714. *Inorganic Per-acids. Part I. The Alkali Perborates.*

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Evidence is given to show that the alkali perborates are true per-salts and do not usually contain hydrogen peroxide as such. The amount of active oxygen in lithium, potassium, rubidium, and cæsium perborates was found to be capable of increase beyond the values given for these perborates by previous workers, and *compounds* agreeing with the formulæ $LiBO_4,H_2O$; KBO_5,H_2O; $RbBO_4,0·5H_2O$ and $CsBO_4,0·5H_2O$ were obtained.

We have already (*Nature*, 1949, **164**, 952) drawn attention to the lack of clear and consistent views regarding the constitution of the alkali perborates. These substances have been regarded by some workers as true per-salts (Bosshard and Zwicky, *Z. angew. Chem.*, 1912, **25**, 938, 993; Menzel, *Z. anorg. Chem.*, 1927, **167**, 193), and by others as addition compounds of hydrogen peroxide and metaborates (Foerster, *Z. angew. Chem.*, 1921, **34**, 354; Krauss and Oettner, *Z. anorg. Chem.*, 1934, **218**, 21). It was also mentioned that the amounts of active oxygen in the alkali perborates reported by previous workers were not in agreement. This resulted from the fact that different types of perborates were investigated, and systematic experiments in this field were lacking. The conclusion we reached was that hydrogen peroxide is not present as such in the compounds prepared Some further details of the investigation of these compounds are now given.

Experimental.

Methods of Analysis.—The alkali perborates were analysed by Menzel's method (*Z. anorg. Chem.*, 1927, **164**, 1). The alkali M_2O was found by titration with acid with methyl-orange as indicator; the B_2O_3 was then found in the same solution by titration with standard sodium hydroxide after addition of mannitol, phenolphthalein being used as indicator. The active oxygen (O_a) was determined by dissolving the perborate in dilute sulphuric acid and titration with potassium permanganate. The water content was found by difference.

I. *Lithium Perborate* (see Table I).—(a) *Preparation by precipitation with alcohol.* The preparation was carried out by Menzel's method of precipitation with alcohol of an aqueous solution of lithium metaborate containing hydrogen peroxide. A more concentrated metaborate solution and an excess of hydrogen peroxide were used, with the aim of obtaining a perborate containing more active oxygen than that prepared by Menzel. The compound $LiBO_2,8H_2O$ was dissolved in varying amounts of 30% hydrogen peroxide ($LiBO_2 : H_2O_2 = 1 : 2$; $1 : 3$; $1 : 5$; $1 : 10$). None of these solutions deposited any solid even after prolonged cooling. On addition of ethyl alcohol to the solution with the ratio 1 : 5, an oily emulsion was obtained, which was kept at <0° until a viscous mass separated. The alcohol was decanted and the viscous material was repeatedly treated with cold absolute alcohol until it was converted into a solid mass, which was spread on a porous plate and dried in vacuum over phosphoric oxide for 14 hours (analysis 1), or for a week (analysis 2). The use of excess of hydrogen peroxide (1 : 10) did not result in an increase in the active oxygen (analysis 3). Table I shows that the active oxygen in the products is greater than that found by Menzel, *viz.*, $B : O_a = 1 : 1$. Dehydration over phosphoric oxide in a vacuum at room temperature caused loss of water without affecting the active oxygen content, and this would not be expected if the additional active oxygen was present in the form of hydrogen peroxide. This additional active oxygen is not extracted from the solid by shaking with dry ether.

Table I.

Analysis No.	Li_2O, %.	B_2O_3, %.	O_a, %.	H_2O, %.	Li.	B.	O_a.	H_2O.
1	14·79	34·76	23·37	27·08	1	1·00	1·47	1·52
	14·62	34·33	23·34	27·71	1	1·01	1·49	1·57
2	15·54	36·24	24·63	23·59	1	1·00	1·48	1·26
	15·49	36·13	24·43	23·95	1	1·00	1·47	1·28
3	14·89	34·72	23·45	26·94	1	1·00	1·47	1·50
	14·82	34·47	23·48	27·23	1	0·99	1·48	1·51
4	13·97	32·56	24·85	28·62	1	1·00	1·65	1·70
	13·86	32·35	24·78	29·01	1	1·00	1·67	1·73
5	12·97	30·27	27·24	29·52	1	1·00	1·95	1·89
	12·92	30·20	27·19	29·69	1	1·00	1·95	1·90
6	15·10	35·16	30·42	19·32	1	1·00	1·88	1·06
	15·14	35·21	30·08	19·57	1	1·00	1·86	1·07
7	14·91	34·73	30·79	19·57	1	1·00	1·93	1·09
	14·95	34·84	30·95	19·26	1	1·00	1·93	1·07
8	14·96	34·81	30·87	19·36	1	1·00	1·93	1·07
	15·03	35·00	31·06	18·91	1	1·00	1·93	1·04
			$LiBO_4,H_2O$ requires		1	1·00	2	1

(b) *Preparation by evaporation of a solution of lithium metaborate in* 30% *hydrogen peroxide under reduced pressure.* The solution in which the ratio was 1 : 2 was evaporated over phosphoric oxide under reduced pressure (5 mm. Hg) at room temperature and the viscous mass obtained was washed with alcohol and ether, whereupon a white crystalline powder, similar in properties to that precipitated by alcohol, was obtained. This contained more active oxygen than before (analysis 4), and the active oxygen increased still further when the ratio $LiBO_2 : H_2O_2$ was 1 : 3 (analysis 5). On dissolving this solid in excess of 30% hydrogen peroxide and evaporating to dryness under reduced pressure, no further increase in active oxygen occurred, there being actually a slight decrease (analysis 6). It thus appears that the lithium perborate obtained with the ratio 1 : 3 is a definite product containing the maximum amount of two atoms of active oxygen per atom of boron. Analyses were made after drying for a week (analysis 7), and after two weeks (analysis 8), over phosphoric oxide in vacuum at room temperature. Dehydration without loss of active oxygen also occurs on heating in vacuum at 45°. The lithium perborate obtained is stable and differs from Menzel's preparation, since it is richer in active oxygen and can readily be dehydrated without loss of active oxygen. The ratio of active oxygen to water indicates that the dehydrated product is a true *per-salt* with the formula $LiBO_4,H_2O$.

II. *Sodium Perborate* (see Table II).—In the patent specification G.P. 256,920 the preparation of sodium perborate with a greater active oxygen content than Tanatar's salt $NaBO_3,4H_2O$ ($B : O_a = 1 : 1$) is claimed. The latter was treated with excess of 30% hydrogen peroxide and the resulting solution allowed to stand for crystallisation, and precipitated with alcohol, or evaporated under reduced pressure. A sodium perborate with high active oxygen is claimed in G.PP. 299,300 and 318,219, but these specifications, apart from reporting the active oxygen content, do not give complete analyses, and it was wrongly assumed that the product is an addition compound of Tanatar's salt and hydrogen peroxide. Le Blanc and Zellmann (*Z. Elektrochem.*, 1923, **29**, 179) assigned the formula $Na(BO_2H_2O_2),2H_2O_2$ to this perborate, which seemed to merit further investigation.

TABLE II.

Analysis No.	Na_2O, %.	B_2O_3, %.	O_a, %.	H_2O, %.	Na.	B.	O_a.	H_2O.
1	25·42	28·53	24·32	21·73	1	1·00	1·85	1·47
	25·28	28·32	24·12	22·28	1	1·00	1·85	1·52
2	27·28	30·76	25·48	16·48	1	1·00	1·81	1·04
	27·34	30·82	25·39	16·45	1	1·00	1·80	1·04
3	25·04	28·16	24·74	22·06	1	1·00	1·93	1·52
	24·78	27·84	24·62	22·76	1	1·00	1·93	1·58
4	24·83	27·88	24·69	22·60	1	1·00	1·92	1·56
	25·12	28·24	24·82	21·82	1	1·00	1·92	1·49
5	26·91	30·32	26·32	16·45	1	1·00	1·89	1·05
	26·83	30·31	26·24	16·62	1	1·00	1·90	1·06
6	20·97	23·71	32·31	23·01	1	1·00	2·99	1·89
	20·78	23·45	32·14	23·63	1	1·00	2·99	1·95
7	23·72	26·58	35·42	14·28	1	1·00	2·90	1·04
	23·84	26·67	35·37	14·12	1	1·00	2·88	1·02

(a) *Preparation by direct separation from aqueous solution.* A 33% sodium metaborate solution was prepared and to this 30% hydrogen peroxide was added ($NaBO_2 : H_2O_2 = 1 : 2$). The solution was cooled below 0° and after a short time a heavy crystalline precipitate was obtained. After separation from the mother-liquor, this was spread on a porous plate and dried in vacuum over phosphoric oxide for 14 hours (analysis 1). It is clear that in this product the proportion of water is not sufficient to hold all the peroxide oxygen as hydrogen peroxide, and still further dehydration occurred in vacuum over phosphoric oxide after a week (analysis 2). Since dehydration occurred to a large extent with negligible loss of active oxygen, the product appears to be a true per-salt. Since this result was not found with Tanatar's sodium perborate, the possibility that this product is an addition compound of hydrogen peroxide and Tanatar's perborate must be excluded, and this conclusion is also supported by the fact that dry ether does not extract active oxygen from the solid. When the ratio $NaBO_2 : H_2O_2$ used was 1 : 3 no heavy precipitation occurred. A small precipitate was slowly formed which was analysed after 14 hours' drying in vacuum over phosphoric oxide (analysis 3). In this case, although the active oxygen content increased, it did not exceed two atoms per atom of boron.

(b) *Preparation by precipitation with alcohol.* When the ratio $NaBO_2 : H_2O_2$ was 1 : 5 no solid separated out by cooling or concentration in vacuum. Addition of ethyl alcohol resulted in the formation of an oily product. After decantation of the alcohol, and treatment with fresh amounts of cold alcohol, a solid was obtained which was analysed after 14 hours' drying over phosphoric oxide in vacuum (analysis 4). This product is similar in properties to that obtained directly from aqueous solution. Further dehydration with negligible loss of active oxygen occurred on keeping for a week in vacuum over phosphoric oxide (analysis 5). Here also the amount of active oxygen did not exceed two atoms per atom of boron.

(c) *Preparation by evaporation under reduced pressure.* Tanatar's perborate $NaBO_3,4H_2O$ was dissolved in excess of 30% hydrogen peroxide ($NaBO_3 : H_2O_2 = 1 : 4$) and the resulting solution was allowed to evaporate under reduced pressure at room temperature (about 19°) over phosphoric oxide. The viscous mass obtained was washed thoroughly with alcohol and ether and the white crystalline solid formed was analysed directly (analysis 6). From the results, it is clear that the active oxygen content in the solid reached three atoms per atom of boron. This product has more tendency to dehydration than Tanatar's salt, as the results obtained after a week's keeping in vacuum over phosphoric oxide show (analysis 7). The amounts of active oxygen and water indicate that the product is a true per-salt, rather than an addition compound of hydrogen peroxide with Tanatar's perborate. At 45° in vacuum, dehydration resulted in appreciable loss of active oxygen and hydrogen peroxide was detected among the decomposition products. Previous workers used much higher temperatures for dehydration. The instability of the product, especially at higher temperatures, explains why hydrogen peroxide was detected by Le Blanc and Zellmann by continuous distillation in vacuum at the temperature at which they prepared this perborate.

III. *Potassium Perborate* (see Table III).—(a) *Preparation by direct separation from aqueous solution.* To 50% potassium metaborate solution prepared from boric acid and potassium hydroxide, 30% hydrogen peroxide was added in different amounts. With the ratio $KBO_2 : H_2O_2 = 1 : 1$ no separation of solid occurred except after long cooling; this solid was very hygroscopic and liquefied on drying on a porous plate. With the ratio 1 : 2 a heavy crystalline precipitate was formed on cooling, which after separation from the mother-liquor was spread on a porous plate and dried for 14 hours over phosphoric oxide in vacuum (analysis 1). With the ratio 1 : 3 a heavy crystalline precipitate was also formed which was dried for 14 hours (analysis 2) and for a week (analysis 3), in the same way. With the ratio 1 : 5 a crystalline precipitate was also formed which was analysed after 14 hours' drying as before (analysis 4). The results show that the ratio 1 : 3 gives a product corresponding in active oxygen content to Bosshard and Zwicky's potassium perborate. The dried product appears to be a true per-salt, and this agrees with the result that no active oxygen is extracted by ether from the solid, and that by gently heating this in vacuum no hydrogen peroxide is evolved. With the ratio 1 : 5, the solid obtained contained a higher proportion of active oxygen not extracted by thorough washing with ether, and this suggests the presence of a higher perborate than that prepared by Bosshard and Zwicky. This compound was prepared by method (b).

TABLE III.

Analysis No.	K_2O, %.	B_2O_3, %.	O_a, %.	H_2O, %.	K.	B	O_a.	H_2O.
1	37·58	28·52	23·28	10·62	1	1·03	1·82	0·74
	37·42	28·29	23·34	10·95	1	1·03	1·83	0·77
2	37·06	27·91	24·92	10·11	1	1·02	1·98	0·71
	36·95	27·85	24·88	10·32	1	1·02	1·97	0·73
3	37·15	27·97	24·96	9·92	1	1·02	1·97	0·70
	37·26	28·08	25·04	9·62	1	1·02	1·97	0·69
4	35·52	26·98	25·72	11·78	1	1·03	2·14	0·87
	35·37	26·88	25·44	12·31	1	1·03	2·11	0·91
5	31·90	23·99	31·82	12·29	1	1·02	2·94	1·01
	31·76	23·87	31·93	12·44	1	1·01	2·94	1·02
6	35·88	27·08	29·08	7·96	1	1·02	2·38	0·59
	35·65	26·83	29·33	8·19	1	1·02	2·41	0·60
				KBO_5,H_2O requires	1	1	3	1

(b) *Preparation by evaporation with excess of* 30% *hydrogen peroxide under reduced pressure.* A mixture of the perborate prepared as above with excess of 30% hydrogen peroxide ($KBO_4 : H_2O_2 = 1 : 4$) was evaporated to dryness under reduced pressure over phosphoric oxide at room temperature. The white crystalline solid obtained was analysed both directly after washing with alcohol and ether (analysis 5) and also after exposure for a week over phosphoric oxide in vacuum (analysis 6). Since this product is soluble with difficulty in water but is soluble in dilute sulphuric acid, a known weight was added to a known excess of standard sulphuric acid and the remaining free acid was titrated with sodium hydroxide solution with methyl-orange as indicator, so giving the alkali content. Mannitol and phenolphthalein were then added and titration with sodium hydroxide continued until the red colour appeared, this titration giving the boric acid content. The composition of the *product* obtained directly corresponds with KBO_5,H_2O with an active oxygen content equal to three atoms per atom of boron. It is less stable than the corresponding sodium salt, or than Bosshard and Zwicky's potassium perborate with only two atoms of active oxygen per atom of boron. These results make it unlikely that the substance rich in active oxygen is an addition compound of hydrogen peroxide and Bosshard and Zwicky's compound.

TABLE IV.

Analysis No.	Rb_2O, %.	B_2O_3, %.	O_a, %.	H_2O, %.	Rb.	B.	O_a.	H_2O.
1	52·62	19·61	17·44	10·33	1	1·00	1·94	1·02
	52·53	19·49	17·35	10·63	1	1·00	1·93	1·05
2	55·00	20·46	18·25	6·29	1	1·00	1·94	1·60
	55·18	20·52	18·31	5·99	1	1·00	1·94	0·56
3	55·46	20·66	18·11	5·77	1	1·00	1·91	0·54
	55·68	20·75	18·21	5·36	1	1·00	1·91	0·50
4	55·05	20·46	18·37	6·12	1	1·00	1·95	0·58
	55·35	20·62	18·34	5·69	1	1·00	1·94	0·53
5	55·16	20·57	18·14	6·13	1	1·00	1·92	0·59
	55·40	20·63	18·27	5·70	1	1·00	1·93	0·54
6	53·07	19·71	21·91	5·31	1	1·00	2·41	0·52
	52·72	19·68	21·86	5·74	1	1·00	2·43	0·57
7	53·99	20·08	20·54	5·39	1	1·00	2·22	0·52
	54·37	20·18	20·37	5·08	1	1·00	2·20	0·48
				$RbBO_4,0·5H_2O$ requires	1	1	2	0·5

IV. *Rubidium Perborate* (see Table IV).—(a) *Preparation by direct separation from aqueous solution.* A 50% rubidium metaborate solution was prepared by mixing equivalent amounts of rubidium carbonate and boric acid, heating them gently until evolution of carbon dioxide and water ceased, and finally fusing the product in a platinum crucible to a clear liquid. The cold mass was extracted with water. On adding to this solution 30% hydrogen peroxide in the ratio $RbBO_2 : H_2O_2 = 1 : 1$, no solid separated. With the ratios 1 : 2 or 1 : 3, a white crystalline precipitate was formed after short cooling. The product with the ratio 1 : 3 was separated from the mother-liquor, washed with alcohol and ether, and analysed directly (analysis 1) or after 14 hours' drying over phosphoric oxide in vacuum at room temperature (analysis 2), or after a week's drying in the same way (analysis 3). The results show that the active oxygen in this product is greater than that in the perborate $RbBO_3,H_2O$ prepared by Christensen (*Danske Vidensk. Selsk. Forh.*, 1904, No. 6). From the active oxygen and water ratio, the compound appears to be a true *perborate.* Gentle heating in vacuum did not give rise to evolution of hydrogen peroxide, and the active oxygen was not extracted from the solid by ether. This product is comparable in active oxygen content with Bosshard and Zwicky's potassium perborate, but it is more readily dehydrated and tends to retain half a molecule of water per atom of boron. The composition of the dried product corresponds to $RbBO_4,0{\cdot}5H_2O$. When the salt was prepared in presence of excess of hydrogen peroxide ($RbBO_2 : H_2O_2 = 1 : 5$), no increase in active oxygen content beyond the above value was found (analysis 4). Precipitation of the mother-liquor with alcohol gave the same perborate (analysis 5).

(b) *By evaporation with excess of* 30% *hydrogen peroxide under reduced pressure.* When the perborate described under (a) was dissolved in excess of 30% hydrogen peroxide ($RbBO_4 : H_2O_2 = 1 : 4$) and the solution evaporated under reduced pressure as before, a solid residue was left, which was analysed directly after being washed with alcohol and ether (analysis 6), and after a week in vacuum over phosphoric oxide (analysis 7). The results show that the active oxygen content of this product is more than that in the first perborate, but it did not reach three atoms per atom of boron, as was the case with the potassium and sodium salts. The product was less stable than that containing only two atoms of active oxygen per atom of boron. The results make it unlikely that this product is an addition compound of hydrogen peroxide and the lower perborate.

TABLE V.

Analysis No.	Ca_2O, %.	B_2O_3, %.	O_a, %.	H_2O_2, %.	Cs.	B.	O_a.	H_2O.
1	63·33	15·60	14·03	7·04	1	1·00	1·95	0·87
	63·19	15·57	13·93	7·31	1	1·00	1·94	0·90
2	63·22	15·61	13·93	7·24	1	1·00	1·94	0·89
	63·34	15·66	13·96	7·04	1	1·00	1·94	0·87
3	64·74	15·95	14·26	5·05	1	1·00	1·94	0·51
	64·95	16·03	14·30	4·72	1	1·00	1·94	0·57
4	65·02	16·02	14·24	4·72	1	1·00	1·93	0·57
	65·28	16·02	14·21	4·49	1	1·00	1·92	0·54
5	64·69	15·98	14·55	4·78	1	1·00	1·98	0·58
	64·89	16·00	14·48	4·63	1	1·00	1·97	0·56
6	62·73	15·37	17·11	4·79	1	1·00	2·40	0·59
	62·95	15·50	17·21	4·34	1	1·00	2·41	0·53
7	64·45	15·92	15·74	3·89	1	1·00	2·15	0·48
	64·04	15·77	15·94	4·25	1	1·00	2·19	0·51
			$CsBO_4,0{\cdot}5H_2O$ requires		1	1·00	2	0·5

V. *Cæsium Perborate* (see Table V).—(a) *Preparation by direct separation from aqueous solution.* A 50% cæsium metaborate solution was prepared by the same method as that used for rubidium metaborate. This solution (unlike those of potassium and rubidium metaborates) readily deposited crystals of cæsium metaborate, but these redissolved on addition of 30% hydrogen peroxide. With hydrogen peroxide in the ratios $CsBO_2 : H_2O_2 = 1 : 1$, $1 : 2$, or $1 : 3$, no separation of perborate occurred on cooling. When the solution with the ratio 1 : 3 was concentrated in vacuum, a crystalline precipitate formed, which was separated from the mother-liquor and washed with alcohol and ether (analysis 1).

(b) *Preparation by precipitation with alcohol.* Most of the perborate was precipitated from the mother-liquor by alcohol. The precipitate was analysed directly after being washed with alcohol and ether (analysis 2), after 14 hours' drying over phosphoric oxide in vacuum at room temperature (analysis 3), and after a week's drying in the same way (analysis 4). The results show that this perborate is comparable in active oxygen content with rubidium perborate, and contains two atoms of active oxygen per atom of boron. It also tends to retain half a molecule of water per atom of boron. The content of active oxygen and water in the dehydrated product indicates that it is a true *per-salt* with the formula $CsBO_4,0{\cdot}5H_2O$. The active oxygen is not extracted from the solid by ether, and hydrogen peroxide is not evolved on gentle heating in vacuum. When hydrogen peroxide was used in the ratio 1 : 5 no solid separated but on addition of alcohol the same perborate was formed as before (analysis 5).

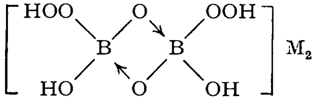
(c) *Preparation by evaporation with excess of* 30% *hydrogen peroxide under reduced pressure.* By dissolving the above perborate in excess of 30% hydrogen peroxide ($CsBO_4 : H_2O_2 = 1 : 4$) and evaporating the solution under reduced pressure, a solid remained which was washed with alcohol and ether and analysed directly (analysis 6), and after a week's drying over phosphoric oxide in vacuum (analysis 7). The results show that, as in the case of rubidium perborate, the active oxygen content is greater than that in the initial perborate, but does not reach three atoms per atom of boron. The compound is also unstable. Nevertheless, it is unlikely that this product is an addition compound of hydrogen peroxide and the first perborate.

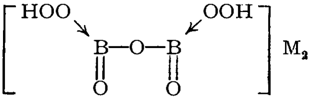
DISCUSSION.

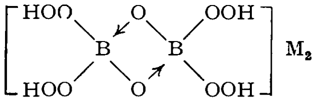
By analogy with Menzel's dimeric formulæ for lower perborates represented by (I) and (II), the dimeric formulæ (III) and (IV) are suggested for perborates containing two atoms of active oxygen per atom of boron. No free hydrogen peroxide is present and the formulæ explain the behaviour of these perborates on dehydration.

In the formulæ the valencies attached to each boron atom are formulated as follows : Three of them originate from the normal three valencies of the boron atom and the fourth by a co-ordinate link directed from the oxygen to the boron atom. Hermans (*Z. anorg. Chem.*, 1925, **142**, 399) regarded all the four links as equivalent.

In (III) there are two atoms of active oxygen and one molecule of constitutional water per atom of boron and this formula may represent sodium and lithium perborates, since it explains their tendency to retain one molecule of water per atom of boron, and their different behaviour from the lower perborates.


(I.)
M = Na or Li.


(II.)
M = K or NH_4.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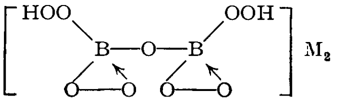
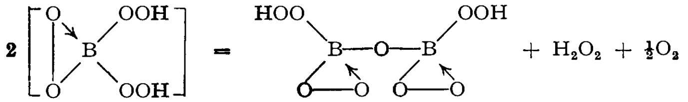

(IV.)
M = Rb or Cs.

In (IV) there are two atoms of active oxygen and 0·5 molecule of constitutional water per atom of boron and this formula may represent rubidium and cæsium perborates. Bosshard and Zwicky's potassium perborate, which tends to retain less than one molecule and more than 0·5 molecule of water on dehydration, may contain anions represented by both formulæ. Higher perborates containing more than two atoms of active oxygen, *e.g.*, KBO_5,H_2O, may be derived from an ion represented as below, and their instability on dehydration may be explained if it is assumed that this anion has a tendency to associate to form anions containing less active oxygen



Conclusions.—(1) A lithium perborate different from that prepared by Menzel and containing two atoms of active oxygen per atom of boron was obtained. It is formulated as $LiBO_4,H_2O$.

(2) The active oxygen content of potassium perborate can reach three atoms per atom of boron, and the unstable product corresponds with KBO_5,H_2O.

(3) Rubidium and cæsium perborates were obtained with higher active oxygen contents than those of the compounds prepared by Christensen. They contain two atoms of active oxygen per atom of boron and correspond with $RbBO_4,0{\cdot}5H_2O$ and $CsBO_4,0{\cdot}5H_2O$, respectively. The existence of unstable rubidium and cæsium perborates containing still more active oxygen was also established

(4) From the contents of water and active oxygen, the perborates with higher active oxygen than one atom per atom of boron seem not to be addition products of hydrogen peroxide and lower perborate or metaborates.

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