Chaotic pH oscillations in the hydrogen peroxide–sulfite–ferrocyanide–hydrogen carbonate flow system

Gyula Rábai,[a] **Akiko Kaminaga**[b] **and Ichiro Hanazaki***[b]

[a] *Institute of Physical Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary*
[b] *Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

Combining the $CO_2(aq) + H_2O \longleftrightarrow H^+ + HCO_3^-$ equilibrium and a slow removal of CO_2 from the solution with an oscillatory H_2O_2–HSO_3^-–$[Fe(CN)_6]^{4-}$ system gives rise to chaotic temporal pH changes in a continuous-flow stirred tank reactor.

A few homogeneous chemical reactions are known to exhibit chaotic changes in species concentrations mostly in continuous-flow stirred tank reactors (CSTR).[1–5] Such phenomena have been discovered by chance, their mechanisms are very complex, and are still not well understood. Here, we present a new systematic approach to design a simple system, capable of displaying chaotic temporal changes in $[H^+]$. In our approach, we utilize CO_2 as a second feedback species in a pH oscillator.[6]

CO_2 is a very sluggish reactant and its direct kinetic role in aqueous solution chemistry is limited, but its strong effect on a pH oscillator through equilibrium (1) (Table 1) is expected. Some H^+ is liberated from $CO_2(aq)$ in the high pH state of oscillations supporting the revival of the positive feedback process in which H^+ is autocatalytically produced. On the other hand, H^+ is removed by HCO_3^- when the pH is low providing a supplementary negative feedback. Such a constant perturbation may desynchronize an oscillatory system into a chaotic

Table 1 Composite reactions and rate laws of the chaotic oscillator

Reactions	Rate laws
(1) $CO_2(aq) + H_2O \longleftrightarrow H^+ + HCO_3^-$	$R_1 = k_1\,[CO_2(aq)]$; $R_{-1} = k_{-1}\,[H^+]\,[HCO_3^-]$
(2) $H_2O_2 + HSO_3^- \longrightarrow H^+ + SO_4^{2-} + H_2O$	$R_2 = (k_2 + k_2'\,[H^+])\,[HSO_3^-]\,[H_2O_2]$
(3) $HSO_3^- \longleftrightarrow H^+ + SO_3^{2-}$	$R_3 = k_3\,[HSO_3^-]$; $R_{-3} = k_{-3}\,[H^+]\,[SO_3^{2-}]$
(4) $CO_2(aq) \longrightarrow CO_2(gas)$	$R_4 = k_4\,[CO_2(aq)]$
(5) $H^+ \longrightarrow$	$R_5 = k_5\,[H^+]$

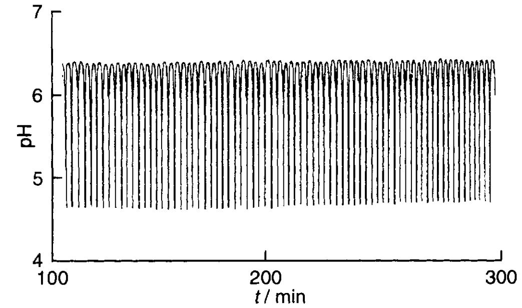

Fig. 1 Measured pH oscillations in the SO_3^{2-}–H_2O_2 reaction in the presence of HCO_3^- in a CSTR. $[H_2O_2]_0$ = 0.010, $[SO_3^{2-}]_0$ = 5.0 × 10^{-3}, $[H^+]_0$ = 4.0 × 10^{-4}, $[HCO_3^-]_0$ = 5.0 × 10^{-4} mol dm^{-3}. k_0 = 2.82 × 10^{-4} s^{-1}. T = 4.0 °C. The cylindrical shaped (id 3.0 cm, height 7.0 cm) reactor was covered (but not sealed) with a plastic cap through which a pH electrode, the input and output tubes (id 0.2 mm) were led. The volume of liquid was 28.0 ml. The reactor was fed with $Na_2SO_3 + H_2SO_4 + NaHCO_3$ (premixed and kept under N_2 to prevent autoxidation, but not bubbled to avoid loss of CO_2) and H_2O_2 solutions by means of a peristaltic pump. The excess of liquid was removed by a second peristaltic pump. The liquid level was controlled by the position of the outlet tubes. An N_2 gas stream of 7 ml min^{-1} was introduced into the liquid to control escape of CO_2.

Table 2 Rate-constant values used in calculations

	T = 25 °C	4 °C[a]	Ref.
k_1/s^{-1}	4.3 × 10^{-2}	1.1 × 10^{-2}	7
k_{-1}/dm^3 mol^{-1} s^{-1}	9.6 × 10^4	2.5 × 10^4	This work
k_2/dm^3 mol^{-1} s^{-1}	7.0	1.54	9, 11
k_2/dm^6 mol^{-2} s^{-1}	1.48 × 10^7	6.5 × 10^6	9, 11
k_3/s^{-1}	3.0 × 10^3	1.0 × 10^3	9
k_{-3}/dm^3 mol^{-1} s^{-1}	5.0 × 10^{10}	1.0 × 10^{10}	9
k_4/s^{-1}		1 × 10^{-3}[b]	This work
k_5/s^{-1}		3.0 × 10^{-2}	This work

[a] Estimated activation energies for the rate constants were used with values available at 25.0 °C to calculate values at 4.0 °C. [b] Measured with a 7 ml min^{-1} N_2 stream under CSTR conditions.

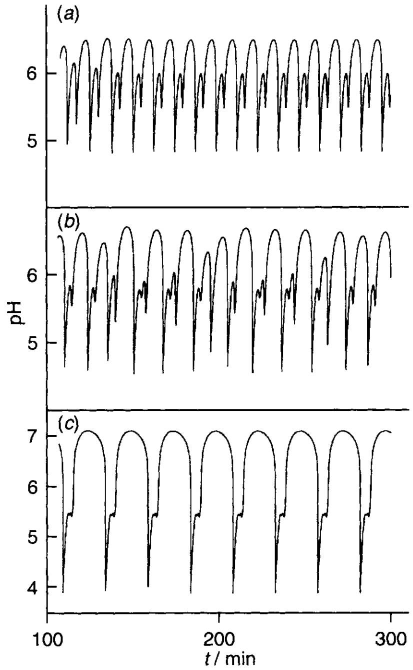

Fig. 2 Calculated pH–time responses at different flow rates. The calculations were carried out by the Runge–Kutta method on the basis of eqns. (1)–(5). Rate constants (at 4 °C) in Table 2 were used. High-frequency regular oscillations (with k_0 = 2.0 × 10^{-4}, not shown), double periods [(*a*) k_0 = 2.4 × 10^{-4}], quarternary periods (k_0 = 2.5 × 10^{-4}, not shown), chaotic traces [(*b*) k_0 = 2.9 × 10^{-4}], triple periods (k_0 = 3.0 × 10^{-4}, not shown), chaotic traces (k_0 = 3.4 × 10^{-4}, see graphical abstract) and bursting-like triple period oscillations [(*c*) k_0 = 6.0 × 10^{-4} s^{-1}] were obtained. $[H_2O_2]_0$ = 0.010, $[SO_3^{2-}]_0$ = 5.0 × 10^{-3}, $[H^+]_0$ = 5.0 × 10^{-4}, $[HCO_3^-]_0$ = 3.0 × 10^{-4} mol dm^{-3}.

state. It is important that reaction (1) is slow[7] compared to the other protonation equilibria. This unique slowness provides a significant time delay which separates the proton consuming pathway from the positive feedback channel. The time delay might be even more pronounced at lower temperature because of the expected differences in activation energies of the two channels. Our preliminary simulations have shown that reaction (1) alone can provide a sufficiently strong negative feedback with appropriate time delay necessary for oscillations to occur: when an autocatalytic H^+-producing reaction is taking place in the presence of HCO_3^-, oscillations are predicted in a CSTR.

Based on the above considerations, we constructed a unique pH oscillator consisting of an autocatalytic oxidation of HSO_3^- by H_2O_2 in the presence of HCO_3^-. Fig. 1 shows pH changes of high frequency (20 periods h^{-1}) measured in a CSTR at 4 °C. The behaviour can be modelled by the rate laws of reactions (1)–(4) shown in Table 1. A measured rate constant (k_1) for the hydration of CO_2 is available.[7] The reverse rate constant (k_{-1}) can be calculated from the apparent equilibrium constant K_1 and k_1 ($K_1 = [H^+][HCO_3^-]/[CO_2] = 4.45 \times 10^{-7}$ mol dm^{-3} at 25 °C[8]). Rate law (R_2) has been established[9–11] for reaction (2) in the pH range 4–8 in an aqueous solution where the predominant sulfur(IV) species are HSO_3^- and SO_3^{2-}. Equilibrium (3) is well characterized: $K_3 = 1.0 \times 10^{-7}$ mol dm^{-3} at 25 °C. We employed mass-action kinetics laws for both the forward and reverse reactions with high rate constants pertinent to K_3. The rate of the escape of CO_2 from the solution surface [eqn. (4)] can be estimated by measuring the pH change of an aqueous CO_2 solution under the experimental conditions. The loss of CO_2 can be approximated by a first-order rate law (R_4). This rate may be controlled experimentally by introducing an inert gas stream into the solution. Rate-constant values are summarized in Table 2. Using the values at 4.0 °C (except $k_4 = 1.2 \times 10^{-3}$ s^{-1}) oscillatory curves can be calculated with reactions (1)–(4) under the conditions given in Fig. 1 (except $[HCO_3^-]_0 = 4.0 \times 10^{-4}$ mol dm^{-3}).

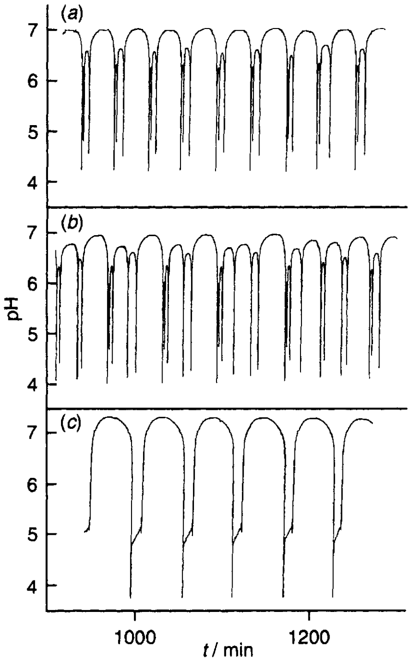

Fig. 3 Measured complex oscillations in the system containing $[Fe(CN)_6]^{4-}$. (*a*) The most characteristic triple periods ($k_0 = 2.97 \times 10^{-4}$), (*b*) chaotic oscillations ($k_0 = 3.64 \times 10^{-4}$), (*c*) bursting-like responses ($k_0 = 4.39 \times 10^{-4}$ s^{-1}) at 4.0 °C in the dark. Input concentrations are the same as in Fig. 1 but $[H^+]_0 = 5.0 \times 10^{-4}$ and $[Fe(CN)_6{}^{4-}]_0 = 1.0 \times 10^{-3}$ mol dm^{-3}; flow rate of N_2: 7.0 ml min^{-1}.

The positive feedback is provided by an autocatalytic production of H^+ during oxidation of HSO_3^-. The negative feedback channel is obviously reaction (1) along the process (4) which eventually removes H^+ in the form of $H_2O + CO_2$. In principle, process (4) would not be inevitable for negative feedback if equilibrium (1) were even slower. For example, the model retains its oscillatory character without process (4) with an arbitrary decrease in the numerical values of k_1 and k_{-1} by an order of magnitude. Of course, this theoretical possibility has no experimental importance in the present system.

Further simulations showed that with an additional channel for the negative feedback [process (5)], the behaviour of the system becomes more complex exhibiting a period doubling route to chaotic responses as the flow rate changes (Fig. 2). Experimentally, the second negative feedback can be introduced by addition of $[Fe(CN)_6]^{4-}$ to the H_2O_2–HSO_3^-–HCO_3^- oscillatory system, which opens another channel for H^+ consumption [eqn. (5′)].

$$2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \rightarrow 2[Fe(CN)_6]^{3-} + 2H_2O \qquad (5')$$

Addition of $[Fe(CN)_6]^{4-}$ may be regarded as creating a combination of two pH oscillators having the same positive feedback since the $[Fe(CN)_6]^{4-}$–H_2O_2–HSO_3^- system itself is an oscillatory one characterized by low frequency (2–3 periods h^{-1}).[9] The route to chaotic pH responses can be measured as a result of the interactions of the two frequencies (20 and 2 periods h^{-1}) (Fig. 3). With two negative feedback channels, chaotic behaviour exists in a surprisingly wide range of flow rate both in the experiments [$k_0 = (3.1–4.4) \times 10^{-4}$ s^{-1}. However, within this range, double and triple period oscillations are also measurable at certain flow rate values under the conditions given in Fig. 3] and in the calculations. Of course, quantitative agreement between the simulated and measured curves is not expected primarily because the kinetics of reaction (5′) are not so simple as assumed in (R_5). In addition to the period doubling route revealed both in the calculations and in the experiments, other chaos-identifying data transformations (*e.g.* next return map) are also supportive, suggesting that the system exhibits true deterministic chemical chaos. Note that this mode of chaos is light-sensitive which offers an opportunity for photoregulation. Further study on the system is now under way in our laboratories.

This work was supported by the Hungarian Science Foundation (OTKA T14440) and the Japan Society for Promotion of Science.

References

1 L. F. Olsen and H. Degn, *Nature*, 1977, **267**, 177.
2 R. A. Schmitz, K. R. Graziani and J. L. Hudson, *J. Chem. Phys.*, 1977, **67**, 3040.
3 M. Orbán and I. R. Epstein, *J. Phys. Chem.*, 1982, **86**, 3907.
4 M. Alamgir and I. R. Epstein, *Int. J. Chem. Kinet.*, 1985, **17**, 429.
5 J. C. Doona and S. I. Doumbouya, *J. Phys. Chem.*, 1994, **98**, 513.
6 Gy. Rábai, M. Orbán and I. R. Epstein, *Acc. Chem. Res.*, 1990, **23**, 258.
7 M. Eigen, W. Kruse, G. Maass and L. De Maeyer, *Prog. React. Kinet.*, 1964, **2**, 285.
8 D. M. Kern, *J. Chem. Educ.*, 1960, **37**, 14.
9 Gy. Rábai, K. Kustin and I. R. Epstein, *J. Am. Chem. Soc.*, 1989, **111**, 3870.
10 W. A. Jaeschke and G. J. Herrmann, *ACS Symp. Ser.*, 1987, **349**, 142.
11 C. Drexler, H. Elias, B. Fecher and K. J. Wannowius, *Ber. Bunsenges. Phys. Chem.*, 1992, **96**, 481.

Received, 3rd July 1996; Com. 6/04639H