56. *Nuclear Resonance Spectra of Some Peroxy-salts.*

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Proton resonance spectra have been recorded at 90° K of crystalline perborates of sodium, potassium, and rubidium, three sodium perpyrophosphates, and sodium percarbonate. The perborates contain most of their hydrogen as water of crystallisation; the small amounts of hydrogen peroxide of crystallisation are not enough to account for all the active oxygen present. They are therefore probably true peroxy-salts. The perpyrophosphates and sodium percarbonate give narrow proton resonance lines, which are consistent with the view that all the hydrogen is present as hydrogen peroxide of crystallisation. These are therefore probably not true peroxy-salts.

When certain borates, carbonates, or pyrophosphates are treated with hydrogen peroxide under appropriate conditions, solids which contain active oxygen can be crystallised from the solutions. This active oxygen has the oxidising properties of hydrogen peroxide.

The perborates and percarbonates have a somewhat variable composition; their stoicheiometry depends rather critically on the conditions of preparation. The formulæ and structures of these compounds have been studied by Partington and Fathallah[1] and others,[2] but there does not appear to be any conclusive evidence which shows whether they contain true peroxyanions or whether their active oxygen is present merely as hydrogen peroxide of crystallisation.

Proton resonance spectra of these compounds were measured in order to determine whether or not hydrogen is present as water or hydrogen peroxide of crystallisation. The absorption curves at low temperatures are very much broader if the protons are in water molecules than if they are in molecules of hydrogen peroxide.

Experimental

Perborates.—*Preparation.* Sodium, potassium, rubidium, and cæsium perborates were prepared by Partington and Fathallah's method.[1] A concentrated solution of the alkali-metal metaborate was added to 30% hydrogen peroxide, and the mixture cooled to −10°. After about 15 min. the perborate crystals were removed and dried.

Analysis. The alkali metal was estimated[3] by titration with 0·1N-sulphuric acid with bromophenol-blue as indicator. This amount of standard acid was then added to another portion of the solution and the concentration of BO_2^- found by titration with 0·1N-sodium hydroxide in the presence of mannitol, with phenolphthalein. The active oxygen (O_a) was determined by titration with potassium permanganate solution.

Sodium perborate. The crystals were dried in a vacuum-desiccator for 16 hr. (P_2O_5) (Found: Na^+, $1{\cdot}00_0$; BO_2^-, $1{\cdot}00_0$; O_a, $1{\cdot}92_3$; H_2O, $1{\cdot}57_6$). The compound approximates to the formula $NaBO_4,\frac{3}{2}H_2O$.

Potassium perborate. The potassium metaborate was prepared from potassium hydroxide and boric acid[4] (Found for the perborate: K^+, $1{\cdot}00_0$; BO_2^-, $1{\cdot}00_0$; O_a, $1{\cdot}73_6$; H_2O, $0{\cdot}67_3$).

Rubidium perborate. Rubidium nitrate was mixed with 2 equiv. of oxalic acid, and the mixture moistened with water and heated gently in a platinum crucible until no more nitrous fumes came off. The residue was converted into the carbonate at 800° in an electric furnace. 1 Equiv. of boric acid was added and the mixture heated to give a clear melt. The cold product was extracted with enough water to give a 50% solution of rubidium metaborate, and the perborate prepared therefrom (Found: Rb^+, 1·00; BO_2^-, 1·00; O_a, 1·90; H_2O, 0·70).

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[1] Partington and Fathallah, *J.*, 1949, 3421.

[2] Menzel, *Z. anorg. Chem.*, 1927, **167**, 193; Bosshard and Zwicky, *Z. angew. Chem.*, 1912, **25**, 938, 993; Carpeni, *Bull. Soc. chim. France*, 1949, 742; Tanata, *Z. phys. Chem.*, 1898, **26**, 132; Bruhat and Dubois, *Compt. rend.*, 1905, **140**, 506.

[3] Menzel, *Z. anorg. Chem.*, 1927, **164**, 1.

[4] Dulesky, *Z. anorg. Chem.*, 1906, **50**, 38.

Sodium perborate tetrahydrate. This was supplied and analysed by Laporte Chemicals Ltd. (Found: Na, 1·00; BO_2^-, 1·00; O_a, 0·94; H_2O, 3·63).

Sodium Perpyrophosphate.—Three samples were supplied and analysed by Laporte Chemicals Ltd. They were $Na_4P_2O_7,H_2O_2$ (Found: O_a, 5·92; P_2O_5, 46·2%), $Na_4P_2O_7,2H_2O_2$ (Found: O_a, 10·39; P_2O_5, 41·7%), and $Na_4P_2O_7,3H_2O_2$ (Found: O_a, 12·93; P_2O_5, 40·8%).

The active oxygen being assumed to be present as H_2O_2 and the P_2O_5 as $Na_4P_2O_7$, the total contents of these samples are then 99·1%, 100·2%, and 103·9% respectively.

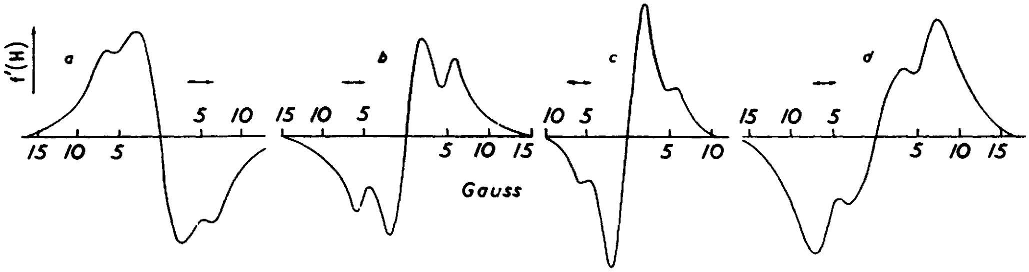
Sodium Percarbonate.—This was supplied and analysed by Laporte Chemicals Ltd. The analysis [Found: Na_2CO_3, 63·7; O_a, 13·0; H_2O (by difference), 23·3%] corresponds approximately to $Na_2CO_4,2H_2O$, although the compound is usually said to be $2Na_2CO_3,3H_2O_2$.

Nuclear Resonance Measurements.—The recording nuclear magnetic resonance spectrometer described previously [5] was used. The amplitude of the radiofrequency field was chosen to be well below the value at which saturation becomes apparent. The spectrometer records the first derivative of the nuclear resonance absorption curve.

RESULTS AND DISCUSSION

Perborates.—The differentials of the absorption curves of proton resonances are shown in Fig. 1. The peak-to-peak amplitude of the modulation field is shown by the double ended arrows. Each curve appears to be a superposition of a broad and a narrower line. The numerical results are summarised in the Table, in which the second moments given have been corrected for the effect of modulation and field inhomogeneity.[6]

FIG. 1. *Derivative of proton resonance of* (*a*) $NaBO_4,\frac{3}{2}H_2O$; (*b*) $KBO_4,\frac{1}{2}H_2O$; (*c*) $RbBO_4,\frac{1}{2}H_2O$; *and* (*d*) $NaBO_3,4H_2O$ *at* 90° K.



The hydrogen atoms of water molecules are about 1·6 Å apart, and crystalline hydrates give a proton resonance spectrum characteristic of these relatively closely spaced pairs of protons. The absorption curve is a broad doublet with a shallow central minimum.[7] The derivative of the absorption curve, which is usually recorded experimentally, has two outer peaks separated by about 12 gauss.

Compound	Temp. (° K)	Second moment (gauss ^{2})	No. of measurements	Derivative curve Separation (gauss) of		Ratio of areas of broad to narrow absorption lines
				inner maxima	outer maxima	
$NaBO_4,\frac{3}{2}H_2O$ Sodium perborate ...	90	20·7 ± 1	7	5·3	12·0	4·5
$KBO_4,\frac{1}{2}H_2O$ Potassium perborate	90	19·7 ± 0·8	4	4·1	11·9	4
$RbBO_4,\frac{1}{2}H_2O$ Rubidium perborate	20	8·9 ± 0·4	9	3·5	11·4	—
$RbBO_4,\frac{1}{2}H_2O$ .... Rubidium perborate	90		Approximately the same as at 20° K			
$NaBO_3,4H_2O$ Sodium perborate tetrahydrate	90	29·5 ± 1	3	6·2	15·5	10

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[5] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; Pratt and Richards, *ibid.*, 1953, **49**, 744.

[6] Andrew, *Phys. Rev.*, 1953, **91**, 425.

[7] Pake, *J. Chem. Phys.*, 1948, **16**, 327.

If the hydrogen atoms in these salts are present either in H–O–O–H molecules or as OH groups, the protons are more widely separated than in a water molecule, and a much narrower proton resonance curve would be obtained.

The derivative curves of the sodium and potassium perborates show a double set of maxima. The outer maxima are separated by about 12 gauss, the separation found in hydrates. It seems reasonable, therefore, to attribute these outer maxima to the presence of water molecules in the crystal lattice, and the inner maxima to protons in OH or HO_2H groups. The relative numbers of protons in the H_2O and OH groups can be estimated by decomposing the observed derivative curve into its two components and comparing the intensities of the corresponding absorption curves. This can be done by superimposing the derivative curve normally obtained from a crystalline salt hydrate [7] on the experimental curve; the narrower line is then obtained by subtraction. This procedure is illustrated in Fig. 2, of which the continuous line is half the experimentally observed derivative curve of sodium perborate tetrahydrate. The broken lines show how the continuous curve can be resolved into the broad (*a*) and the narrow (*b*) component. The two components of the resolved derivative curve can be integrated separately and give the absorption curves shown in Fig. 3 for $NaBO_4,\frac{3}{2}H_2O$. The relative areas of these two curves give the approximate ratio of the number of protons in the two situations. In this case the area under the broad doublet is 4·5 times that under the narrower curve.

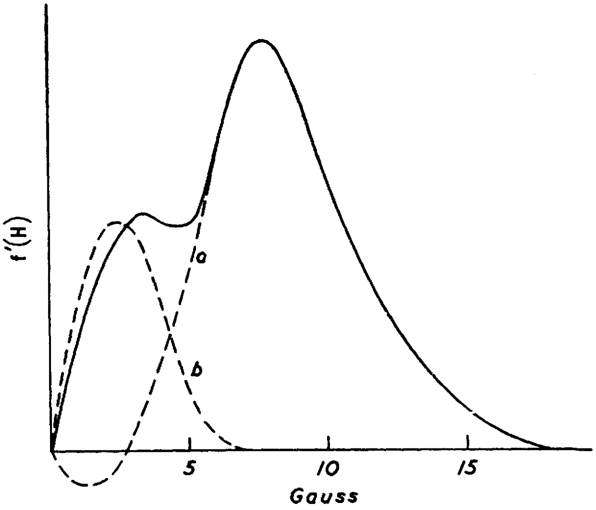
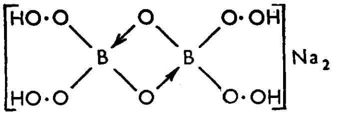
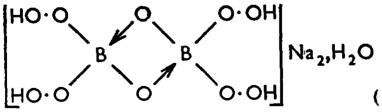


FIG. 2. *Resolution of half the derivative curve of* $NaBO_3,4H_2O$ *into two components* (90° K).

Partington and Fathallah [1] obtained a compound approximating to $NaBO_4,H_2O$ by drying the above perborate *in vacuo* (P_2O_5) and attributed to it the structure (I), so that by analogy the structure of $NaBO_4,\frac{3}{2}H_2O$ would be (II). If this formula is correct, then the ratio of the number of doublet protons to that of Q "singlet" protons = 2/4 = 0·5.

(I)





(II)

However, the above results indicate that this ratio is about 4·5, and are therefore inconsistent with this formula. Most of the protons are present in the form of pairs in water molecules and the small number of singlet protons is not sufficient to account for all the active oxygen present as hydrogen peroxide of crystallisation. This compound is, therefore, probably a true hydrate of a peroxy-salt which contains some hydrogen peroxide of crystallisation.

Potassium perborate. $KBO_4,\frac{1}{2}H_2O$. The derivative curve was resolved into two components as in the case of the sodium compound, and the areas of the integrated components compared (Fig. 3*b*). The doublet : singlet ratio was 4. It is, therefore, probable that this compound is a true peroxy-salt with the hydrogen atoms present as water molecules, but with some hydrogen peroxide of crystallisation.

Rubidium perborate. $RuBO_4,\frac{1}{2}H_2O$. The protons in this sample were very readily saturated and the signals were rather weak. It is clear, however, that the derivative curve is much narrower than in the above salts, and the shape of the outer portions of the curve did not correspond closely to that usually observed with hydrates. This might be due to reorientation of the water molecules in the crystal lattice (although the curve was not significantly changed on cooling from 90° K to 20° K) or to the absence of water molecules. The signals were not good enough to warrant a more detailed discussion.

FIG. 3. *Two components of the absorption curve of proton resonance of* (*a*) $NaBO_4,\frac{3}{2}H_2O$, (*b*) $KBO_4,\frac{1}{2}H_2O$, *and* (*c*) $NaBO_3,4H_2O$ *at* 90° K.

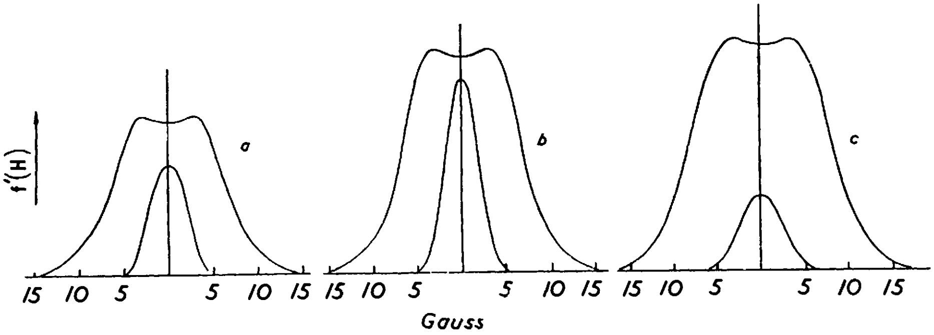
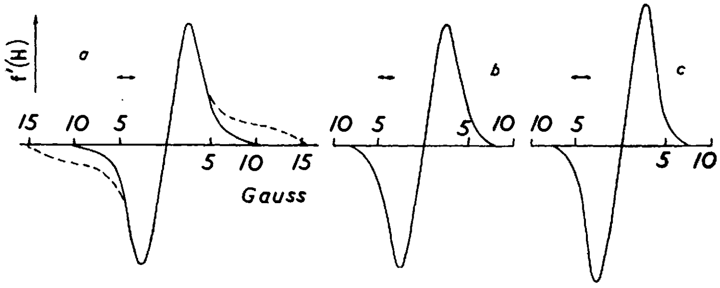


FIG. 4. *Derivative of proton resonance of* (*a*) $Na_4P_2O_7,H_2O_2$, (*b*) $Na_4P_2O_7,2H_2O_2$, *and* (*c*) $Na_4P_2O_7,3H_2O_2$ *at* 90° K.



Sodium perborate tetrahydrate. The derivative curve was resolved into two components (Fig. 2) and after integrating these (Fig. 3*c*), the relative areas of the doublet and singlet curves were found to be about 10 : 1. If this compound is formulated as $NaBO_2,H_2O_2,3H_2O$, the doublet : singlet ratio would be 3, and so on the above evidence the formula $NaBO_3,4H_2O$ is preferable.

General.—The perborates, with the possible exception of the rubidium salt, give proton resonance spectra which indicate that they are true hydrates of peroxy-salts. They all appear to contain hydrogen peroxide of crystallisation, but not enough to account for the total active oxygen found. The difficulty of obtaining pure salts with accurate analyses may be associated with the instability of the peroxyanion and the ability of hydrogen peroxide to replace water of crystallisation.

The Perpyrophosphates.—Sodium perpyrophosphate I, $Na_4P_2O_7,H_2O_2$. The first measurements on this sample gave derivative curves with long tails (Fig. 4*a*, broken curve).

It was suspected that these tails might arise from the broad contribution of the protons in moisture, so the sample was dried *in vacuo* (P_2O_5) for 3 days. The broad edges of the derivative curve were no longer observed, and the final result is shown in Fig. 4*a* (continuous curve). The second moment was $6{\cdot}3 \pm 0{\cdot}5$ gauss ^{2} (9 measurements), and the line width was 5·33 gauss.

Sodium perpyrophosphate II, $Na_4P_2O_7,2H_2O_2$. The derivative curve obtained is shown in Fig. 4*b*. The second moment was $5{\cdot}5 \pm 0{\cdot}3$ gauss^2 (8 measurements) and the line width 5·40 gauss.

Sodium perpyrophosphate III, $Na_4P_2O_7,3H_2O_2$. The derivative curve is shown in Fig. 4*c*; the second moment was $4{\cdot}1 \pm 0{\cdot}2$ gauss^2, and the line width 5·30 gauss.

The derivative curves of these samples are all very similar. The line widths are the same and the curves differ only slightly near the outer edges. These differences might be due to small amounts of water which could not be removed. Sodium perpyrophosphate I could be written either as $Na_4P_2O_8,H_2O$ or as $Na_4P_2O_7,H_2O_2$. The absence of the broad line characteristic of water of crystallisation suggests that the first formula is incorrect and that the active oxygen is present as hydrogen peroxide of crystallisation, which gives a narrow proton resonance line. The close similarity of the proton resonances in the other two salts suggests that they too consist of sodium pyrophosphate with molecules of hydrogen peroxide of crystallisation.

It was found that the active oxygen in these compounds could be extracted with ether, even when it had been dried with lithium hydride, and the presence of hydrogen peroxide in the ether was demonstrated by the addition of sodium dichromate solution, when the characteristic blue colour developed. Only small amounts of the active oxygen of the perborates could be extracted with ether.

Sodium Percarbonate.—The derivative curve obtained at 90° K is narrow and similar in appearance to those of Fig. 4. The second moment was $4{\cdot}0 \pm 0{\cdot}2$ gauss^2 (6 measurements) and the line width was 5·33 gauss.

The compound clearly does not contain an appreciable proportion of protons as water molecules since the resonance is narrow. The composition $Na_2CO_4,2H_2O$ is, therefore, probably incorrect. The formula usually assigned to this compound, $2Na_2CO_3,3H_2O_2$, is consistent with the narrow nuclear resonance line obtained.

Conclusion.—The perborates appear to be true peroxy-salts with water of crystallisation. They all contain some hydrogen peroxide of crystallisation but not enough to account for all the active oxygen.

The perpyrophosphates and percarbonates studied do not contain appreciable amounts of water of crystallisation, and the hydrogen is present as hydrogen peroxide of crystallisation.

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