pH and Temperature Pulses during the Periodic Decomposition of Hydrogen Peroxide

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Among the large number of homogeneous, liquid-phase, and non-enzymic reactions only two are so far known to be periodic in nature; they are the decomposition of H_2O_2 by IO_3^- and I_2[1-4] and of malonic acid by Ce^{3+}, Ce^{4+}, and BrO_3^-.[5-7] Owing to their complexity, neither reaction has so far been given a satisfactory mechanism; only one aspect of the former reaction, *i.e.* the periodic change in $[I_2]$ ([ ] means mol/*l*), has been qualitatively reproduced[8] *via* computer for a hypothetical mechanism.

In our reinvestigation[9] of the IO_3^- - I_2 - H_2O_2 system, we have found pulses in $[I^-]$ that are closely related to previously discovered pulses[1,3,4] in $[I_2]$ and dO_2/dt (rate of oxygen evolution). We have now succeeded in finding pulses also in pH and in temperature. To find these new pulses, it was necessary to have sensitive measuring instruments and to choose the proper reaction conditions. As evidence for this, we mention that Peard and Cullis,[3] apparently the first to look for pH pulses, failed to find them.

Reaction mixtures (140 cc) consisting of approximately 0.6M KIO_3, 0.052M $HClO_4$, and 0.5M H_2O_2 were subjected to both pH and temperature measurements. The reaction vessel, which was surrounded by a water jacket at 50°C, was equipped as needed with instruments for the measurements. Recording of pH was by means of a glass electrode connected to a mV recorder *via* a digital pH/mV meter. Temperature recording was by means of Cu-constantan thermocouple connected to a mV recorder *via* a microvoltometer. Supplementary measurements of $[I_2]$, pI, and dO_2/dt were made with a spectrophotometer, an iodide selective electrode,[10] and a mass flowmeter, respectively.

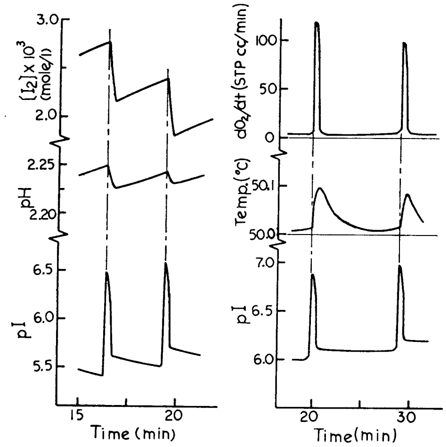

Fig. 1. Pulses in pI, pH, $[I_2]$, temperature, and dO_2/dt. pH pusles were perceptible for the first hour. Replenishment of 0.3M H_2O_2 at time= 150 min resulted in their reappearance at time= 180 min.

Figure 1 shows the observed pulses in pH and temperature and the concomitant pulses in $[I_2]$, pI, and dO_2/dt. Preliminary analysis of the data supports the view that the pH decrease results mainly from the reaction $I_2+5H_2O_2=2H^++2IO_3^-+4H_2O$, the incomplete dissociation of HIO_3 being considered. The heat evolved during the temperature pulses appears to result from the reaction just given (responsible for the $[I_2]$ decrease) and from $H_2O_2=H_2O+\frac{1}{2}O_2$ (responsible for the oxygen evolution). Work is continuing on the relationship of the pulses and their interpretation in terms of known reactions.

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