

SHORT COMMUNICATIONS

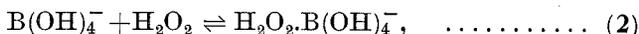
BORATE BUFFERS IN HYDROGEN PEROXIDE REACTIONS*

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During a recent investigation of a peroxide oxidation reaction (Wilson and Harris 1960), interference from borate buffers was noted. These observations provide evidence for the relative electrophilicity of hydrogen peroxide and perborate species. An interpretation of the structure of the latter is proposed. The properties of aqueous solutions containing hydrogen peroxide and boric acid or borates have been investigated by distribution, cryoscopy, and conductance (Menzel 1923, 1927), pH (Edwards 1953), and polarographic behaviour (Kern 1955). The authors conclude that borates, but probably not boric acid, combine with hydrogen peroxide or its anion, forming peroxy compounds. Results over a range of hydrogen peroxide concentrations appear to require the existence of more than one such compound. The probable structure of these species has been stated only in very broad terms. Thus Kern speaks of "the formula $\text{H}_2\text{O}_2\cdot\text{B}(\text{OH})_4^-$ for the perborate species", and Kemp (1956) uses either this formula or such non-committal expressions as $\text{NaBO}_3\cdot 4\text{H}_2\text{O}$ (for the solid).

Peroxides and hydroperoxides of a number of elements, including boron, have been synthesized by Davies and co-workers (Buncel and Davies 1958; Davies and Moodie 1958; Abraham and Davies 1959; Davies and Hall 1959; Davies and Hare 1959; Davies and Packer 1959) using reactions of nucleophilic substitution in compounds such as BCl_3 . It is now suggested that the species formed from borates or boric acid arise from nucleophilic substitution by hydrogen peroxide (or its anion) and that their structures are, in consequence, analogous to such anions as $\text{B}(\text{OH})_4^-$ and BCl_4^- . Then the equation for the formation of the simplest member should be written as (1) rather than as (2).

The borate ion

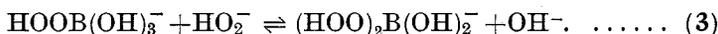


will be much less susceptible to nucleophilic attack than boric acid, since it lacks a vacant orbital. Equation (1) shows that in solutions of boric acid alone, formation of $\text{HOOB}(\text{OH})_3^-$ from H_2O_2 is accompanied by a mole of strong acid. The pH measurements by Edwards show this effect quite well. Measurements of conductance also reveal it (Menzel 1927, unpublished data). In less strongly acid solutions, reaction (1) would be expected to occur through the HO_2^- ion. This should be a much stronger nucleophile than H_2O_2 here, as it is found to be in nucleophilic attack of peroxide on benzonitrile (Wiberg 1953).

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The variation with pH of the extent of formation of perborate is adequately explained by the present hypothesis. The small decrease in conductivity found for borate solutions with increasing hydrogen peroxide concentration is also reasonable if an anion such as $\text{HOOB}(\text{OH})_3^-$ is replacing $\text{B}(\text{OH})_4^-$. Edwards and Menzel have both reported evidence for the binding of more than one peroxide group per boron atom. Presumably this involves displacement of an hydroxyl ion as in (3):



Kern has drawn attention to the fact that fairly satisfactory equilibrium constants have been found in the various investigations within restricted ranges of concentration (e.g. 33 calculated for the present eqn. (2)) at moderately low concentrations of hydrogen peroxide. His conclusion may be applied to (1), leading to a value of approximately 1.9×10^8 for the equilibrium constant* at 18 or 25 °C.

The formation of peroxyborates has important kinetic consequences which have not always been recognized. Some reactions in which hydrogen peroxide functions as an electrophile may be very substantially accelerated in the presence of a borate buffer. For example, the following values have been obtained for the overall rate constant for oxidation of thiocyanate ion by hydrogen peroxide at varying concentrations of borax buffer.

Borax Concentration (M)	Observed Rate Constant (l. mole min ⁻¹)	k_2 (l. mole min ⁻¹)
0.01	0.117, 0.105	0.22 ; 0.25
0.02	0.178	0.29
0.05	0.254, 0.255	0.32

Values of the rate constant for reaction between thiocyanate ion and perborate, calculated with the equilibrium constant given above and assuming the rate expression (4) are also given:

$$-d(\text{H}_2\text{O}_2)/dt = k_1(\text{H}_2\text{O}_2)(\text{SCN}^-) + k_2(\text{Perborate})(\text{SCN}^-) \quad \dots \dots (4)$$

The value of k_1 is 0.031 l. mole⁻¹ min⁻¹ (Wilson and Harris 1960). The values of k_2 show a definite trend, which may be elucidated in further investigations. They suffice to demonstrate that the specific reaction rate of perborate ion is 7–10 times that of hydrogen peroxide. It is apparent that measurements at a single concentration of borax would be very misleading indeed. Extrapolation to low buffer concentration is not easy.

Where hydrogen peroxide functions as a nucleophile, interference is also possible, but now perborate appears to be less reactive than HO_2^- . Kern (1955) observed polarographic behaviour in which perborate did not contribute. Wiberg (1953) reports no acceleration of rate with benzonitrile when borate buffers were used. Kern also noted that the rate of decomposition of hydrogen peroxide in borate buffers decreased with increasing borate concentration. Preliminary

* Using a value of 5.79×10^{-10} for the dissociation constant of boric acid (Kemp 1956, p. 14).

experiments using iodometric titration confirm this, although some workers appear not to have observed the phenomenon (Erdey 1953). Use of borate buffers in reactions which involve hydrogen peroxide should only be made with care.

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