pH Oscillation in the Closed System of H_2O_2–$Fe(CN)_6{}^{4-}$–Acetonitrile–Water

Gyula Rábai

Institute of Physical Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary

Regular pH oscillations with small amplitude are observed during the decomposition of hydrogen peroxide in the presence of ferrocyanide ions in an unbuffered mixture of water–acetonitrile under closed conditions in the dark.

Hydrogen peroxide has played a major role in the field of oscillatory chemical reactions for 70 years. Its acidic iodate catalysed decomposition[1] was the first example of a handful of inorganic chemical reactions to oscillate in a closed homogeneous solution.

A large body of information now exists about this system, and several new reactions of H_2O_2 have recently been found to be oscillatory mostly in a continuous flow stirred tank reactor (CSTR). Despite the discovery of new CSTR systems, still very few model reactions that have do not exchange matter with their surroundings (batch conditions) are available for detailed study. In addition to the above mentioned iodate-catalysed decomposition[1] the only batch oscillator of H_2O_2 was observed in the H_2O_2–SCN^-–Cu^{2+} system.[2] Taking into consideration that both iodate and thiocyanate ions are known to participate in H_2O_2 free oscillators, the following questions

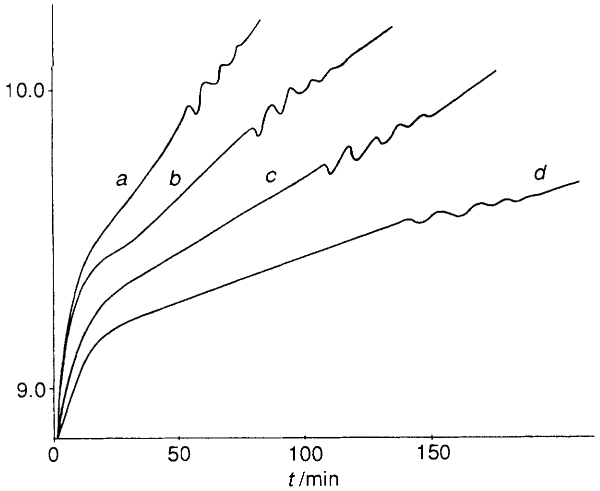

Fig. 1 Typically oscillatory pH–time curves in the [acetonitrile] (10%)-[$Fe(CN)_6^{4-}$] (0.05 mol dm^{-3})-[H_2O_2] (0.75 *a*, 1.0 *b*; 1.12 *c*; 1.25 *d*; M) system at 25 °C in darkness

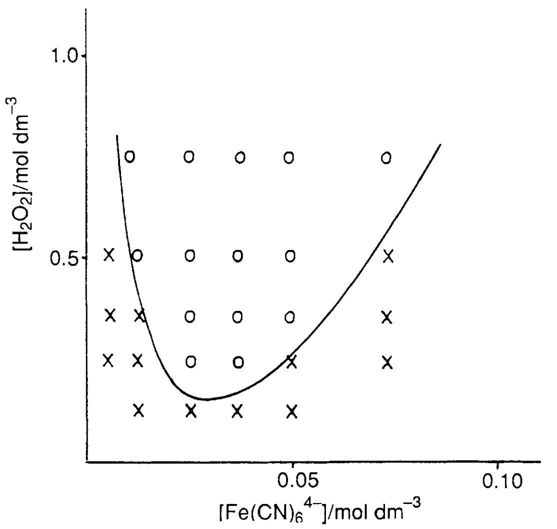

Fig. 2 Initial compositions of reaction mixture in the [H_2O_2]-[$Fe(CN)_6^{4-}$] plain showing oscillatory (O) and non-oscillatory (×) kinetics. T = 25 °C; [acetonitrile] = 10%; in darkness.

arise: Does hydrogen peroxide play a crucial role, or is its partner responsible for these oscillations? Is there a common feature of the mechanisms of different H_2O_2 oscillators necessary for the oscillation to occur? In order to answer these questions and to understand the general thermodynamic and kinetic basis of H_2O_2 oscillators, discovery of further reactions of this type is still of great importance. Herein we report on the disproportionation of H_2O_2 in the presence of ferrocyanide ions and acetonitrile, which is of interest as a new H_2O_2 oscillator in batch.

In our experiments 33% aqueous H_2O_2 was used. A stock solution of 0.10 mol dm^{-3} $K_4Fe(CN)_6$ was prepared and stored under argon in darkness as described previously.[3] All the kinetic experiments were performed in a thermostatted glass vessel of volume 50 ml equipped with a pH electrode and a magnetic stirrer. Since the kinetics of the reaction were sensitive to visible light, the reactor was protected from light. Acetonitrile and the ferrocyanide solution were premixed immediately prior to the kinetic runs. We found that when a solution of $K_4Fe(CN)_6$ in aqueous acetonitrile was mixed at room temperature, in darkness with an aqueous solution of H_2O_2, a slow reaction occurs indicated by a moderate O_2 gas evolution. In Fig. 1, we show representative pH–time oscillatory curves at different hydrogen peroxide concentrations. After a pre-oscillatory period the kinetic traces appear to include regular damped temporal oscillations, or at least a stepwise increase in pH with a period of 5–10 min. Although the amplitude is very small, there seems to be no reason to doubt veracity of this oscillation. It can be reproduced easily and exactly. In addition to the pH measurements we followed simultaneously the changes in redox potential using Pt electrode, and found it to show regular oscillations with small amplitude (3–4 mV). Oscillation could be observed in a rather broad range of initial reactant concentrations. The oscillatory and non-oscillatory regions in the [H_2O_2]-[$Fe(CN)_6^{4-}$] plain at constant acetonitrile concentration are shown in Fig. 2. No definite upper boundary of the oscillatory region could be measured. It is, however, important to note that the higher the [H_2O_2], the longer the pre-oscillatory period of the pH–time curves is observed. This means that the excess of hydrogen peroxide must be removed by a non-oscillatory catalytic decomposition before oscillations can start.

Efforts have been made to observe periodicity in the rate of gas formation by means of volumetric measurement. However, the amplitude of oscillation in the rate of gas formation seems to be too small to be observed by this method unambiguously. Total volume of oxygen formed during the reaction was found to be 96–98% of the stoichiometric amount based on eqn. (1). Simultaneously a small part of ferrocyanide is oxidized to ferricyanide ions [eqn. (2)].

$$2\,H_2O_2 \rightarrow O_2 + 2\,H_2O \qquad (1)$$

$$H_2O_2 + 2\,Fe(CN)_6^{4-} \rightarrow 2\,Fe(CN)_6^{3-} + 2\,OH^- \qquad (2)$$

Since the oxidizing properties of hydrogen peroxide depend upon pH,[4] reaction (2) stops at pH 9.5–10. Reaction (2) is essentially stoichiometric, and no significant catalytic decomposition of hydrogen peroxide occurs in the presence of hexacyanoiron complexes in darkness,[5] so the complete decomposition of H_2O_2 is not due to the presence of $Fe(CN)_6^{4-}$. Control experiments establish that the addition of OH^- to H_2O_2 in a water–acetonitrile mixture results in the moderate base-catalysed disproportionation of H_2O_2 to water and oxygen[6] even in the absence of ferrocyanide ions, but no oscillations could be observed. It seems reasonable to assume that one of the roles of ferrocyanide ions in the oscillations is to supply the system with OH^- by reaction (2). Since, according to our experiments, $Fe(CN)_6^{4-}$ cannot be replaced by the simple addition of base to the system, but its presence is essential for the oscillations to occur, there must be another role of $Fe(CN)_6^{4-}$. We do not wish to speculate here on the possible detailed mechanism of reaction except to point out that a mechanism proposed[3] for the oscillatory reaction of H_2O_2 with $Fe(CN)_6^{4-}$ in CSTR can also reflect oscillation in batch, but there is no good agreement between the calculated and experimentally found curves. A detailed mechanism is under construction and will be published in a forthcoming paper.†

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† This system is not a so called pH-regulated oscillator[7] because of the very small changes in pH. Here, the pH serves as an indicator of oscillation, and the phenomenon is governed kinetically by species other than H^+ or OH^-.