Light-Induced Route to Chaos in the $H_2O_2-HSO_3^--HCO_3^--Fe(CN)_6^{4-}$ Flow System

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High-frequency pH oscillations observed in the H_2O_2-HSO_3^--$HCO_3^--Fe(CN)_6^{4-}$ flow system in the dark at 5 °C undergo period-doubling cascades to chaos upon continuous irradiation with visible light of increasing intensity. A reverse period-doubling route from chaos to low-frequency limit cycle oscillations is also observable upon further increasing the light power. Such a unique photoresponse may open the way for controlling the chaotic behavior by light.

Responses of different kind to the continuous photoillumination or short light pulse perturbations are observed in homogeneous chemical oscillators.[1] Changes in the periodic time and amplitude, induction and inhibition of oscillations, transitions between steady and oscillatory states in bistable systems, and phase shift are known as the most common photoresponses. Since the selective alteration of the rate of a photosensitive composite reaction is possible by illumination, the use of the light power as an external control parameter appears to be a powerful tool for obtaining unambiguous mechanistic insights in a complex dynamic system. An obviously interesting relevant question is whether photosensitive periodic oscillations can be driven into chaotic state by using light power as the bifurcation parameter. The opposite problem is whether a chaotic state can be regulated into simple limit cycle oscillations or into steady states by illumination. Here, we show an experimental example that both transitions can be induced by photoillumination in an appropriate dynamic system.

In our experiments we used a recently designed chaotic $H_2O_2-HSO_3^--Fe(CN)_6^{4-}-HCO_3^-$ system in a continuous flow stirred tank reactor (CSTR).[2] This system consists of two oscillatory subsystems which share a common positive feedback loop: the autocatalytic oxidation of HSO_3^- by H_2O_2 (reaction 2 in Table 1). The negative feedback consists of, at least, two channels: (i) protonation of HCO_3^- coupled with an escape of CO_2, which eventually removes some of the H^+ in the form of $H_2O + CO_2$ (reactions 1 and 4), and (ii) the oxidation of ferrocyanide by H_2O_2 (reaction 5), which also consumes proton. Due to the multichannel negative feedback, the system can exhibit regular pH oscillations of two very different frequencies depending on the conditions. For example, the high-frequency oscillations (20−25 periods h^{-1}, characteristic for channel i) are supported by slow flow rate, while higher flow rate is favorable for low-frequency oscillations (1−2 periods h^{-1}, characteristic for channel ii). As a result of the interaction of the two frequencies, complex periodic behavior and chaos are also exhibited if favorable input concentrations and flow rates are maintained in the dark at 4−5 °C. The existence of chaos is demonstrated in Figure 1 by a fraction of the measured pH time series and the corresponding next return map. Other chaos-identifying data transformations were also supportive. The dynamic behavior is expected to be sensitive to light because

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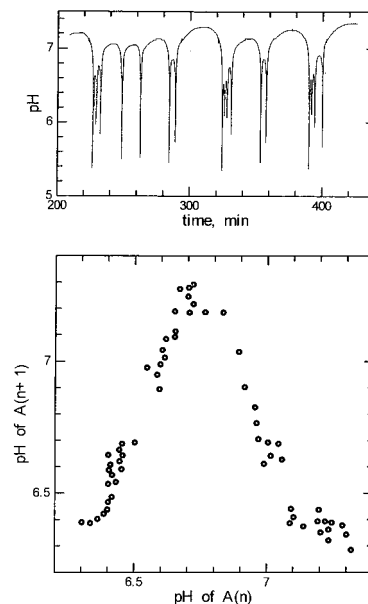
Figure 1. A fraction of the chaotic time series of pH (top), and the pH in a maximum as a function of the pH in the previous maximum (bottom) collected during a 10 h CSTR run in the dark. Input concentrations in the combined feed: $[H_2O_2]_0 = 0.011$, $[SO_3^{2-}]_0 = 5.0 \times 10^{-3}$, $[H^+]_0 = 5.0 \times 10^{-4}$, $[HCO_3^-]_0 = 5.0 \times 10^{-4}$, $[Fe(CN)_6^{4-}]_0 = 2.0 \times 10^{-3}$ M; $k_0 = 2.82 \times 10^{-4}$ s^{-1}; $T = 5.0$ °C. The cylindrical shaped (i.d. 3.0 cm, 7.0 cm tall) black plastic reactor with a liquid volume of 28.0 mL was covered (but not sealed) with a cap through which a pH electrode, the input and output tubes (i.d. 1.0 and 2.0 mm, respectively), and an optical cable were led. The reactor was immersed in a water bath to maintain $T = 5.0 \pm 0.1$ °C in the reaction mixture. The reactor was fed by means of a peristaltic pump with solutions of H_2O_2 and $Na_2SO_3 + H_2SO_4 + NaHCO_3 + K_4Fe(CN)_6$ (premixed, prethermostated for 12 h and kept from light under N_2, but not bubbled to avoid any loss of CO_2!). Another pump served for removing the excess of liquid. The solution in the reactor was stirred by a magnetic stirrer with approximately 500 rpm. The liquid level could be controlled by the position of the outlet tubes. A N_2 gas stream of 7.0 ± 0.4 mL min^{-1} was introduced into the liquid to control CO_2 escape.

the $H_2O_2-Fe(CN)_6^{4-}$ composite reaction (reaction 5) is known to be highly photosensitive.[3] Our systematic experiments have revealed that a photoinduced period-doubling route from simple high-frequency pH oscillations to chemical chaos and a reverse period-doubling route from chaos to low-frequency regular oscillations are observable. First, we optimized the experimental conditions that supported high-frequency regular oscillations in the dark (Figure 2, bottom). Then, the reaction mixture was continuously illuminated with visible light of different intensity and the pH responses were measured. Before steady responses of a given kind were obtained, we had observed a 2−3 h long transient period after changing the light power. This indicated that the system responded slowly to any change in the illumination intensity. Sustained period 2 oscillations consisting of alternating 8 and 16 min sections appeared with 0.70 mW light power. When the light intensity was increased step by step, more complex period 4 oscillations composed of alternating sequences of 24−6−18−12 min sections at 1.15 mW and stable chaotic pH time series were observed (Figure 2). Chaotic behavior was supported by a rather wide range of light power (1.4−2.0 mW). Windows of stable period 3 oscillations within the region of chaos (for example at 1.6 mW) were found. However, the width of these windows hardly exceeds 0.1 mW. Such periodic windows are a universal feature of the period-
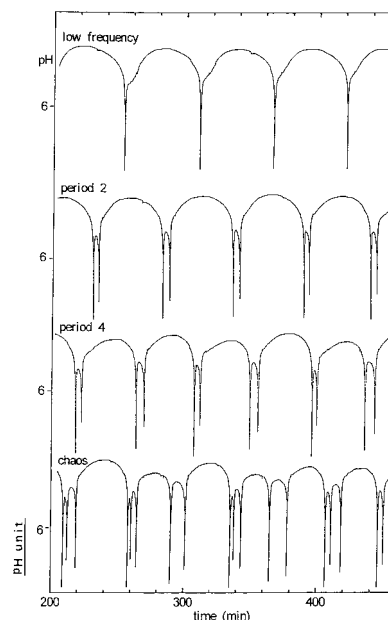
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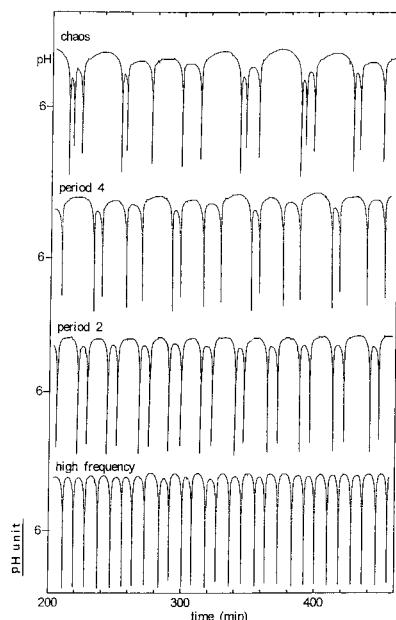
Figure 2. Light-induced period-doubling cascades to chaos measured in a CSTR. Light power from the bottom is 0.0 (dark), 0.70, 1.15, and 1.55 mW, respectively, where the power refers to the incident light power into the reactor. The stirring seems to be fast enough to distribute the irradiated volume on a time scale shorter than the reaction events. Input concentrations are the same as in Figure 1 except $[Fe(CN)_6^{4-}]_0 = 1.0 \times 10^{-3}$ M, $k_0 = 2.07 \times 10^{-4}$ s^{-1} and $T = 5.0$ °C. A Hayashi Luminar Ace LA-150SX type 150W halogen light source provided the visible light (>390 nm) of variable intensity, which was led to the reactor through the optical cable. Diameter of the light beam and the optical path length in the solution were 1.0 and 2.6 cm, respectively.

doubling route to chaos and are also found in other reactions.[4] Unstable period 5 oscillations as fractions of chaotic traces (Figure 3, bottom) have also been detected under illumination. The dynamic behavior undergoes a reverse period-doubling route from the chaotic state to low-frequency regular oscillations with increasing further the light power. Shown in Figure 3 are chaos, period 4, period 2, and low-frequency period 1 oscillations which were supported by light power of 1.70, 2.05, 3.1, and 5.15 mW, respectively. If the power exceeded 8 mW, oscillations were completely inhibited and a high pH (7.3) steady state set in. Transition from the dark chaotic state (Figure 1) to the low-frequency oscillatory state can also be induced by continuous illumination. Similar responses to those shown in Figure 3 were obtained. To our knowledge, this unique photoresponse has never been observed in chemical reaction systems before. Nevertheless, these light-induced transitions from chaotic state to limit cycle oscillatory state are not the realization of the recently developed concept of "controlling chaos".[6] This concept suggests small, carefully selected, time-dependent perturbations on a parameter to stabilize one of the infinitely many unstable limit cycle oscillations of which chaos is composed. It remains to be seen whether such small, time-dependent variation in the light power can stabilize one of these limit cycles under the conditions which support chaos otherwise.

A simple scheme has been suggested for this system (Table 1), which was used to simulate the chaotic behavior.[2] Reaction 5 contributes to the multichannel negative feedback as it removes some of the hydrogen ion and a part of the H_2O_2. Its rate

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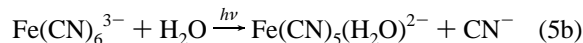(6) Ott, G.; Grebogi, C.; Yorke, J. A. *Phys. Rev. Lett.* **1990**, *64*, 1196.

Figure 3. Reverse period-doubling cascades from chaos (bottom) to low-frequency regular oscillations (top) under continuous illumination. Light power from the bottom: 1.70, 2.05, 3.10, and 5.15 mW, respectively. Other conditions are the same as in Figure 2. Note the transient period 5 oscillations as a fraction of the chaotic traces in the bottom curve.

Table 1. Composite Reactions of the Chaotic Oscillator

Reactions	Rate laws
(1) $CO_2(aq) + H_2O$ $\leftrightarrow H^+ + HCO_3^-$	$R_1 = k_1[CO_2(aq)]$; $R_{-1} = k_{-1}[H^+][HCO_3^-]$
(2) $H_2O_2 + HSO_3^-$ $\to H^+ + SO_4^{2-} + H_2O$	$R_2 = (k_2 + k_2'[H^+])[HSO_3^-][H_2O_2]$
(3) $HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$	$R_3 = k_3[HSO_3^-]$ $R_{-3} = k_{-3}[H^+][SO_3^{2-}]$
(4) $CO_2(aq) \to CO_2(gas)$	$R_4 = k_4[CO_2(aq)]$
(5) $2Fe(CN)_6^{4-} + H_2O_2 + 2H^+$ $\to 2Fe(CN)_6^{3-} + 2H_2O$	see text

increases upon illumination because of the photoaquation of the hexacyano iron(II)/(III) complexes.[3]

$$Fe(CN)_6^{4-} + H_2O \xrightarrow{h\nu} Fe(CN)_5(H_2O)_3^- + CN^- \quad (5a)$$

$$Fe(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Fe(CN)_5(H_2O)^{2-} + CN^- \quad (5b)$$

The monoaquapentacyano complexes accelerate the reaction between ferrocyanide and hydrogen peroxide.[5] The contribution of reaction 5 to the negative feedback loop is overwhelming under strong illumination, and the system shows low-frequency oscillations characteristic for the $H_2O_2-HSO_3^--Fe(CN)_6^{4-}$ subsystem or high pH steady state. In the dark, reaction 5 is relatively slow, its contribution to the negative feedback is small, and high-frequency oscillations are exhibited which are characteristic for the $H_2O_2-HSO_3^--HCO_3^-$ subsystem. The released cyanide ion may also modify the dynamic features, because it takes up proton in the pH interval of the oscillations.