PROTON MAGNETIC RESONANCE OF HYDROGEN PEROXIDE OF CRYSTALLIZATION IN SOME SODIUM PERPHOSPHATES

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Until recently it has been considered sufficient for an inorganic compound to have an oxygen bridge, \(-\text{O-O-}\), for it be called a peroxide. However the synthesis of new peroxy-compounds and especially the more detailed study of their structures and properties has shown that at least nine groups of compounds can be distinguished among them: 1) hydroperoxides, 2) peroxides, 3) superoxides, 4) ozonides, 5) peroxy acids and their salts, 6) peroxy-complexes which are not derived from peroxy acids or their salts, 7) hydrates of peroxides, 8) peroxyhydrates, and 9) hydrates of peroxyhydrates [1]. In the past, for example, it was not always possible to establish unambiguously whether a given compound was a derivative of a peroxy acid, the simple product of the addition of a molecule of hydrogen peroxide to a molecule of salt, i.e., a peroxyhydrate of the salt, or the product of the simultaneous addition to the salt of molecules of water and hydrogen peroxide, i.e., a hydrated peroxyhydrate. A basis for distinction was the Reisenfeld-Likhavskii test, according to which peroxy-salts ("true peroxides") liberated iodine almost instantaneously from KI solution at pH 7.5 to 8.0, whereas addition compounds (the peroxyhydrates and hydrated peroxyhydrates) did not liberate iodine under these conditions, but the hydrogen peroxide in solution decomposed with evolution of oxygen. Partington and Fatallach [2] cast doubt on the validity of this test.

A whole range of compounds of the peroxyhydrate type has recently been synthesized, but the structures of these compounds and the nature of the hydrogen peroxide in them has not been adequately studied. Whereas different modes of bonding of water have been established [3, 4] the experimental material for similar compounds of hydrogen peroxide is much too limited to establish any classification. It is most probably correct to describe them as hydrogen bonded compounds.

There is only one reference to the \(^1H\) NMR spectra of peroxy compounds. Sodium, potassium, and rubidium perborates, sodium perpyrophosphate, and sodium percarbonate were studied [5]. Analysis of the spectra showed that the perborates were basically hydrates of the corresponding perborates with a small amount of hydrogen peroxide of crystallization—they had the formula \(\text{Na}_2\text{BO}_3\cdot\text{mH}_2\text{O}\cdot(0.1-0.25)\text{H}_2\text{O}_2\). The perpyrophosphate and the percarbonate were peroxyhydrates of the simple salts and had the formulae \(\text{Na}_4\text{P}_2\text{O}_7\cdot\text{mH}_2\text{O}_2\) (\(m = 1, 2, 3\)) and \(\text{Na}_2\text{CO}_3\cdot1.5\text{H}_2\text{O}_2\).

We have observed the \(^1H\) NMR spectra for which the following formulae have been proposed on the basis of a series of their chemical and physicochemical properties: \(\text{Na}_6\text{HPO}_4\cdot1.5\text{H}_2\text{O}\); \(\text{Na}_2\text{HPO}_4\cdot2.5\text{H}_2\text{O}_2\); \(\text{Na}_3\text{PO}_4\cdot4.5\text{H}_2\text{O}_2\); \(\text{Na}_3\text{P}_2\text{O}_7\cdot3\text{H}_2\text{O}_2\). The preparation and some of the properties of these compounds are described elsewhere [6, 7]. The spectra were recorded on a \(^1\text{H}-\text{NMR}-60\) spectrometer with a field of about 6000 Oe. The spectra of some of the compounds studied at room temperature and about \(-100^\circ\) are given in the Fig. 1.

At low temperature all the spectra coincided, and the spectrum of \(\text{Na}_4\text{P}_2\text{O}_7\cdot3\text{H}_2\text{O}_2\) was almost identical with that published previously [5]. All the other spectra have been obtained for the first time. The second moments \(S_2\) [8] calculated from the spectra are cited in the table.

The values obtained show that the first three compounds are pure peroxyhydrates of the corresponding salts, i.e., they contain hydrogen peroxide of crystallization, but no water of crystallization. This follows because the well known \(^1H\) NMR spectrum of water of crystallization should have a second moment of 20-25 Oe\(^2\) in a polycry-
stalline sample at low temperature [8]. The comparatively large value of the second moment for the fourth compound indicates that it contains some water of crystallization. From the value of the second moment and the form \(^1\)H NMR spectrum this compound has the formula Na\(_3\)PO\(_4\)·4H\(_2\)O\(_2\)·2H\(_2\)O.

It is possible to estimate the mean interprotonic distances in these compounds from the second moments by using Van Vleck's formula [9], which has the form \(S^2 = 358.1 \cdot r^{-6} \) (\(S^2\) in Oe\(^2\), \(r\) in Å) for protons in a polycrystalline sample. Hence the interprotonic distances in these compounds range from \(r = 1.73\) to \(r = 2.08\) Å.

The distance between the hydrogen atoms in the hydrogen peroxide molecule is 2.13 ± 0.09 Å [10]. From this distance the intramolecular part of the second moment is 3.25 Oe\(^2\), i.e., about half the observed value, and the rest is explained by intermolecular interactions.

All the discussion above indicates that there are hydrogen bonds between the hydrogen peroxide units in these compounds, and that associates of the type

\[ \text{Na}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O} \]