butyl. To this end it is desirable towards the close of the operation, to examine from time to time the contents of the mortar, by placing a drop on a watch-glass, acidifying with hydrochloric acid, and testing with a dilute solution of bichromate of potassium. The appearance of a feeble blue colour indicates that sufficient peroxide has been added. The substance is mixed with a small quantity of water, and the solution agitated repeatedly with ether, which dissolves the peroxide of butyl. This operation is readily effected in a burette provided with a glass stopcock. The ethereal solution is then repeatedly washed, first with dilute hydrochloric acid, then with a weak solution of carbonate of sodium, until it has a strong

alkaline reaction, and then again with water until the alkaline reaction disappears. The solution is filtered and allowed to evaporate in a current of air at a low temperature. An oily residue is left, which is to be washed once or twice with a small quantity of water, in which it is only slightly soluble. It is then removed with a pipette, and allowed to stand for some time in contact with a few fragments of chloride of calcium. The substance thus prepared is pure peroxide of butyl.

This peroxide was analysed with oxide of copper in the usual manner.

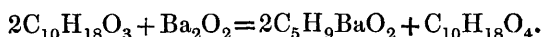
Two analyses gave per cent.,

	I.	II.		Theory requires
Carbon.....	55·21	55·11	$C_8 = 96$	55·172
Hydrogen....	8·29	8·28	$H_{14} = 14$	8·046
Oxygen.....	36·50	36·61	$O_4 = 64$	36·782
	<hr/> 100·00	<hr/> 100·00	<hr/> 174	<hr/> 100·000

A drop of the peroxide of butyl heated on a watch-glass decomposes with a slight explosion. Suspended in water, it possesses the oxidizing properties of the acetic peroxide.

Peroxide of Valeryl.

The peroxide of valeryl is prepared by the action of anhydrous valerianic acid on hydrated peroxide of barium, the result of the reaction being expressed by the equation



The method of preparation is in all respects the same as that by which the peroxide of butyl is prepared.

The peroxide of valeryl is a dense oily fluid, heavier than water. It gives a slight explosion when heated, and possesses the oxidising properties of the other analogous peroxides.

The substance dried by means of chloride of calcium was analysed with the following results:—

	I.	II.		Theory requires
Carbon.....	59·05	59·39	$C_{10} = 120$	59·40
Hydrogen	9·17	9·17	$H_{18} = 18$	8·91
Oxygen	31·78	31·44	$O_4 = 64$	31·69
	<hr/> 100·00	<hr/> 100·00	<hr/> 202	<hr/> 100·00

Peroxide of Camphoryl.

The action of the anhydrides of the bibasic acids on the alkaline peroxides affords a remarkable illustration of the profound difference by which this group is distinguished from the anhydrides of the monobasic acids. In the latter case we have seen that the monobasic anhydride decomposes with the alkaline peroxide, forming the peroxide of the radical and the barium-salt of the corresponding acid. In the case of the bibasic anhydride, a combination takes place of the anhydride with the peroxide, with the formation of a new and peculiar compound, which we may regard as the barium-salt of the peroxide of the bibasic radical. The compounds thus formed have but little permanence; and although in several cases we have evidence of their formation, in only one example, namely that of camphoric acid, have I been able to effect the analysis of the compound.

If hydrated peroxide of barium be gradually added to anhydrous succinic acid, and carefully mixed with it in a small quantity of water, the mixture becomes fluid; but long before the addition of the equivalent quantity of peroxide of barium, oxygen gas is evolved. If the fluid be filtered when this effervescence commences, it will be found to have the following properties:—

1. The solution is alkaline. It may be assumed, therefore, to contain but little, if any, succinate of barium, which is insoluble in water.

2. The solution, rendered acid, gives no blue colour with bichromate of potassium, and does not discolour permanganic acid. It therefore contains no peroxide of hydrogen. If peroxide of barium be mixed with hydrated succinic acid, a solution is obtained, containing peroxide of hydrogen with the above characteristic reactions.

3. The solution bleaches indigo, gives a precipitate of peroxide of manganese with a solution of acetate of manganese, oxidises ferrocyanide of potassium, and evolves chlorine when boiled with hydrochloric acid.

4. When the solution is boiled, oxygen gas is evolved, and a crystalline precipitate formed of succinate of barium.

Similar results are obtained if hydrated peroxide of barium be mixed with lactide, the lactic anhydride. The peroxide is rapidly dissolved, and a powerfully bleaching solution is obtained, pos-

sessing the same oxidising properties as that procured from succinic anhydride. The solution is, however, excessively unstable; even when cooled by ice, it is in a constant state of decomposition, and although it doubtless contains the lactic peroxide, I have been unable to effect its analysis.

With the camphoric anhydride I have been somewhat more successful. The anhydrous camphoric acid used in the following experiments, was prepared by the oxidation of camphor by means of nitric acid. It is better not to attempt the prior preparation of a pure camphoric acid, which is attended with much difficulty, but after the product of the oxidation of camphor has been once or twice crystallised, to distil the crude acid. After two distillations and two or three crystallisations from alcohol of the distilled product, the camphoric anhydride is obtained quite pure.

A portion (about 3 grms.) of anhydrous camphoric acid thus prepared, was triturated in a mortar with ice-cold water, and the equivalent quantity of hydrated peroxide of barium was gradually added to the same, fragments of ice being mixed with the solution. No evolution of gas was observed during the experiment. The filtered solution was rather alkaline, doubtless from the trace of baryta present in the peroxide. The solution, rendered acid, had the following properties. It gave no blue reaction with chromic acid, nor did it discolour permanganic acid. It bleached indigo, oxidised ferrocyanide of potassium, and decomposed hydriodic acid. The residue from which the solution was filtered was small in amount, and contained a little peroxide of barium. The solution when boiled evolves oxygen. Evaporated to dryness, it leaves a residue, which, dissolved in water, gives a precipitate with a solution of acetate of lead. This precipitate was suspended in water, and decomposed by sulphide of hydrogen. The acid thus separated was analysed after one crystallisation. It was pure camphoric acid.

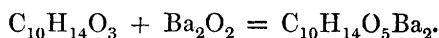
A solution of the camphoric peroxide thus prepared was analysed in the following manner:—

1. A measured quantity of the solution was rendered acid, and titred by means of a standard solution of iodine.

2. To another measured quantity of the same, a solution of carbonic acid in water was added. The liquid was raised to the boiling-point, filtered, and precipitated by sulphuric acid. The addition of the carbonic acid effects the removal of a small quantity of baryta, invariably present through the decomposition of the peroxide of barium.

3. Another portion of the solution, similarly treated, was precipitated by acetate of lead, and the precipitate collected and weighed. The precipitate thus obtained is pure camphorate of lead.

The results thus obtained agree with the hypothesis that the solution contains the substance $C_{10}H_{14}O_5Ba_2$,—the reaction taking place according to the equation,



For we should have, assuming the camphoric acid to be correctly determined by precipitation with acetate of lead, in 1000 parts of the solution,

Experiment I.

	Atomic weight.	Ratio calculated.	Found.
$C_{10}H_{14}O_3$	182	25·12	25·12
O	16	2·20	2·07
Ba_2O	153	21·12	21·51

Experiment II.

$C_{10}H_{14}O_3$	182	21·43	21·43
O	16	1·88	1·96
Ba_2O	153	18·00	17·88*

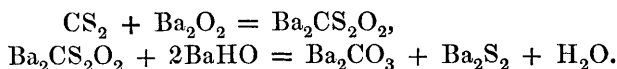
The oxygen-determinations show that, even in this case, there is a gradual, although but slight, decomposition of the substance taking place during the time which the determinations occupy. But this peroxide is far more stable than the corresponding succinic and lactic peroxides. I have made several unsuccessful attempts to analyse these substances by methods similar to the above; but, from the excessive instability of the solutions, I have been obliged to abandon the attempt. In the case of the lactic peroxide, for example, three successive determinations required 60·8, 54·3, and 48·6 cub. centims. of the standard iodine-solution, showing so rapid a change as to render hopeless the accurate determination of the oxygen. These substances stand, as it were, upon the very verge of chemical possibility, and have only a momentary and fugitive existence.

* Mean of two determinations 16·5 and 19·22.

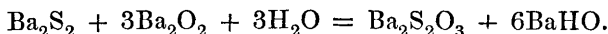
That in the above reaction the oxygen is transferred from the peroxide of barium to the anhydrous camphoric acid—in other words, that the compound formed is to be regarded as the barium-salt of the peroxide of camphoryl, and not as the camphorate of the peroxide of barium, is shown by the reactions of the solution. The action of acids upon it does not form peroxide of hydrogen, and the action of alkalies does not reproduce the peroxide of barium. These reactions would take place if the solution contained the salt of the peroxide.

The analogy of the bisulphide of carbon to the anhydrous acids induced me to try its action on the alkaline peroxide. When bisulphide of carbon suspended in water is agitated with hydrated peroxide of barium, the peroxide is dissolved, with formation of a yellow solution. The solution when filtered is at first clear; but on standing, and more rapidly on boiling, a precipitate of carbonate of barium is formed. The solution contains a sulphide of barium. If sulphide of hydrogen be passed through water in which peroxide of barium is suspended, a clear yellow solution is formed similar in appearance to the preceding.

I have not fully investigated the reaction; but the experiments point to the conclusion that, in the first instance, we have formed the combination of bisulphide of carbon and peroxide of barium, which subsequently decomposes into carbonate of barium and bisulphide of barium, according to the equations,



The reaction is undoubtedly complicated by the action of the bisulphide of barium on the peroxide. This solution, in presence of an excess of peroxide, becomes colourless, hyposulphite of barium being probably formed—



In the case of the action of carbonic acid on peroxide of barium, I could detect no indication of the formation of a higher oxide of carbon.

The previous investigation has placed beyond doubt the existence of a new and extensive group of chemical substances, the peroxides of the radicals of the organic acids, a group in all probability as numerous as the anhydrides of the acids, and charac-

terised by singular properties, which have never hitherto been discovered in any combination of carbon, and which greatly enlarge our view of the system of analogies by which the organic and inorganic worlds of chemistry are connected.

The transition is obvious from the peroxide of the acid radical to the peroxide of the basic radical. The question is immediately suggested whether, by corresponding processes, we may not be able to procure the peroxides of ethyl, of ethylene, of the compound ammoniums. I am yet occupied with this subject, and will now only remark that the peroxide of the glycol series appears undoubtedly to be formed. The bromide of ethylene does not, indeed, decompose the hydrated peroxide of barium; but this peroxide is immediately acted on by the diacetate, and a solution is formed having a most pungent odour, containing no peroxide of hydrogen, but possessing the usual characteristics of the organic peroxides. I have not made many experiments with the compound ammonias. A solution of hydrated oxide of tetramylammonium, evaporated *in vacuo* with a solution of pure peroxide of hydrogen, gave a residue which did not appear to contain even a trace of a substance resembling an alkaline peroxide. But this by no means renders it impossible that the same experiment may in other cases be more successful; for great differences are found in the stability of the peroxides of very analogous metals; the peroxide of potassium is quite decomposed on evaporation *in vacuo*, whereas the hydrated peroxide of sodium can be readily thus obtained.
