396. *Inorganic Per-acids. Part II. The Alkali Percarbonates.*

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The contradictory experimental work on the alkali percarbonates has been re-investigated. The new compounds $CsOOH,H_2O_2$, $KHCO_4$, $RbHCO_4$, $Rb_2C_2O_6$, and Li_2CO_4,H_2O were obtained. The compounds $NaHCO_4$, $Na_2C_2O_6$, $K_2C_2O_6$, $K_2CO_4,2\frac{1}{2}H_2O$, $K_2CO_4,H_2O_2,1\frac{1}{2}H_2O$, $K_2CO_4,2H_2O_2,H_2O$, $Rb_2CO_4,2\frac{1}{2}H_2O$, $Rb_2CO_4,H_2O_2,2H_2O$, $Rb_2CO_4,2H_2O_2,H_2O$, and Cs_2CO_4,H_2O_2,H_2O were confirmed. The supposed isomeric compounds $Na_2CO_4,1\frac{1}{2}H_2O$ and $Na_2CO_3,H_2O_2,\frac{1}{2}H_2O$ were shown to be identical. The compounds $Na_2C_2O_6,H_2O_2$ and $Na_2C_2O_6,C_2H_5OH$ were not confirmed. The validity of the Riesenfeld test for differentiating between true percarbonates and carbonates with hydrogen peroxide of crystallisation is denied.

THE literature on the alkali percarbonates is very confused and contradictory, and it seems desirable first to give a short summary of the methods of preparation which have been used and then to consider briefly the supposed differentiation of the products into two groups, the true percarbonates regarded as salts of percarbonic acids, and the carbonate peroxyhydrates regarded as addition compounds of carbonates and hydrogen peroxide and sometimes water as well.

(1) Constam and Hansen (*Z. Elektrochem.*, 1896—1897, **3**, 137; Hansen, *ibid.*, p. 445) obtained sky-blue solid potassium perdicarbonate $K_2C_2O_6$ by anodic oxidation of concentrated potassium carbonate at $-10°$. They interpreted the reaction as due to the discharge of KCO_3' ions, but this is very improbable, since Löwenherz (*Z. physikal. Chem.*, 1895, **18**, 77) found that potassium carbonate is completely ionised in fused Glauber's salt into $2K^{\cdot}$ and CO_3''. Better yields and a purer product were obtained by Riesenfeld and Reinhold (*Ber.*, 1909, **42**, 4377), the poor yield found by Brown (*J. Amer. Chem. Soc.*, 1905, **27**, 1222) being no doubt due to faulty procedure. Constam and Hansen also obtained a solid thought to be rubidium perdicarbonate $Rb_2C_2O_6$ and oxidising solutions supposed to contain the sodium and ammonium salts. Solutions of the lithium and the sodium salt were obtained by Riesenfeld and Reinhold

and by LeBlanc and Zellmann (*Z. Elektrochem.*, 1923, **29**, 179, 192), who confirmed an observation of Salzer (*ibid.*, 1902, **8**, 900) that the yield is much better with normal sodium carbonate than with sodium hydrogen carbonate. Solutions which were merely assumed to contain percarbonates were obtained by Fichter and Bladergoen (*Helv. Chim. Acta*, 1927, **10**, 566) by the action of fluorine on solutions of sodium, potassium, and rubidium carbonates. It is seen that the only well-established electrolytic percarbonate is the potassium salt. This, and the oxidising solutions, liberate immediately iodine from neutral potassium iodide solution, and in the case of the potassium salt the iodine is equivalent to the whole of the active oxygen. The structure of the electrolytic perdicarbonates proposed by Constam and Hansen is $M_2[-O{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}O-]$.

(2) Another type of percarbonate was isolated by Tanatar (*Ber.*, 1899, **32**, 1544). By dissolving sodium carbonate in 3% hydrogen peroxide and precipitating the products with alcohol he obtained two solids to which he gave the formulæ $Na_2CO_4,1\frac{1}{2}H_2O$ and $Na_2CO_4,\frac{1}{2}H_2O_2,H_2O$ (formed with excess of hydrogen peroxide). These liberated hydrogen peroxide in solution, slowly decomposing with evolution of oxygen, and gave hydrogen peroxide with acids. From thermochemical measurements, Tanatar concluded that the solids were, not carbonate peroxyhydrates, but salts of permonocarbonic acid H_2CO_4. Several patent specifications describe the preparation of sodium percarbonates by similar methods (Merck, G.P. 213,457/1907; Klopfer, G.P. 297,797/1914; Henkel & Cie., G.P. 303,556/1915; D. G. S. Scheideanst. Roessler, G.P. 342,046/1915; Wade, B.P. 152,366/1920; Noll, B.P. 202,985/1923; Shotterbeck, G.P. 560,460/1927; Walters, B.P. 565,653/1944; Slater and Wood, B.P. 568,754/1945). Tanatar failed to obtain the corresponding potassium salts in a pure form, the solid obtained being regarded as a mixture of $K_2CO_4,3H_2O$ and K_2CO_3. Kasanetzky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 202, 388; *Abs.*, 1902, **82**, ii, 317, 500) by using 25% hydrogen peroxide obtained $K_2CO_3,2H_2O_2,\frac{1}{2}H_2O$ and $K_2CO_3,3H_2O_2$, which he regarded as $K_2CO_5,2\frac{1}{2}H_2O$ and $K_2CO_6,3H_2O$, an ammonium salt $(NH_4)_2CO_4,2H_2O$, and (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1110; *Abs.*, 1915, **108**, ii, 334) an unstable cæsium compound $Cs_2CO_3,2H_2O_2$. Peltner (*Ber.*, 1909, **42**, 1777) obtained the compound $RbOOH,H_2O_2$ and the unstable rubidium percarbonates $Rb_2CO_4,2\frac{1}{2}H_2O$, $Rb_2CO_4,H_2O_2,2H_2O$, and $Rb_2CO_4,2H_2O_2,H_2O$. By the action of excess of hydrogen peroxide on potassium and sodium hydrogen carbonates and precipitation with alcohol Kazanetzky (*J. Russ. Phys. Chem. Soc.*, 1903, **36**, 57; *Abs.*, 1913, **84**, ii, 366) obtained an evolution of carbon dioxide and the solid compounds $K_2CO_5,2\frac{1}{2}H_2O$, $Na_2CO_4,1\frac{1}{2}H_2O$, and $Na_2CO_4,\frac{1}{2}H_2O_2,H_2O$ (previously prepared by Tanatar from sodium carbonate). LeBlanc and Zellmann (*loc. cit.*) assumed that in this case sodium hydrogen carbonate forms the normal carbonate and carbonic acid in solution ($2NaHCO_3 = Na_2CO_3 + H_2CO_3$), the carbonate reacts with hydrogen peroxide to form Tanatar's salt, and the carbonic acid to form permonocarbonic acid which decomposes ($H_2CO_4 = H_2O + CO_2 + \frac{1}{2}O_2$). It would seem simpler, however, to suppose that the carbonic acid decomposes directly.

(3) A third group of reactions make use of the action of carbon dioxide on sodium peroxide hydrate $Na_2O_2,8H_2O$ (or sodium peroxide with less water than this), or sodium hydrogen peroxide NaOOH or its compound with hydrogen peroxide (Bauer, G.P. 145,746/1903; F.P. 331,937/1903; Merck, G.P. 188,569/1905; Wolffenstein and Peltner, *Ber.*, 1908, **41**, 280), or carbonyl chloride on sodium peroxide (Blankart, Dissert., Techn. Hochsch., Zurich, 1922). Wolffenstein and Peltner, by slowly passing carbon dioxide into a mixture of sodium peroxide and ice kept at or below 0°, and adding more sodium peroxide during the reaction, until the calculated increase in weight was reached, obtained $Na_2CO_4,1\frac{1}{2}H_2O$, the reaction being described as "subtle." By the further action of carbon dioxide on this, or directly by saturating hydrated sodium peroxide with carbon dioxide, they obtained $Na_2C_2O_6$, which they regarded as an anhydride of $NaHCO_3 + NaHCO_4$ but containing water, which they supposed was present as $Na_2CO_4,1\frac{1}{2}H_2O$. The action of carbon dioxide on sodium hydrogen peroxide NaOOH prepared by Tafel's method (*Ber.*, 1894, **27**, 2297) by the action of sodium peroxide on alcohol, which they regarded as "Natrylhydrat" $O{:}Na{\cdot}OH$, gave a product regarded as a mixture of $NaHCO_4$, Na_2CO_5, and $Na_2C_2O_6$, or of $NaHCO_4$, Na_2CO_4, and Na_2CO_5, or as $Na_2C_2O_7,H_2O$. Another specimen of sodium hydrogen peroxide prepared by the addition of sodium ethoxide to aqueous-alcoholic hydrogen peroxide was regarded as "Natriumtrioxyhydrat" $Na{\cdot}OOH$ and was supposed to give a different product with carbon dioxide, *viz.*, impure $NaHCO_4$ which was more stable to dehydration than that obtained with $O{:}Na{\cdot}OH$ and hence was regarded as isomeric with it. The supposed difference was almost certainly caused by a difference in the rates of drying of the two products, and there is no evidence that more than one form of NaOOH exists. They found that by the action of the calculated amount of carbon dioxide on partly

hydrated "O:Na·OH" hydrated Na_2CO_5 is formed. Dry sodium peroxide and sodium hydrogen peroxide do not react with dry carbon dioxide. Wolffenstein and Peltner emphasise that the amount of water present in their $Na_2C_2O_6$ does not allow the active oxygen to be present as hydrogen peroxide, and this must *a fortiori* apply to the nearly dry $K_2C_2O_6$ first described in the present communication.

Kamtikar and Husain (*J. Osmania Univ. Coll.*, 1934, 2, 39; *Chem. Abstr.*, 1936, **30**, 4112) regarded $Na_2C_2O_6$ and $Na_2CO_4,1\frac{1}{2}H_2O$ prepared by the above methods as mixtures of Na_2CO_3, $NaHCO_3$, and a small amount of active oxygen probably in the form of Na_2O_2 or NaOOH. Both previous work in this field and the experiments now described negative this assumption. The preparations are far from simple. Wolffenstein and Peltner found that, in the preparation of Na_2CO_4 from carbon dioxide and hydrated sodium peroxide, if the water content is too small so much heat is evolved that the whole is decomposed, whilst with too much water the end product is moist and during the reaction the mass cakes together, the absorption of gas is too slow, and the percarbonate is decomposed The reaction between carbon dioxide and sodium hydrogen peroxide they say is "tremendously sensitive"; the solid must be mixed with 26—30% of powdered ice, cooled in ice and salt, and the carbon dioxide passed in slowly. A local rise in temperature above 0° or a momentarily too rapid supply of carbon dioxide led to rapid and complete decomposition of the product. Even during drying of the moist product decomposition may occur, the lid of the desiccator being blown off, although when dry the solid is fairly stable. Failure to obtain satisfactory products in this field is very easy.

Riesenfeld and Mau (*Ber.*, 1911, **44**, 3589, 3595), on the basis of the Riesenfeld test (see below), concluded that $Na_2C_2O_6$ and Na_2CO_4 are true percarbonates, whilst $NaHCO_4$ is $Na_2C_2O_6,H_2O_2$ and Na_2CO_5,H_2O is Na_2CO_4,H_2O_2, the compounds $Na_2C_2O_6$ and $Na_2C_2O_6,H_2O_2$ liberating the same amount of iodine from neutral potassium iodide solution. By passing dry carbon dioxide into sodium peroxide in absolute alcohol (containing NaOOH and $NaOC_2H_5$) at 0—5° until the mixture gave no colour with phenolphthalein they claimed to have obtained $Na_2C_2O_6,C_2H_5OH$, which is the same as Wolffenstein and Peltner's compound except that it contains alcohol of crystallisation, and if sodium peroxide hydrate was used $Na_2C_2O_6,\frac{1}{2}H_2O$ was obtained. By adding 30% hydrogen peroxide to the suspension of sodium peroxide in alcohol, either before or after passing in carbon dioxide, they claimed to have obtained $Na_2C_2O_6,H_2O_2$, and, whereas $Na_2C_2O_6$ liberated iodine equivalent to half the active oxygen, this liberated only a quarter. Kamtikar and Husain (*loc. cit.*) regarded the first compound as $Na_2CO_3,NaHCO_3,H_2O_2,xC_2H_5OH$, but we have shown that it is a mixture of $NaHCO_4$ and sodium monoethyl carbonate $NaO·CO·OC_2H_5$, obtained by Beilstein (*Annalen*, 1859, **112**, 124; Faurholt, *Z. physikal. Chem.*, 1927, **126**, 227) but apparently unknown to Riesenfeld and Mau. This compound is precipitated by carbon dioxide from sodium ethoxide solution and is insoluble in alcohol. Riesenfeld and Mau, using a potassium peroxide with the empirical formula K_2O_3 but probably a mixture of K_2O_2 and KO_2, in place of sodium peroxide, obtained a compound $K_2C_2O_6$ which, as solid or in solution, differed from the electrolytic compound in liberating only about half the iodine equivalent to its active oxygen. This compound was formulated as $M_2[-O·O·CO·O·CO·O-]$. This type of isomerism is confirmed by experiments now described.

LeBlanc and Zellmann (*loc. cit.*) limited true percarbonates to salts of the monobasic permonocarbonic acid H_2CO_4 and the dibasic perdicarbonic acid $H_2C_2O_6$, which are derivatives of hydrogen peroxide HOOH in which one or both hydrogen atoms are replaced by the group O:C(OH), and they are hydrolysed by water as follows:

$$M_2C_2O_6 + H_2O = MHCO_4 + MHCO_3$$
$$MHCO_4 + H_2O = MHCO_3 + H_2O_2$$

The extensive liberation of iodine by $K_2C_2O_6$ was regarded as due to the rapid formation of $KHCO_4$ (then unknown as a solid, but described below). Wolffenstein and Peltner's compounds $Na_2C_2O_6$ and $NaHCO_4$ with 15% potassium iodide solution at −10° did not evolve oxygen, and only $NaHCO_4$ liberated iodine at once, whereas at 0° both liberated iodine immediately. The liberation of iodine by $Na_2C_2O_6$ at 0° was delayed by addition of sodium hydrogen carbonate, presumably owing to suppression of the formation of $NaHCO_4$. If both hydrogen atoms in HO·O·CO·OH are replaced by a metal the actve oxygen is no longer in the form of a true percarbonate but is easily detached as hydrogen peroxide of crystallisation. Although the extraction of hydrogen peroxide by ether from Tanatar's salt was only slight it was supposed (as we think incorrectly) that this was not $Na_2CO_4,1\frac{1}{2}H_2O$ but $Na_2CO_3,H_2O_2,\frac{1}{2}H_2O$. Wolffenstein and Peltner's Na_2CO_5 they regarded as a mixture of NaOOH and $NaHCO_4$.

It is clear from what precedes that the whole field of the chemistry of the alkali percarbonates stood in need of re-investigation. The following questions seemed to us to call for attention. (1) Is the salt $Na_2CO_4,1\frac{1}{2}H_2O$ described by Wolffenstein a chemical individual, and, if it is, does it differ from Tanatar's salt with the same formula? (2) Do the perdicarbonates $M_2C_2O_6$ exist in one form only, as stated by LeBlanc and Zellmann, or in two as stated by Riesenfeld and Mau? (3) Has the sodium percarbonate prepared from sodium peroxide and hydrogen peroxide in alcohol by the action of carbon dioxide the formula $Na_2C_2O_6,H_2O_2$ as stated by Riesenfeld and Mau, or is it a salt of H_2CO_4, and do other salts of this acid exist? (4) Is the test with neutral potassium iodide, claimed by Riesenfeld to distinguish true peroxides from hydrogen peroxide of crystallisation, reliable? Before passing to the experimental part, a few words may be said about the Riesenfeld test.

The distinction made by Riesenfeld and Reinhold and by Riesenfeld and Mau between the two types of compound is based on a reaction first studied by Bredig and Walton (*Z. Elektrochem.*, 1903, **9**, 114; later investigations of it do not concern us), who found that hydrogen peroxide liberates hardly any iodine from neutral potassium iodide solution, but evolves oxygen gas. This was explained as a catalytic effect of the hypoiodite ion formed as an intermediate product:

$$H_2O_2 + I' = H_2O + IO' \text{ (slow)} \quad . . . . \quad \text{(i)}$$

$$H_2O_2 + IO' = H_2O + O_2 + I' \text{ (very rapid)} \quad . . . . \quad \text{(ii)}$$

Riesenfeld and Reinhold found that electrolytic percarbonates liberate iodine immediately from 30% potassium iodide solution by the reaction:

$$C_2O_6'' + 2I' = 2CO_3'' + I_2 \quad . . . . \quad \text{(iii)}$$

whilst the solid compounds which they regarded as carbonates with hydrogen peroxide of crystallisation did not liberate iodine but produced an evolution of oxygen. The conclusion drawn was criticised by Tanatar (*Ber.*, 1910, **43**, 127), who pointed out that only solids or freshly prepared solutions gave the test and attributed the different behaviour of the two types of salt to the hydrolysis of the first to form an alkali hydrogen carbonate (HCO_3') which did not react with free iodine and hence did not prevent its appearance, and the hydrolysis of the second to form a normal carbonate (CO_3'') which reacted with iodine to form a hypoiodite, the latter reacting with hydrogen peroxide, also formed by hydrolysis, with evolution of gaseous oxygen. Riesenfeld (*Ber.*, 1910, **43**, 566) then showed that $K_2C_2O_6$ liberates an appreciable amount of iodine even in presence of sodium carbonate in the ratio $K_2C_2O_6 : 2Na_2CO_3$, whereas Tanatar's salt evolved oxygen only in presence of sodium hydrogen carbonate in the ratio $Na_2CO_4 : 2NaHCO_3$, although the first solution was more alkaline than the second. These results were confirmed by Tanatar (*Ber.*, 1910, **43**, 2149), who found different results with solid percarbonates and hence concluded that, since both the solutions (especially after being kept for some time) evolve oxygen, the liberation of iodine by $K_2C_2O_6$ is more rapid than its hydrolysis to form H_2O_2, whilst the reverse is true in the case of Na_2CO_4. Krauss and Oettner (*Z. anorg. Chem.*, 1934, **218**, 21) distinguished between reactions in neutral or acid and those in alkaline solutions; in the first, liberation of iodine occurs both with percarbonate and with carbonate peroxyhydrate according to the reaction:

$$H_2O_2 + 2I' = I_2 + 2OH' \quad . . . . \quad \text{(iv)}$$

whilst in the second the iodine reacts further:

$$I_2 + 2OH' = I' + IO' + H_2O \quad . . . . \quad \text{(v)}$$

the hydrogen peroxide present in the solution or formed by hydrolysis then reacting according to (ii). These conclusions were modified by Liebhafsky (*ibid.*, 1934, **221**, 25), who found that in neutral solution reaction (iv) is negligible, the main change being catalytic liberation of oxygen, whilst a true persalt such as $K_2S_2O_8$ liberates iodine without liberation of oxygen. In presence of buffer solutions to maintain a suitable pH the Riesenfeld test may serve to distinguish such widely different compounds as hydrogen peroxide and persulphate, but its extension to transition cases (*e.g.*, to weak peracids such as the percarbonic acids) is of doubtful value. The latter conclusion was also reached by Menzel (*ibid.*, 1927, **167**, 193) in the case of perborates, since so many factors are involved in the use of the solid salt, such as the rate and extent of hydrolysis and of solution, the pH of the solution, etc. A readily soluble per-salt will form sufficient ions in solution to liberate iodine from iodide before complete hydrolysis and formation of hydrogen peroxide occurs, whereas a sparingly soluble salt, or one which dissolves slowly, may hydrolyse before sufficient per-ions are present to react with the iodide.

The marked hydrolysis of per-salts of weak acids such as boric, carbonic, and silicic makes it doubtful if the Riesenfeld test, when carried out with solutions, has any validity in such cases. It may be mentioned that the existence of free percarbonic acid in solution in ether (Bach, *Chem. Zentr.*, 1897, II, 828) was shown by Wolffenstein and Peltner (*loc. cit.*) to be improbable.

The results obtained in the present investigation were as follows.

Lithium permonocarbonate Li_2CO_4,H_2O was prepared by the action of carbon dioxide on lithium peroxide perhydrate $Li_2O_2,H_2O_2,3H_2O$ or on lithium peroxide Li_2O_2 in presence of water; it is not formed by the action of hydrogen peroxide on lithium carbonate. Excess of carbon dioxide reduces the active oxygen without affecting the $Li_2O : CO_2$ ratio, which is explained by assuming the formation of unstable $Li_2C_2O_6$ or $LiHCO_4$, which could not be prepared.

The formation of disodium perdicarbonate $Na_2C_2O_6$ by the action of carbon dioxide on sodium peroxide hydrate was confirmed, but the compound described as $Na_2C_2O_6,C_2H_5{\cdot}OH$ was shown to be a mixture of sodium hydrogen permonocarbonate $NaHCO_4$ and sodium monoethyl carbonate $NaO{\cdot}CO{\cdot}OC_2H_5$. Sodium hydrogen permonocarbonate prepared from carbon dioxide and the compound $NaOOH,\frac{1}{2}H_2O_2$ was shown to lose carbon dioxide more readily than $Na_2C_2O_6$ and to form a product almost identical with Tanatar's salt; hence its formulation as $Na_2C_2O_6,H_2O_2$ is thought to be incorrect. Hydrogen peroxide has hardly any action on sodium hydrogen carbonate below 0°, but the evolution of carbon dioxide and the formation of $Na_2CO_4,\frac{1}{2}H_2O_2,H_2O$ at room temperature was confirmed. In presence of alcohol this absorbs carbon dioxide only if water is present, the active oxygen content being diminished. The distinction between $Na_2CO_4,1\frac{1}{2}H_2O$ and $Na_2CO_3,H_2O_2,\frac{1}{2}H_2O$ on the basis of Riesenfeld's test is shown to be unsatisfactory. When prepared from sodium peroxide octahydrate it behaves in the same way as Tanatar's salt, suggesting that in presence of sufficient water $Na_2C_2O_6$ and $Na_2O_2,8H_2O$ react to form a uniform substance, $Na_2CO_4,1\frac{1}{2}H_2O$ and $Na_2CO_3,H_2O_2,\frac{1}{2}H_2O$ being identical.

Potassium hydrogen permonocarbonate $KHCO_4$ was obtained by saturating an alcoholic suspension of potassium hydrogen peroxide with carbon dioxide at low temperature, and also from hydrogen peroxide and potassium monomethyl carbonate; it is much less stable than the sodium salt ($RbHCO_4$ is also unstable and $CsHCO_4$ could not be obtained). Hydrogen peroxide and sodium monomethyl or monoethyl carbonate or potassium monoethyl carbonate gave products containing active oxygen but probably partly hydrolysed. The formation of $K_2CO_4,2\frac{1}{2}H_2O$, $K_2CO_4,H_2O_2,1\frac{1}{2}H_2O$, and $K_2CO_4,2H_2O_2,H_2O$ from potassium carbonate and hydrogen peroxide in the ratios 1 : 1, 1 : 2, and 1 : 3 was confirmed. In alcohol all three absorbed carbon dioxide to form the same product $K_2C_2O_6$, which was obtained almost anhydrous by drying it in a vacuum over phosphoric oxide. Evidence for the formation of a small amount of $KHCO_4$ with excess of hydrogen peroxide was found.

Rubidium hydrogen permonocarbonate $RbHCO_4$ was confirmed; it is very unstable and sensitive to dehydration. With excess of hydrogen peroxide evidence of the formation of a substance containing more active oxygen was found but it could not be isolated. The three compounds $Rb_2CO_4,2\frac{1}{2}H_2O$, $Rb_2CO_4,2H_2O_2,H_2O$, and $Rb_2CO_4,H_2O_2,2H_2O$ were confirmed. In alcohol they absorb carbon dioxide in the same way as the potassium salts. With the first, absorption of carbon dioxide occurs with slight loss of active oxygen to form $Rb_2C_2O_6$ but this salt could not be obtained anhydrous. The active oxygen retained after carbonation of the second and third is greater than in the case of the potassium salts, and rubidium hydrogen permonocarbonate $RbHCO_4$ seems to be formed in appreciable amounts.

Cæsium hydrogen peroxide perhydrate $CsOOH,H_2O_2$ was prepared by the action of hydrogen peroxide on alcoholic cæsium hydroxide; with carbon dioxide it does not form $CsHCO_4$ but gives Cs_2CO_4,H_2O_2,H_2O.

EXPERIMENTAL.

I. *Lithium Permonocarbonate* Li_2CO_4,H_2O.—This compound, previously unknown, could not be obtained by the action of hydrogen peroxide on lithium carbonate, on account of the sparing solubility of the latter, but was prepared by the action of carbon dioxide on lithium peroxide perhydrate and on lithium peroxide in presence of water. In the analyses of the products, lithium oxide Li_2O was determined by titration with acid using methyl-orange as indicator, active oxygen (O_a) by titration with permanganate in acid solution, carbon dioxide gravimetrically by liberation and absorption in alkali, and water by difference.

1. *Action of hydrogen peroxide on lithium carbonate.* On keeping lithium carbonate in contact with 30% hydrogen peroxide for some time and filtering, it was found that the solid did not contain active oxygen but was unchanged lithium carbonate. The same result was found by using excess of hydrogen peroxide and keeping the mixture for a long time at room temperature or below 0°. From the mother-liquor, alcohol precipitated only lithium carbonate.

2. *Action of carbon dioxide on lithium peroxide perhydrate.* The preparation of lithium peroxide perhydrate ($Li_2O_2,H_2O_2,3H_2O$) was carried out as described by De Forcrand (*Compt. rend.*, 1900, **130**, 1465). Cold alcohol was added to a cold concentrated aqueous solution of lithium hydroxide containing the requisite amount of hydrogen peroxide. The compound separated as minute colourless crystals, which were washed with alcohol and ether after separation from the mother-liquor. On passage of stream of carbon dioxide dried by concentrated sulphuric acid slowly over this substance with continuous stirring, the mass being maintained below −10°, the carbon dioxide was smoothly absorbed and towards the end of the reaction the already dry mass became moist. The end of the reaction is indicated when the increase in weight corresponds to the absorption of one molecule of carbon dioxide per mol. of Li_2O. The pasty mass was washed with alcohol and the crystalline white solid analysed after being washed with ether (analysis 1, Table I) and after drying for several hours in a vacuum over phosphoric oxide (analysis 2). The results show that a lithium percarbonate was formed. The product dried in a vacuum corresponds to Li_2CO_4,H_2O. Only half the active oxygen in the lithium peroxide perhydrate is found in the solid percarbonate, the rest being eliminated as hydrogen peroxide and removed during the washing. This salt is soluble in water to give an alkaline solution. Dry ether does not extract any active oxygen from it. On addition of the solid to concentrated neutral potassium iodide solution a slight liberation of iodine occurred, accompanied by a strong evolution of oxygen, which according to Riesenfeld and Reinhold would indicate that the product is an addition product of hydrogen peroxide and lithium carbonate. Since, however, it is not formed from hydrogen peroxide and lithium carbonate, it seems to be a true percarbonate, and the evolution of oxygen may owe its origin to free hydrogen peroxide formed by hydrolysis and to the alkaline reaction (hypoidite is formed which reacts with hydrogen peroxide, evolving oxygen). The experiment was repeated but at the end of the reaction excess of 30% hydrogen peroxide was added. No increase in active oxygen content was found (analysis 3, directly after washing with alcohol and ether; analysis 4, after drying in a vacuum over phosphoric oxide for several hours). The salt has, therefore, no tendency to add hydrogen peroxide. The solid gradually lost active oxygen, and after a week the active oxygen content fell to 11·0%. The aqueous solution is very unstable, losing the whole of its active oxygen within a few hours. The active oxygen content is also affected by continued passage of carbon dioxide after one molecule of carbon dioxide is absorbed per mol. of Li_2O. In this way products were obtained with less active oxygen but at the same time no further increase in the ratio $CO_2 : Li_2O$ was observed. Analysis 5 corresponds to a product obtained after passing carbon dioxide for an hour after one molecule of carbon dioxide had been absorbed per mol. of Li_2O. This behaviour is best explained by assuming the formation of an unstable compound $Li_2C_2O_6$ or $LiHCO_4$, which decomposes as soon as formed :

$$2Li_2C_2O_6 = 2Li_2CO_3 + O_2 + 2CO_2$$
$$2LiHCO_4 = Li_2CO_3 + CO_2 + H_2O_2 + \tfrac{1}{2}O_2$$

A similar behaviour was noticed by Wolffenstein and Peltner in the preparation of barium percarbonate, and is in harmony with the fact that lithium hydrogen carbonate, like the alkaline-earth hydrogen carbonates, is unstable, in contrast to other alkali-metal hydrogen carbonates

3. *Preparation from lithium peroxide* (Li_2O_2). Li_2O_2 was obtained by "dehydrating" $Li_2O_2,H_2O_2,3H_2O$ over phosphoric oxide in a vacuum, as described by De Forcrand. The preparation of lithium percarbonate from this peroxide was carried out in the same way as before; to obtain a good yield, the appropriate amount of water must be present. Analysis 6 was found when $Li_2O_2 : H_2O$ was 1 : 2, analysis (7) when the ratio was 1 : 3, and (8) when it was 1 : 5. The results show that the same percarbonate is formed, in good yield, when three molecules of water are present per Li_2O_2. The reaction therefore proceeds as follows :

$$Li_2O_2\,aq. + CO_2 = Li_2CO_4\,aq.$$

The product obtained in this way is identical in properties with that prepared from lithium peroxide perhydrate.

TABLE I.

Analysis no.	Li_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	Li_2O.	CO_2.	O_a.	H_2O.
1	25·1	36·8	13·2	24·9	1	0·99	0·98	1·65
2	27·4	40·1	14·4	18·05	1	1·00	0·98	1·09
3	24·8	36·4	13·2	25·6	1	1·00	0·99	1·71
4	27·8	40·7	14·45	17·0	1	0·99	0·97	1·01
5	25·2	37·6	11·9	—	1	1·01	0·88	—
6	29·6	43·1	12·5	14·8	1	0·99	0·79	0·83
7	28·4	41·4	13·5	16·7	1	0·99	0·89	0·98
8	29·4	43·0	12·2	15·4	1	0·99	0·76	0·87
			Calc. for Li_2CO_4,H_2O :		1	1	1	1

II. *Sodium Percarbonates.*—In the following experiments, the determinations of Na_2O, CO_2, O_a, and H_2O were carried out as described above unless otherwise stated. The solids formed in the reactions were washed with alcohol and ether and dried on porous plates in a vacuum over the drying agents specified unless otherwise stated. Since some of the compounds are very sensitive to small changes in drying procedure, these details are given when required.

1. *Disodium perdicarbonate* $Na_2C_2O_6$. In the preparation Wolffenstein and Peltner's procedure was closely followed, carbon dioxide being passed slowly into hydrated sodium peroxide and the temperature kept below 0° until the weight no longer increased. The product was dried over phosphoric oxide for a day. (The moist product rapidly loses carbon dioxide and oxygen.) Analyses 1 and 2 in Table II refer to this compound. The results confirm those of Wolffenstein and Peltner and the amount

of water is too small for the active oxygen to exist as hydrogen peroxide, or the carbon dioxide as $NaHCO_3$. Dry ether had no effect on the active oxygen content. The solid liberated iodine and oxygen from concentrated neutral potassium iodide solution. Analyses 3 and 4 refer to solid kept for a month in a desiccator; loss of active oxygen and some carbon dioxide occurred but to a much smaller extent than with $NaHCO_4$ (see below), and the solid still liberated much iodine from iodide solution. The rapid loss of carbon dioxide from the moist product suggests the formation of $NaHCO_4$ by hydrolysis according to the scheme of LeBlanc and Zellmann.

TABLE II.

Analysis no.	Na_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	Na_2O.	CO_2.	O_a.	H_2O.
1	38·8	49·0	7·7	4·4	1	1·78	0·77	0·39
2	38·9	48·9	7·8	4·3	1	1·76	0·78	0·38
3	41·8	48·2	5·8	4·2	1	1·62	0·54	0·35
4	41·5	48·45	5·7	4·4	1	1·64	0·53	0·36
Calc. for $Na_2C_2O_6$:					1	2	1	

Riesenfeld and Mau's method was also used, dry sodium peroxide in absolute alcohol being saturated with dry carbon dioxide below 0° until phenolphthalein gave no colour. The product was dried for a short time. Na_2O and CO_2 were determined by titration with methyl-orange and phenolphthalein. The results are shown in Table III.

TABLE III.

Analysis no.	Na_2O, %.	CO_2 %.	O_a, %.	Na_2O.	CO_2.	O_a.
1	29·2	37·4	4·8	1	1·81	0·64
2	29·5	38·25	5·2	1	1·83	0·69

This product when distilled with water gave alcohol even after repeated washing with ether and when kept lost carbon dioxide much more rapidly than that prepared by the first method. Its properties suggest that it is a mixture of the unstable $NaHCO_4$ and sodium monoethyl carbonate $NaO{\cdot}CO{\cdot}O{\cdot}C_2H_5$, and not $Na_2C_2O_6,C_2H_5{\cdot}OH$ as stated by Riesenfeld and Mau. It is probable that sodium peroxide first reacts with alcohol as follows:

$$Na_2O_2 + C_2H_5{\cdot}OH = NaOOH + NaO{\cdot}C_2H_5$$

and the two products react simultaneously with carbon dioxide:

$$NaOOH + CO_2 = NaHCO_4$$

$$NaOC_2H_5 + CO_2 = NaO{\cdot}CO{\cdot}O{\cdot}C_2H_5$$

An equimolecular mixture of these products would have the same composition as $Na_2C_2O_6,C_2H_5{\cdot}OH$. This mechanism is confirmed by the experiment described in (2).

2. *Sodium hydrogen monopercarbonate* $NaHCO_4$. The method of LeBlanc and Zellmann was used, except that $NaOOH,\frac{1}{2}H_2O_2$ prepared according to Wolffenstein and Peltner was used instead of NaOOH. A mixture of 30% hydrogen peroxide and alcohol was added to alcoholic sodium ethoxide ($H_2O_2 : Na = 2 : 1$). The oily precipitate solidified on cooling. The solid washed with alcohol and ether gave Na_2O 41·9, 41·8%, O_a 29·9, 29·8%, *i.e.*, Na : O_a 1 : 1·39 and 1 : 1·38; $NaOOH,\frac{1}{2}H_2O_2$ requires 1 : 5. The solid (2 g.) was suspended in 75% alcohol (100 ml.), and carbon dioxide passed in below −10° until phenolphthalein gave no colour. The product was dried over phosphoric oxide for a short time. The results 1 and 2 in Table IV show that the solid is $NaHCO_4$. The product was free from alcohol, was not affected by dry ether, and liberated iodine and oxygen from potassium iodide solution. Rapid drying caused sudden decomposition, but this did not occur on slow drying. The results 3 and 4 for a specimen kept for a month show that carbon dioxide and active oxygen are lost more rapidly than from $Na_2C_2O_6$; the final product behaves like Tanatar's salt:

$$2NaHCO_4 = Na_2CO_4 + H_2O + CO_2 + \tfrac{1}{2}O_2.$$

TABLE IV.

Analysis no.	Na_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	Na.	CO_2.	O_a.	H_2O.
1	31·3	41·6	14·9	12·15	1	0·94	0·92	0·67
2	31·2	40·6	14·8	13·4	1	0·92	0·91	0·74
3	41·0	34·6	11·7	12·6	1	0·59	0·55	0·53
4	41·4	35·1	11·5	12·1	1	0·59	0·54	0·50
5	30·5	41·1	14·3	14·1	1	0·95	0·91	0·79
6	30·2	40·2	14·3	15·4	1	0·94	0·92	0·87
7	23·9	29·6	11·1	*	1	0·88	0·90	*
8	23·3	28·6	11·0	*	1	0·87	0·92	*
Calc. for $NaHCO_4$:					1	1	1	0·50

* Contains alcohol.

The procedure of Riesenfeld and Mau, said to give $Na_2C_2O_6,H_2O_2$, was then followed. 30% Hydrogen peroxide was added to alcoholic sodium peroxide before saturating the mixture with carbon dioxide. The product was easily freed from alcohol by washing with ether, and analyses 5 and 6 show that it was $NaHCO_4$: $C_2H_5ONa + H_2O_2 = NaOOH + C_2H_5OH$; $NaOOH + CO_2 = NaHCO_4$. When 30%

hydrogen peroxide was added after the reaction with carbon dioxide a slimy product was formed, not easily freed from alcohol by washing with ether and resembling the product containing active oxygen formed by addition of hydrogen peroxide to sodium monoethyl carbonate suspended in alcohol. In this reaction the carbon dioxide forms sodium monoethyl carbonate with the sodium peroxide and alcohol, and the hydrogen peroxide added subsequently reacts with this to give the slimy product which contaminates the $NaHCO_4$. Contrary to Riesenfeld and Mau's statement, the results are quite different according as hydrogen peroxide is added before or after passage of carbon dioxide, and confirm the conclusion that the compound described by them as $Na_2C_2O_6,H_2O_2$ is really a mixture of $NaHCO_4$ and sodium monoethyl carbonate.

3. *Action of hydrogen peroxide on sodium hydrogen carbonate.* The gradual addition of excess of solid sodium hydrogen carbonate to 10% or 30% hydrogen peroxide at room temperature or below 0° gave a solid free from active oxygen. But if the solid was set aside at room temperature in contact with the solution for about 4 hours Tanatar's salt $Na_2CO_4,\frac{1}{2}H_2O_2,H_2O$ was formed, provided that sufficient hydrogen peroxide was used. The change was very slow below 0°. On passage of carbon dioxide into an alcoholic suspension of Tanatar's salt, no $NaHCO_4$ or $Na_2C_2O_6$ was formed, the gas being absorbed only in presence of water, and active oxygen being lost simultaneously.

4. *Disodium permonocarbonate* $Na_2CO_4,1\frac{1}{2}H_2O$. This was prepared by Wolffenstein and Peltner's method. Carbon dioxide was passed slowly into 7·8 g. of sodium peroxide and 5 g. of water cooled below 0° until the increase in weight corresponded with the formation of Na_2CO_4. The washed product was dried in a vacuum for a short time. The analytical results were :

Analysis no.	Na_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	Na_2O.	CO_2.	O_a.	H_2O.
1	40·7	29·2	9·5	20·7	1	1·01	0·90	1·75
2	40·8	30·0	9·4	19·8	1	1·04	0·89	1·67

The product was unstable and differed in this respect from Tanatar's salt, but was more stable when not fully dried. It liberated iodine and oxygen from concentrated neutral potassium iodide solution. The product from $Na_2O_2,8H_2O$ behaved like Tanatar's salt in not liberating iodine, and it is concluded that the action of carbon dioxide on sodium peroxide hydrate containing less than $8H_2O$ gives Tanatar's salt, $Na_2C_2O_6$ (liberating iodine), and unchanged sodium peroxide hydrate. But, with sufficient water, $Na_2C_2O_6$ and sodium peroxide hydrate react to form Tanatar's salt. Riesenfeld and Mau's supposition that the product is a definite percarbonate different from Tanatar's salt, on the basis of a slight liberation of iodine, is considered very unlikely.

III. *Potassium Percarbonates.*—1. *Action of hydrogen peroxide on potassium carbonate.* Potassium carbonate was dissolved in 30% hydrogen peroxide in different proportions below −5° and excess of alcohol added. The oily products solidified on cooling; they were washed as usual and dried for a short time over calcium chloride in a vacuum. The white crystalline solids were readily soluble, the solutions decomposing rapidly. When the solids were added to concentrated neutral potassium iodide solution oxygen was evolved but no iodine liberated. The solids slowly decomposed but no yellow colour developed (as with $KHCO_4$, see below). The analyses are given in Table V.

TABLE V.

Ratio $K_2CO_3 : H_2O_2$.	K_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	K_2O.	CO_2.	O_a.	H_2O.
(*a*) 1 : 1	46·5	21·7	7·7	24·2	1	0·99	0·97	2·71
	46·7	21·7	7·8	23·7	1	1·00	0·98	2·65
			Calc. for $K_2CO_4,2\frac{1}{2}H_2O$:		1	1	1	2·5
(*b*) 1 : 2	43·4	20·25	14·3	22·05	1	1·00	1·94	2·65
	43·45	20·3	14·4	21·8	1	1·00	1·94	2·62
			Calc. for $K_2CO_4,H_2O_2,1\frac{1}{2}H_2O$:		1	1	2	2·5
(*c*) 1 : 3	38·65	18·2	18·8	24·4	1	1·01	2·85	3·29
	39·0	18·1	19·0	23·9	1	0·99	2·87	3·19
(*d*) 1 : 5	38·7	18·0	18·9	24·4	1	0·99	2·86	3·28
			Calc. for $K_2CO_4,2H_2O_2,H_2O$:		1	1	3	3

2. *Effect of carbon dioxide on the above products.* Carbon dioxide when passed into alcoholic suspensions of the above products was absorbed and the same substance was formed in all cases. The temperature was kept below −10° until phenolphthalein gave no colour. In case (*a*) practically all the active oxygen was retained, in (*b*) only half, and in (*c*) only a third. The products in all cases contained $K_2C_2O_6$ and water. They were unstable, losing nearly half the active oxygen in a week. They were unchanged by dry ether but easily soluble in water to form unstable solutions. The solids liberated considerable quantities of iodine from concentrated neutral potassium iodide solution. Drying over phosphoric oxide in a vacuum for a few hours caused loss of water and some active oxygen. The analytical results exclude the possibility that the products (*a*)—(*d*) consist of potassium hydrogen carbonate with hydrogen peroxide of crystallisation and since they all form $K_2C_2O_6$, which can be obtained nearly anhydrous, by the action of carbon dioxide they are probably as formulated, and not $K_2CO_3,H_2O_2,1\frac{1}{2}H_2O$, $K_2CO_3,2H_2O_2,\frac{1}{2}H_2O$, and $K_2CO_3,3H_2O_2$. The absorption of carbon dioxide by them would then proceed as follows ($x = 0$, 1, or 2) :

$$K_2CO_4,xH_2O_2\,aq. + CO_2 = K_2C_2O_6\,aq. + xH_2O_2$$

The analyses of the products from (*a*)—(*c*) are given in Table VI, the effects of drying being shown in the last two lines.

TABLE VI.

Initial substance.	K_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	K_2O.	CO_2.	O_a.	H_2O.
(*a*)	43·2	38·8	6·8	11·2	1	1·92	0·93	1·35
	44·2	39·2	7·05	9·5	1	1·90	0·94	1·13
(*b*)	43·0	39·0	7·2	10·8	1	1·93	0·98	1·31
	43·8	39·4	7·1	9·65	1	1·92	0·96	1·15
(*c*)	43·7	39·1	7·3	9·9	1	1·91	0·99	1·18
	43·0	38·3	7·2	11·4	1	1·91	0·99	1·38
(*a*)	47·9	42·85	6·8	2·4	1	1·91	0·84	0·26
(*b*)	47·8	43·0	6·9	2·3	1	1·92	0·85	0·25
			Calc. for $K_2C_2O_6$:		1	2	1	

3. *Potassium hydrogen permonocarbonate* $KHCO_4$. (i) Although LeBlanc and Zellmann pointed out the possibility of the formation of this compound in the hydrolysis of $K_2C_2O_6$ it was not isolated. We obtained ***potassium hydrogen permonocarbonate*** $KHCO_4$ by the action of carbon dioxide on an alcoholic suspension of potassium hydrogen peroxide perhydrate, $KOOH,\frac{1}{2}H_2O_2$, made according to D'Ans and Friederich (*Z. anorg. Chem.*, 1912, **73**, 325). A mixture of 30% hydrogen peroxide and alcohol was added to a solution of potassium ethoxide in absolute alcohol cooled below −10° ($K : H_2O_2 = 1 : 1$). The oily product solidified after cooling for some time. Carbon dioxide was passed into the alcoholic suspension, the temperature being kept below −10°. When phenolphthalein was no longer coloured the fine crystalline precipitate was filtered off rapidly, washed with cold ether, and analysed as rapidly as possible. Results 1 and 2 in Table VII are for two specimens. The solid is very unstable unless kept below 0°. It liberates much iodine as well as oxygen from concentrated neutral potassium iodide solution. On drying it decomposes rapidly, becoming pinkish-yellow and leaving potassium hydrogen carbonate. The colour may be due to $K_2C_2O_7$ but this was not isolated

(ii) A similar product was obtained by the action of 30% hydrogen peroxide on potassium monomethyl carbonate $CH_3O{\cdot}CO{\cdot}OK$ in methyl alcohol. This was precipitated on passing dry carbon dioxide into a solution of potassium methoxide in methyl alcohol. When phenolphthalein gave no colour, 30% hydrogen peroxide was added ($K : H_2O_2 = 1 : 2$) with stirring, the temperature being kept below −10°. The product was washed thoroughly with dry ether and was free from methyl alcohol. The analyses are 3 and 4 in Table VII. Unless anhydrous methyl alcohol was used, partial hydrolysis of potassium monomethyl carbonate occurred and the product formed with hydrogen peroxide was deficient in active oxygen.

(iii) Some evidence for the formation of very small amounts of $KHCO_4$ from $K_2C_2O_6$ and excess of hydrogen peroxide by the reaction $K_2C_2O_6 + H_2O_2 = 2KHCO_4$ was obtained. Carbon dioxide was passed to saturation into an alcoholic suspension of $K_2CO_4,2H_2O_2,H_2O$ in presence of excess of 30% hydrogen peroxide ($K : H_2O_2 = 1 : 4$) and the washed product gave the analyses 5 and 6 in Table VII. The active oxygen content is more than that required for $K_2C_2O_6$. The product was sensitive to dehydration and developed a slight yellow colour, observed with $KHCO_4$.

TABLE VII.

Analysis no.	K_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	K.	CO_2.	O_a.	H_2O.
1	38·95	33·9	12·1	15·1	1	0·93	0·91	1·01
2	39·9	33·7	12·5	13·9	1	0·90	0·92	0·91
3	40·2	34·5	12·2	13·0	1	0·92	0·89	0·85
4	39·85	34·7	12·4	13·1	1	0·93	0·91	0·83
5	41·8	37·8	8·0	12·4	1	0·96	0·56	0·78
6	42·6	38·3	8·3	10·9	1	0·96	0·57	0·67
			$KHCO_4$ requires		1	1	1	0·5

IV. *Rubidium Percarbonates.*—1. *Action of hydrogen peroxide on rubidium carbonate.* The method of Peltner was closely followed and his results confirmed. Rubidium carbonate was dissolved in 30% hydrogen peroxide, the liquid being cooled below −5°, and excess of absolute alcohol added. The oily product solidified on cooling and the white crystalline solids were washed as usual and dried for some time over calcium chloride. Rubidium was determined as sulphate. The properties of the products were similar to those of the corresponding potassium salts. Analyses are in Table VIII.

TABLE VIII.

Ratio $Rb_2CO_3 : H_2O_2$.	K_2O, %.	CO_2, %.	O_a, %.	H_2O, %.	Rb_2O.	CO_2.	O_a.	H_2O.
(*a*) 1 : 1	63·65	15·3	5·3	15·75	1	1·02	0·98	2·56
	62·8	14·9	5·3	16·0	1	0·99	0·97	2·61
			Calc. for $Rb_2CO_4,2\frac{1}{2}H_2O$:		1	1	1	2·5
(*b*) 1 : 2	58·2	13·6	9·5	18·7	1	0·99	1·91	3·37
	58·4	13·7	9·7	18·2	1	1·00	1·93	3·23
			Calc. for $Rb_2CO_4,H_2O_2,2H_2O$:		1	1	2	3
(*c*) 1 : 3	57·0	13·4	13·5	16·1	1	1·01	2·76	2·93
	56·4	13·2	13·2	17·2	1	1·00	2·74	3·13
			Calc. for $Rb_2CO_4,2H_2O_2,H_2O$:		1	1	3	3

2. *Preparation of* $Rb_2C_2O_6$. An alcoholic suspension of compound (*a*) in Table VIII was saturated below −10° with carbon dioxide. The white crystalline product was rapidly washed and analysed. Results 1 and 2 in Table IX indicate an absorption of almost one mole of CO_2 per mole of Rb_2CO_3 with slight loss of active oxygen, and formation of ***rubidium perdicarbonate*** $Rb_2C_2O_6$. This was much less stable than $K_2C_2O_6$ and on dehydration over phosphoric oxide lost all its active oxygen in a few hours without development of a yellow colour. It liberated a considerable amount of iodine and also oxygen from neutral concentrated potassium iodide solution.

3. *Formation of* $RbHCO_4$. An alcoholic suspension of compound (*b*) in Table VIII was treated as under (2). The results 3 and 4 in Table IX show an absorption of nearly one mole of CO_2 per mole of Rb_2CO_3 and an active oxygen content of more than one atom. The product was less sensitive to dehydration than $Rb_2C_2O_6$ but was affected and developed a yellow colour which suggests the presence of ***rubidium hydrogen permonocarbonate*** $RbHCO_4$. The latter was obtained in good yield by saturating an alcoholic suspension of (*c*) in Table VIII with carbon dioxide, the analyses being 5 and 6 in Table IX. It was also prepared from RbOOH obtained by the method of Peltner (*Ber.*, 1909, **42**, 1777) by adding 30% hydrogen peroxide mixed with absolute alcohol to an absolute-alcoholic solution of rubidium hydroxide (Rb : H_2O_2 = 1 : 1) cooled below −10°, the precipitated oil solidifying on cooling. The alcoholic suspension was saturated with carbon dioxide. The analyses of the washed product, made rapidly, are 7 and 8 in Table IX. The solid liberated much iodine and also oxygen from neutral concentrated potassium iodide solution; it was unstable on dehydration, leaving potassium hydrogen carbonate.

4. *Rubidium percarbonate with higher active oxygen content.* In the preparation of $RbHCO_4$ from RbOOH with the ratio Rb : H_2O_2 = 1 : 2 the product contained somewhat more active oxygen, as shown in analyses 9 and 10 in Table IX. A similar increase was found on saturating with carbon dioxide an alcoholic suspension of $Rb_2CO_4,2H_2O_2,H_2O$ in excess of hydrogen peroxide, and another percarbonate seems to be formed (but not in a pure state), which like $RbHCO_4$ and $Rb_2C_2O_6$ contains $2CO_2$ per Rb_2O but more active oxygen.

TABLE IX.

Analysis no.	Rb_2O, %.	CO_2, %.	O_a ,%.	Rb_2O.	CO_2.	O_a.
(*a*) 1	59·6	26·9	4·5	1	1·92	0·89
2	59·0	26·4	4·5	1	1·90	0·90
			$Rb_2C_2O_6$ requires	1	2	1
(*b*) 3	57·2	25·85	7·6	1	1·92	1·56
4	56·4	25·2	7·8	1	1·90	1·61
(*c*) 5	54·6	24·1	8·3	1	1·88	1·78
6	57·6	25·7	8·9	1	1·90	1·80
(*d*) 7	56·9	24·9	8·8	1	1·86	1·80
8	56·7	24·55	8·7	1	1·84	1·78
			$RbHCO_4$ requires	1	2	
(*e*) 9	52·4	22·7	10·9	1	1·84	2·42
10	53·4	23·4	11·6	1	1·85	2·53

V. *Cæsium Percarbonate.*—On addition of 30% hydrogen peroxide mixed with alcohol to a solution of cæsium hydroxide in absolute alcohol (Cs : H_2O_2 = 1 : 1) an oil was formed which slowly solidified. After the salt had been washed with alcohol and ether the cæsium was determined as sulphate and the active oxygen by permanganate titration. The results correspond with ***cæsium hydrogen peroxide perhydrate*** $CsOOH,H_2O_2$: Cs, 59·5, 60·2; O_a, 12·9, 13·5; Cs : O_a, 1 : 1·80, 1 : 1·86; $CsOOH,H_2O_2$ requires 1 : 2.

On saturation of an alcoholic suspension of this compound with carbon dioxide at −10° the solid dissolved. Ether precipitated a white crystalline solid which did not liberate iodine from concentrated neutral potassium iodide solution but only oxygen. It slowly decomposed without formation of a yellow colour. The following analyses show that the compound was not $CsHCO_4$ as expected, but cæsium permonocarbonate peroxide hydrate Cs_2CO_4,H_2O_2,H_2O, described by Kasanetzky.

Cs_2O, %.	CO_2, %.	O_a, %.	Cs_2O.	CO_2.	O_a.
68·2	10·7	7·5	1	1·00	1·94
67·7	10·5	7·3	1	1·00	1·91
	Calc. for Cs_2CO_4,H_2O_2,H_2O :		1	1	2

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