XVIII. *On the Peroxides of the Radicals of the Organic Acids.*
By Sir B. C. BRODIE, *Bart., F.R.S., Professor of Chemistry in the University of Oxford.*

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 also of these substances is 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 characterized by well-marked reactions.

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

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

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 extracted 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. The following experiments leave little doubt that in this reaction the baryta is oxidized to the condition, not of peroxide, but of sesquioxide of barium.   When oxygen is passed over baryta, the action does not appear to be absolutely arrested at this point, but nevertheless only small quantities of peroxide are formed.

Expt. I. 4·726 grms. of baryta were powdered, and mixed with one-third that weight of chlorate of potassium.   The mixture was thrown by degrees into a platinum crucible, heated to low redness.   After the first ignition, which proceeded without any external increase of temperature, the crucible was heated somewhat more strongly, so as to ensure the decomposition of the chlorate of potassium.   The mass was powdered, mixed with water, and dissolved in very dilute hydrochloric acid, to which the hydrate was added.   The solution was rendered feebly alkaline by the addition of baryta water, which precipitated the traces of iron and alumina invariably contained in the baryta.   The solution was then rapidly filtered, and immediately rendered acid; and by the addition of water, it was brought to the bulk of 500 cub. centims.   10 cub. centims. of this solution, titred with a standard solution of permanganate, of which 1 part was equivalent to 0·000516 grm. of oxygen, required in two experiments 8·6 and 8·7 parts of that solution.   Since

8·65 parts of permanganate were equivalent to 0·0004465 grm. of oxygen, 0·22325 grm. of oxygen were contained in the 500 cub. centims. of solution of peroxide of barium; 100 parts of baryta had therefore absorbed 4·718 parts of oxygen.

In three other experiments conducted in a similar manner, in which respectively 5 grms. of baryta were mixed with $\frac{1}{3}$, with $\frac{2}{3}$, and with an equal weight of chlorate of potassium, precisely the same result was obtained.

Expt. II. 5·084 grms. of baryta were mixed with $\frac{1}{4}$ that weight of perchlorate of potassium: the experiment was otherwise conducted precisely as before. 9·8 cub. centims. of the resulting solution of peroxide required 10 parts of permanganate. 1 part of the permanganate employed was equivalent to 0·000548 grm. of oxygen. Hence 100 parts of baryta had combined with 5·375 parts of oxygen. In the case of the formation of the sesquioxide of barium, 100 parts of baryta would combine with 5·228 parts of oxygen.

When lime or strontia were 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, $Ba_2 O_2$, 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.
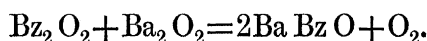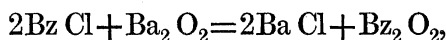
Peroxide of Benzoyl, $C_{14} H_{10} O_4$.

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 pre-
cautions 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 satis-
factory results. In one experiment, for example, from 20 grms. of chloride of benzoyl,
15·2 grms. of the crude peroxide, as dried under the air-pump, were obtained, corre-
sponding to 88·26 per cent. of the theoretical yield. If an excess of water be present,
the amount of peroxide of benzoyl obtained is greatly reduced. The hydration of the
peroxide of barium appears to be essential to the reaction. An equivalent quantity
of peroxide of barium, mixed with anhydrous benzoic acid dissolved in ether and heated
for five or six hours in a water-bath, was entirely without action. The same appeared
to be the case with equivalent quantities of chloride of benzoyl and peroxide of barium
under the same circumstances.

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 in which
the peroxide of benzoyl is formed is immediately succeeded by a second reaction in which
that substance is destroyed, according to the equations

$$2Bz\,Cl + Ba_2\,O_2 = 2Ba\,Cl + Bz_2\,O_2,$$
$$Bz_2\,O_2 + Ba_2\,O_2 = 2Ba\,Bz\,O + O_2.$$

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 crystallized 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 benzole.

This substance gave on analysis the following results :—

I. 0·3975 grm. of substance gave

Carbonic acid . . . . 1·0103
Water . . . . 0·1513

II. 0·4412 grm. of the same substance, twice recrystallized, gave

Carbonic acid . . . . 1·1213
Water . . . . 0·1661

These numbers give, as the percentage composition,

	I.	II.
Carbon . . .	69·31	69·31
Hydrogen . .	4·23	4·18
Oxygen . . .	26·46	26·51
	100·00	100·00

The numbers required by theory are

C_{14} =168		69·42
H_{10}= 10		4·13
O_4 = 64		26·45
242		100·00

I have repeatedly prepared and analysed this substance with the same results.

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

$$Bz_2 O_2 + 2KHO = 2Bz KO + H_2 O + O.$$
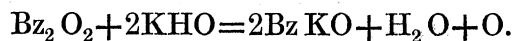
If the peroxide of benzoyl be heated, it is decomposed with a slight explosion. By mixing the finely powdered peroxide with sand the action may be moderated; under these circumstances carbonic anhydride is evolved. The decomposition commences at about 85° C. I have estimated the loss of weight which 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

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

evolved from one equivalent of the peroxide, $C_{14}H_{10}O_4$, would be 18·18 per cent. The substance formed by the removal of one equivalent of carbonic anhydride from the peroxide of benzoyl, $C_{13}H_{10}O_2$, would be isomeric with the benzoate of phenyl.

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 extracting 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 brought 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.

I. 0·4167 grm. of the substance gave

$$\text{Carbonic acid . . . 0·7735 grm.}$$
$$\text{Water . . . . . 0·0969 grm.}$$

II. 0·433 grm. of the same substance, at a temperature of 18° C., and a barometric pressure of 758·5 millims., gave 32·5 cub. centims. of nitrogen gas. This corresponds to a weight of 0·0374 grm. of nitrogen.

We have as the results of these determinations,

$$\text{Carbon . . . . . 50·60}$$
$$\text{Hydrogen . . . . 2·58}$$
$$\text{Nitrogen . . . . 8·49}$$
$$\text{Oxygen . . . . . 38·33}$$
$$\overline{\text{100·00}}$$

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 $C_{14}H_8(NO_2)_2O_4 = C_{14}H_8N_2O_8$, and requires

$$C_{14} = 168 \qquad 50{\cdot}60$$
$$H_8 = 8 \qquad 2{\cdot}41$$
$$N_2 = 28 \qquad 8{\cdot}43$$
$$O_8 = \underline{128} \qquad \underline{38{\cdot}56}$$
$$332 \qquad 100{\cdot}00$$

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.

GERHARDT did not succeed in procuring in a state of purity the anhydrous nitro-benzoic acid *, on account of the facility with which it decomposes water. The nitro-benzoic peroxide stands to the acid in the same relation as does the peroxide of benzoyl to the anhydrous benzoic acid.

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.

0·3798 grm. of the substance gave 1·020 grm. of carbonic acid and 0·2392 grm. of water. These numbers give per cent.,

$$\text{Carbon} \quad . \quad . \quad . \quad . \quad 73{\cdot}24$$
$$\text{Hydrogen} \quad . \quad . \quad . \quad 7{\cdot}00$$
$$\text{Oxygen} \quad . \quad . \quad . \quad . \quad \underline{19{\cdot}76}$$
$$\phantom{\text{Oxygen} . . . . }100{\cdot}00$$

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

$$C_{20} = 240 \qquad 74{\cdot}23$$
$$H_{22} = 22 \qquad 6{\cdot}75$$
$$O_4 = \underline{64} \qquad \underline{19{\cdot}02}$$
$$326 \qquad 100{\cdot}00$$

The peroxide of benzoyl itself is mixed with traces of some substance which it is very difficult to remove by crystallization, and which lowers the percentage of carbon in the analyses; and, notwithstanding the difference of 1 per cent. in the carbon from that required by theory, we may assume the substance to be the peroxide of cumenyl.

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.

* Annales de Chimie, iii. p. 37 & 321.

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

$$2C_4 H_6 O_3 + Ba_2 O_2 = 2C_2 H_3 Ba O_2 + C_4 H_6 O_4.$$
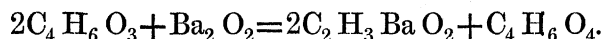
The reaction is attended with an elevation of temperature which causes the ether to boil; the temperature is not to be allowed to reach this point. After standing some time, the solution is filtered from the gelatinous residue, which does not contain a trace of peroxide of barium, and the ether is distilled 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. 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 effected.

An undetermined quantity of the peroxide of acetyl was placed in a little water at the bottom of the bulb-apparatus used for the estimation of oxygen in peroxide of barium, which I have described in a former paper. 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 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 grm.

The solution precipitated by sulphuric acid gave 1·776 grm. of sulphate of barium.

Experiment II. The loss of oxygen estimated as before was 0·137 grm.

The solution precipitated by sulphuric acid gave 1·944 grm. 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 paralleled 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 oxidizes 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 characterized. It does not reduce an acid 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

$$2C_8 H_{14} O_3 + Ba_2 O_2 = 2C_4 H_7 Ba O_2 + C_8 H_{14} O_4.$$
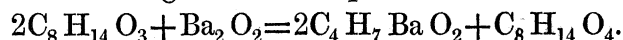
The experiment may be advantageously conducted as follows:—

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 the solution 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.

I. 0·3562 grm. of the substance gave 0·721 grm. of carbonic acid and 0·2668 grm. of water.

II. 0·3144 grm. of the substance gave 0·6355 grm. of carbonic acid and 0·2344 grm. of water.

These analyses give per cent.,

	I.	II.
Carbon . . .	55·21	55·11
Hydrogen . .	8·29	8·28
Oxygen . . .	36·50	36·61
	100·00	100·00

Theory requires

C_8 = 96	55·172	
H_{14} = 14	8·046	
O_4 = 64	36·782	
174	100·000	

A drop of the peroxide of butyl 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

$$2C_{10}H_{18}O_3 + Ba_2O_2 = 2C_5H_9BaO_2 + C_{10}H_{18}O_4.$$
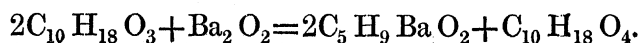
The method of preparation is in all respects the same as that by which the peroxide of butyl is prepared.

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

The substance, dried by means of chloride of calcium, gave to analysis the following numbers :—

I. 0·3055 grm. of the substance gave 0·6615 grm. of carbonic acid and 0·2523 grm. of water.

II. 0·4005 grm. of the substance gave 0·873 grm. of carbonic acid and 0·3310 grm. of water.

These numbers give as the percentage constitution of the substance,

	I.	II.
Carbon . . .	59·05	59·39
Hydrogen . .	9·17	9·17
Oxygen . . .	31·78	31·44
	100·00	100·00

Theory requires

$$C_{10} = 120 \qquad 59·40$$
$$H_{18} = 18 \qquad 8·91$$
$$O_4 = 64 \qquad 31·69$$
$$\overline{202} \qquad \overline{100·00}$$

Peroxide of Camphoryl.

The action of the anhydrides of the bibasic acids on the alkaline peroxides affords a remarkable illustration of the profound differences 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 baryta 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 baryta 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, oxidizes ferrocyanide of potassium, and boiled with hydrochloric acid evolves chlorine.

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, possessing the same oxidizing properties as that procured from the succinic anhydride. This 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 crystallized, to distil the crude acid. After two distillations and two or three crystallizations from alcohol of the distilled product, the camphoric anhydride is obtained quite pure. The substance was analysed with the following results :—

		Calculated.		Found.
C_{10}	. . .	120	65·93	65·51
H_{14}	. . .	14	7·69	7·87
O_3	. . .	48	26·38	26·62
$C_{10} H_{14} O_3$	.	182	100·00	100·00

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 slightly 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, oxidized 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 after one crystallization analysed. It was pure camphoric acid.

		Calculated.		Found.
C_{10}	. . .	120	60·00	60·37
H_{16}	. . .	16	8·00	8·13
O_4	. . .	64	32·00	31·50
$C_{10} H_{16} O_4$	.	200	100·00	100·00

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.

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, as is shown by the following determination:—

0·5901 grm. of the precipitate, ignited in a porcelain crucible, gave 0·3257 grm. of oxide of lead. Hence 100 parts gave 55·19 parts of oxide of lead. 100 parts of neutral camphorate of lead, $C_{10} H_{14} O_4 Pb_2$, contain 55 parts of oxide.

Experiment I.—(1) One part of this solution required for its titration in two concordant experiments, 12·98 cub. centims. of a standard solution of iodine, which contained in 1 cub. centim. 0·002531 grm. of iodine. Hence 1000 parts of the solution of camphoric peroxide contained 2·07 grms. of oxygen.

(2) Six parts of the same solution, treated in the manner described, gave 0·1949 grm. of sulphate of barium. Hence 1000 parts of the solution contained 21·511 grms. of baryta, $Ba_2 O$.

(3) Six parts of the same solution, treated as described, gave 0·3354 grm. of camphorate of lead. Hence 1000 parts of the solution contained 25·12 grms. of anhydrous camphoric acid, $C_{10} H_{14} O_3$.

Experiment II.—(1) In a similar experiment made with another solution, one part titred with the same standard solution of iodine was equivalent to 12·26 cub. centims. of the iodine solution. In a second experiment, one part of the same was equivalent to 12·317 cub. centims. of the same iodine solution. Hence, on the mean of the two experiments, 1000 parts of the solution contained 1·97 grm. of oxygen.

(2) Six parts of the solution gave 0·1508 grm. of sulphate of barium. Ten parts of the solution gave 0·2927 grm. of sulphate.

From the first determination, 1000 parts of the fluid contained 16·5 grms. of baryta; from the second, 1000 parts of the fluid contained 19·22 grms. of baryta. The mean of these two determinations (in which doubtless there is some error) gives 17·88 grms. of baryta in 1000 parts of fluid.

(3) Six parts of the solution gave 0·3354 grm. of camphorate of lead. Hence 1000 parts of the solution contained 21·43 grms. of anhydrous camphoric acid.

These numbers 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

$$C_{10}H_{14}O_3 + Ba_2O_2 = C_{10}H_{14}O_5Ba_2.$$
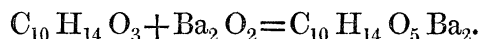
For we should have, assuming the camphoric acid to be correct as determined by precipitation with acetate of lead in 1000 parts of the solution,

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, for example, of the lactic peroxide, 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.

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

---

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

reproduce the peroxide of barium. These reactions must 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 the formation of a yellow solution. The solution when filtered is at first clear; but on standing, and more rapidly on boiling, a precipitate is formed of carbonate of barium. The solution contains a sulphide of barium. If sulphide of hydrogen be led 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

$$CS_2 + Ba_2 O_2 = Ba_2 C S_2 O_2,$$

$$Ba_2 C S_2 O_2 + 2 Ba HO = Ba_2 CO_3 + Ba_2 S_2 + H_2 O.$$
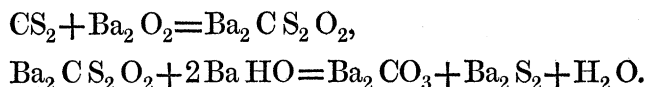
The reaction is undoubtedly complicated by the action of the bisulphide of barium on the peroxide. This solution in presence of an excess of peroxide becomes colourless, hyposulphite of barium being probably formed,
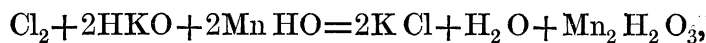
$$Ba_2 S_2 + 3 Ba_2 O_2 + 3 H_2 O = Ba_2 S_2 O_3 + 6 Ba HO.$$
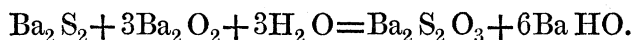
In the case of the action of carbonic acid on peroxide of barium, I could detect no indication of the formation of a higher oxide.

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 characterized by singular properties, which have never hitherto been discovered in any
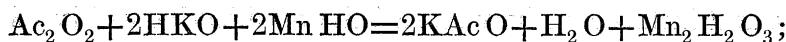
---

* The question regarded as one of notation may be considered as, whether we are to write the formula of the compound $(C_{10} H_{14} O_3)'' \left.\begin{matrix} Ba' \\ Ba' \end{matrix}\right\} O_2$, or $(C_{10} H_{14} O_2)'' \left.\begin{matrix} {}^5Ba'' \\ Ba'' \end{matrix}\right\} O_3$, or on the dualistic method as $C_{10} H_{14} O_3$, $Ba_2 O$, or $C_{10} H_{14} O_2$, $Ba_2 O_2$.

If we are to write the formula of the sesquioxide and its hydrate as $\begin{matrix} Fe_2''' \\ Fe_2''' \end{matrix} O_3$, and $2 \begin{matrix} H_3 \\ Fe_2''' \end{matrix} \right\} O_3$, we must in consistency write the formula of the peroxide and its hydrate thus, $\begin{matrix} Na'' \\ Na'' \end{matrix} O_2$ and $2 \begin{matrix} H_2 \\ Na'' \end{matrix} O_2$. (Chem. Soc. Q. J. vol. xiv. p. 280.) The normal salt of the peroxide would be the body derived from the peroxide by the substitution of the equivalent quantity of the acid radical for the equivalent of sodium. The compound of one equivalent of camphoric anhydride with one equivalent of the peroxide of barium, would be an oxide intermediate between the protoxide and peroxide, just as the magnetic oxide, and its derivatives, is intermediate between the protoxide and sesquioxide.
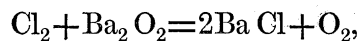
combination of carbon, and which greatly enlarge our view of the system of analogies by which the organic and inorganic worlds of chemistry are connected. These bodies are, so to say, the organic representatives of chlorine. Indeed no compound substance, unless perhaps the peroxide of hydrogen, can be compared with them in chemical similarity to that element. The solution of these peroxides in water can hardly be discriminated from a solution of chlorine; the solution bleaches indigo, oxidizes the protosalts of iron and manganese, decomposes the alkaline peroxides, is decomposed by the action of sunlight, and breaks up with water into the hydrated acid and oxygen. We have
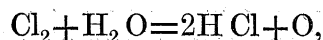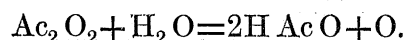
$$Cl_2 + 2HKO + 2Mn\,HO = 2K\,Cl + H_2\,O + Mn_2\,H_2\,O_3,$$

and

$$Ac_2\,O_2 + 2HKO + 2Mn\,HO = 2KAc\,O + H_2\,O + Mn_2\,H_2\,O_3;$$

also

$$Cl_2 + Ba_2\,O_2 = 2Ba\,Cl + O_2,$$

and

$$Bz_2\,O_2 + Ba_2\,O_2 = 2Ba\,Bz\,O + O_2;$$

also

$$Cl_2 + H_2\,O = 2H\,Cl + O,$$
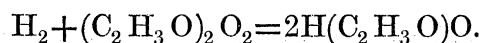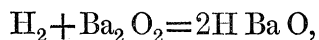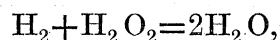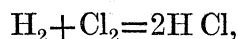
and

$$Ac_2\,O_2 + H_2\,O = 2H\,Ac\,O + O.$$
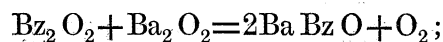
No parallel can be more complete.

In writing the formula of water and of hydrochloric acid, HO and HCl, it was implicitly assumed that the atom of oxygen stood in the same relation in regard to the molecule of water as does the atom of chlorine in regard to the molecule of hydrochloric acid. This view can no longer be maintained. Peroxide of hydrogen, and not oxygen, is the analogue of chlorine. We have

$$H_2 + Cl_2 = 2H\,Cl,$$
$$H_2 + H_2\,O_2 = 2H_2\,O,$$
$$H_2 + Ba_2\,O_2 = 2H\,Ba\,O,$$
$$H_2 + (C_2\,H_3\,O)_2\,O_2 = 2H(C_2\,H_3\,O)O.$$

The remarkable point in the case of the organic peroxides is not only that this analogy is an analogy of the forms of decomposition, but that the same similarity of properties which exists in hydrochloric acid and acetic acid is found also in chlorine and the peroxide of acetyl; and precisely the same reasons, derived from similarity of chemical properties, which lead us to place in the same class of "acids" hydrochloric acid and acetic acid, compel us also to group together chlorine and the peroxide of acetyl. These bodies are the analogues of chlorine in the same sense in which the nitrogen base is the analogue of potash, and in a closer sense than that in which ethyl is the analogue of hydrogen.

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 of 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 in other cases may 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.