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Carbon Dioxide-mediated Decomposition of Hydrogen Peroxide in Alkaline Solutions

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Rapid hydrogen peroxide decomposition in aerated alkaline solutions is described, the maximum rate being attained at pH values between 11.5 and 11.7, where the peroxide ($pK_a = 11.7$) is *ca.* 50% unprotonated. The reaction proceeds with the release of protons and is strictly dependent upon the continuous presence of carbon dioxide, but not of carbonate anions, in the peroxide solutions. The following two-step mechanism is proposed: (1) formation of percarbonic acid (H_2CO_4) by condensation of CO_2 with the undissociated peroxide (H_2O_2) and (2) reduction of the acid by perhydroxyl anions (HO_2^-).

In previous papers^{1,2} describing a photochemical system for hydrogen peroxide production with flavin as photosensitizer, semicarbazide as electron donor and oxygen as electron acceptor, we found an anomalous and drastic decrease in the efficiency of the photoproduction of H_2O_2 at pH *ca.* 12, and the stability of H_2O_2 was found to be a function of pH. Hydrogen peroxide decomposition is a very complex reaction and it has been studied extensively for many years. The decomposition may take place spontaneously, but it is accelerated by the presence of catalysts such as metal ions (Fe, Cu, Mn),^{3–5} metal oxide (OsO_4),⁶ metal complexes (metallotetraphenylporphyrins, iron–EDTA)^{7,8} or enzymes (catalase, peroxidases). Two mechanisms have been proposed for the spontaneous decomposition of H_2O_2 ,^{3–5,9} but neither has been readily accepted.

This paper deals with the effect of carbon dioxide on the decomposition of H_2O_2 in alkaline solutions, which, to the best of our knowledge, has not been described previously.

EXPERIMENTAL

The kinetics and rates of the decomposition of hydrogen peroxide were studied in a cylindrical glass vessel of 2 cm diameter. The hydrogen peroxide (30%, analytical grade, Merck) solutions were prepared immediately prior to the experiments at a final concentration of 20–22 mmol dm⁻³ in 10 cm³ of doubly distilled water.

The H_2O_2 solutions had a continuous stream of air, nitrogen (99.99%), oxygen (99.9%) or carbon dioxide (99.5%) passed through them, the flow rate of the gas stream being controlled by a Century Vit flowmeter and maintained at 0.1 dm³ min⁻¹. In some experiments, the air was previously passed through a saturated $Ba(OH)_2$ solution to remove CO_2 .

The pH of the H_2O_2 -containing solutions, especially that of the unbuffered ones, was continuously monitored during the experiments with a Radiometer pH-meter and kept at the desired value by addition of a small amount of concentrated NaOH or HCl solution.

The H_2O_2 content was determined by enzymatic reduction of the peroxide with *o*-dianisidine, as described previously,¹⁰ the absorbance of the complex so formed being measured at 440 nm with a Pye Unicam SP8–100 spectrophotometer.

All the chemicals were reagent grade and used without further purification.

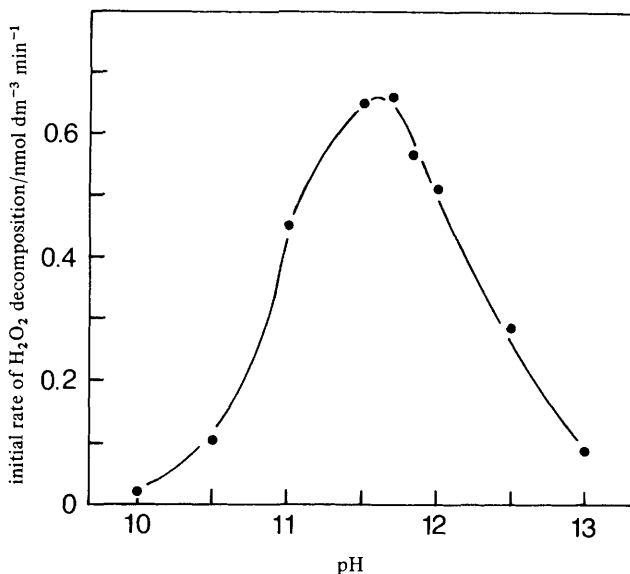


Fig. 1. Dependence on pH of decomposition of hydrogen peroxide in aerated solutions. 10 cm³ solutions containing 20 mmol dm⁻³ H₂O₂ at the indicated pH were continuously aerated at a flow rate of 0.1 dm³ min⁻¹, the peroxide content being measured as described in the experimental section. The solutions were buffered either with borate (pH 10.0, 10.5 and 11.0) or with phosphate (pH 11.0, 11.5, 11.7, 12.0 and 12.5) at a final concentration of 0.6 mol dm⁻³. At pH 13.0 the solution was unbuffered but contained 0.1 mol dm⁻³ NaOH. In all cases the pH was continuously monitored throughout the experiments with a pH-meter and adjusted when necessary.

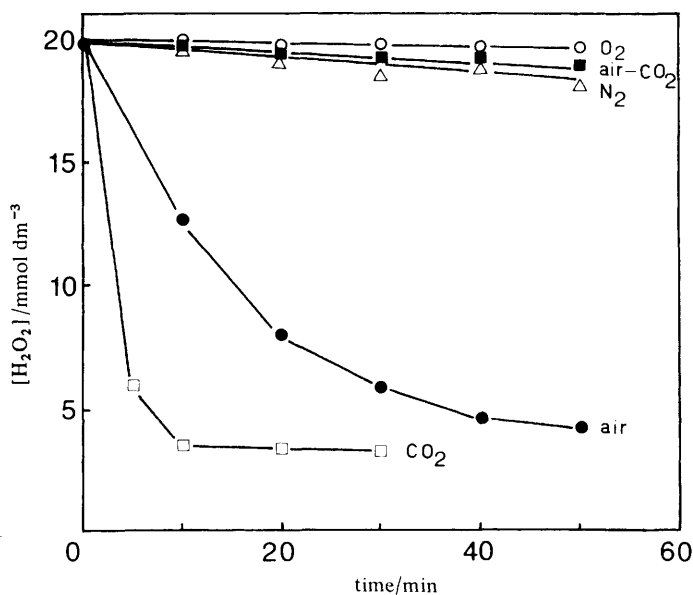


Fig. 2. Kinetics of decomposition of hydrogen peroxide at pH 12 under different gases. Nitrogen, oxygen, carbon dioxide or air either with or without CO₂ were passed through unbuffered solutions containing 20 mmol dm⁻³ H₂O₂ in a final volume of 10 cm³. The pH was initially adjusted to 12 and maintained constant throughout each experiment. The H₂O₂ content was measured at the indicated times.

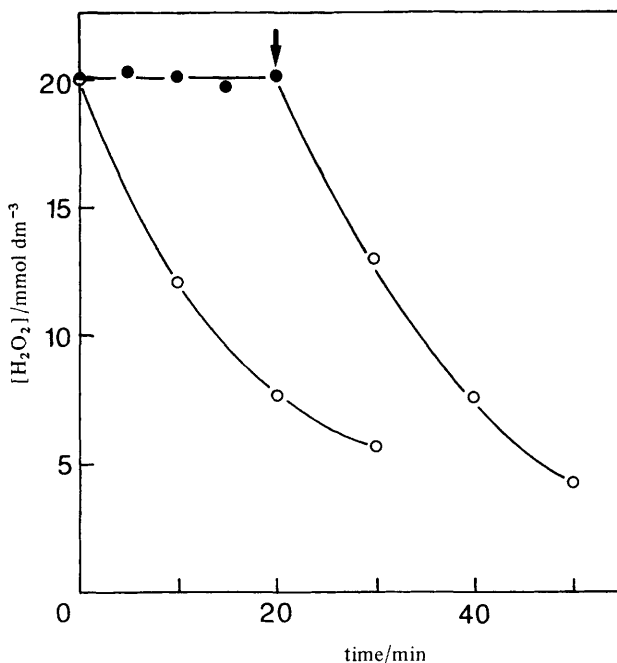


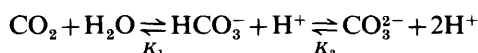
Fig. 3. Requirement of carbon dioxide (but not of carbonate anions) for decomposition of hydrogen peroxide at pH 12. Either air (O) or CO₂-free air (●) were passed through 10 cm³ solutions containing 20 mmol dm⁻³ H₂O₂ and 0.5 mol dm⁻³ carbonate buffer at pH 12. The arrow indicates the moment when the air stream, initially free of CO₂, was passed directly through the peroxide solution without passing through the Ba(OH)₂ solution. The pH was maintained at 12 throughout the experiments. The H₂O₂ content was determined at the indicated times.

RESULTS AND DISCUSSION

As shown in fig. 1, H₂O₂ decomposed rapidly in aerated solutions containing the peroxide at a concentration of 20 mmol dm⁻³, the maximum rate (0.7 mmol dm⁻³ min⁻¹) being attained at pH values between 11.5 and 11.7. Significant decomposition of H₂O₂ was not observed at pH < 10 or > 13. As the first pK_a value of H₂O₂ is 11.7, coinciding with the pH region at which H₂O₂ decomposition reached a maximum, it seems likely that the presence of both peroxide molecules and perhydroxyl anions is necessary for the process to take place, in accordance with the uncatalysed mechanism reported previously.^{5,9}

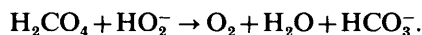
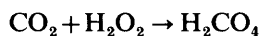
However, when the H₂O₂-containing solutions, at pH 12, had either oxygen or nitrogen passed through them, no decomposition of H₂O₂ was observed. In contrast, when carbon dioxide was used, the peroxide decomposed at a very high rate (see fig. 2). H₂O₂ decomposition did not occur when the solutions had CO₂-free air, obtained by passing the air stream through a saturated solution of barium hydroxide, passed through them (see also fig. 2). From this we deduced the effect of carbon dioxide on the decomposition of H₂O₂ in alkaline solutions.

Note, however, that in aqueous solutions CO₂ is diluted and hydrated to H₂CO₃, quickly losing one or two protons, depending on the pH of the solution, as shown in the following simplified reactions

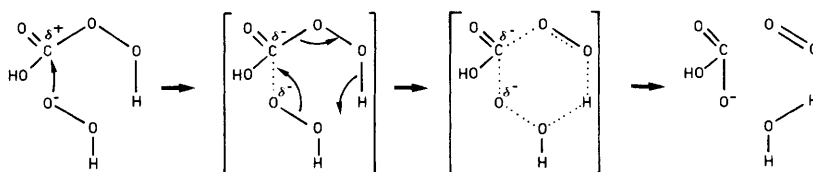


where pK_1 and pK_2 are 6.3 and 10.3, respectively.¹¹ As the CO₂-dependent decomposition of H₂O₂ was observed to be especially high at pH 11–12, where almost all the CO₂ is present as CO₃²⁻ anions, it was investigated whether decomposition of H₂O₂ occurs in the presence of such anions. The results obtained are shown in fig. 3, where it can be seen that peroxide decomposition at pH 12 does not take place in the presence of carbonate unless the solutions have air containing CO₂ passed through them. If the carbonated solutions of H₂O₂ had CO₂-free air passed through them, the decomposition reaction was much slower. These findings mean that CO₂, but not carbonate anions, is the species responsible for catalysing the decomposition of H₂O₂.

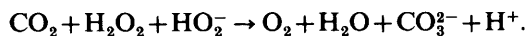
In view of these results, it appears that one possible explanation would be the oxidation of HO₂⁻ by percarbonic acid, previously formed by reaction of CO₂ with H₂O₂:



The last reaction can be visualized as taking place as the result of a nucleophilic attack of perhydroxyl anions on percarbonic acid, as shown in the following scheme:

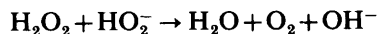


According to the proposed mechanism, and as we were working at pH 12, the decomposition reaction must involve the release of protons, since the bicarbonate anion, at that pH, will lose its proton to form carbonate anion. The total reaction, at pH 12, would be as follows:



In order to check this hypothesis, the set of experiments shown in fig. 4 was carried out. The pH of unbuffered solutions containing H₂O₂, initially adjusted to 12, decreased, as the peroxide was decomposing, at a higher rate than that of similarly treated solutions without H₂O₂ in which the pH decrease was only due to CO₂ contained in the air being passed through the solutions.

These results support the above mechanism but contradict that described previously by Abel,¹² in which the decomposition of the peroxide proceeds through the uncatalysed reaction of perhydroxyls with undissociated peroxide molecules



and brings about the concomitant release of hydroxyl anions.

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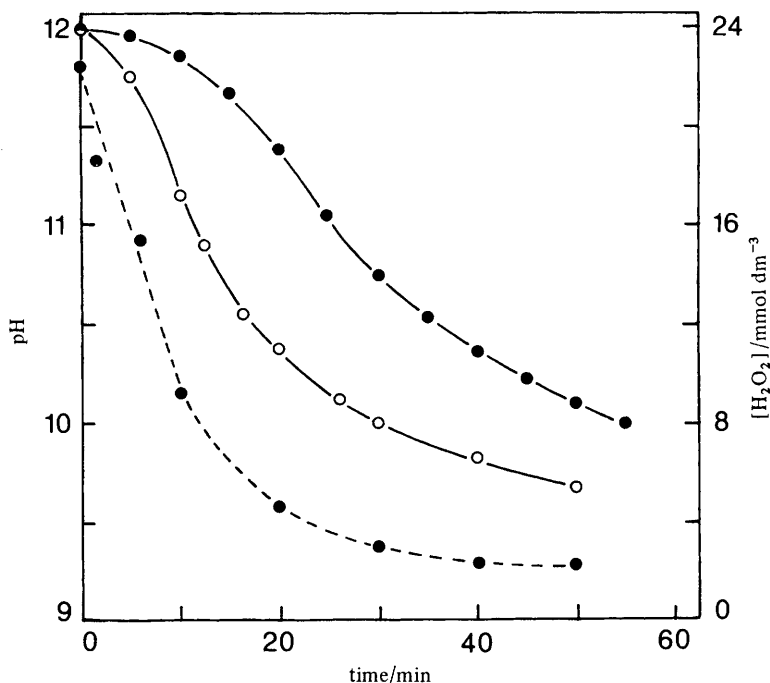


Fig. 4. Decrease of pH during the CO₂-mediated decomposition of hydrogen peroxide in unbuffered solutions. A 10 cm³ solution containing 22 mmol dm⁻³ H₂O₂, whose pH was initially adjusted to 12 by addition of NaOH, was continuously aerated at a flow rate of 0.1 dm³ min⁻¹. Its H₂O₂ content (●---●) and pH (○—○) were measured at the indicated times. The pH of another aerated solution containing only 10 cm³ of distilled water was adjusted to 12 and its decrease also plotted (●—●).

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