

Temperature compensation in the oscillatory hydrogen peroxide–thiosulfate–sulfite flow system

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Received (in Cambridge, UK) 13th August 1999, Accepted 23rd August 1999

A simple controlling mechanism assuming reasonable activation energies for the reaction steps is used to simulate temperature compensation of the period length of the large amplitude sustained pH oscillations observed experimentally in a H_2O_2 – $\text{S}_2\text{O}_3^{2-}$ – SO_3^{2-} – H^+ aqueous flow reaction system under optimized conditions.

The period length of the rhythm in many biological clocks is largely unaffected by temperature changes which occur in a certain physiological range.^{1–3} This behavior is called temperature compensation, and it is very important for the correct timing of numerous periodic processes (for example, light and dark periods in photoperiodic responses) that would be, by and large, independent of environmental factors such as, for example, temperature. Such behavior is in contrast to that observed in chemical oscillators where an increase in temperature leads generally to a significant increase in the frequency,^{4–6} since all the composite reactions accelerate as expected from the Van't Hoff's rule. An old unanswered question is whether temperature compensation is confined to circadian and ultradian rhythms, or whether homogeneous chemical oscillators may be able to act similarly.⁷

According to recent theoretical considerations, temperature compensation can be obtained in simple oscillator models, such as the Brusselator,⁷ the Oregonator,⁸ or the Goodwin model.⁹ The theory states that temperature compensation in a reaction kinetic network requires an appropriate balance in activation energy-weighted rate constant sensitivities between opposing processes. In order to find experimental evidence for the theory, we have studied the temperature sensitivity of several pH oscillators¹⁰ and found that a recently designed H_2O_2 – $\text{S}_2\text{O}_3^{2-}$ – SO_3^{2-} – H^+ system¹¹ exhibited temperature compensation under certain conditions.

In our experiments, we used a water-jacketed cylindrical-shaped glass vessel with a liquid volume of 12.5 ml as a continuous-flow stirred tank reactor (CSTR). The CSTR was equipped with a Horiba electrode to measure the pH and the temperature inside the reactor. The time–pH data were collected by a computer through a pH meter and an A/D converter with a sampling rate of 1 Hz. A 1.0 cm long Teflon-covered stirrer bar was used to ensure uniform mixing. Two input solutions were prepared daily: one contained 0.0270 M H_2O_2 , the other contained all the remaining components, such as 0.010 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.0040 M Na_2SO_3 and 5.0×10^{-4} M H_2SO_4 , together. The input solutions were kept from air to avoid any effect of O_2 and CO_2 . The reactor was fed with these solutions by means of an EYELA peristaltic pump. The mixing ratio was 1.0:1.0, so the input concentrations in the combined feed were half of those in the input solutions.

Our first task was to determine the temperature range where regular pH oscillations were exhibited. Shown in Fig. 1 is a state diagram spanned in the normalized flow rate (k_0)– T plane. The range of oscillations is rather narrow at low k_0 values. It is shifted to the higher temperatures and widens significantly as k_0 increases. At $k_0 = 4.0 \times 10^{-3} \text{ s}^{-1}$ the range is as wide as 10 °C.

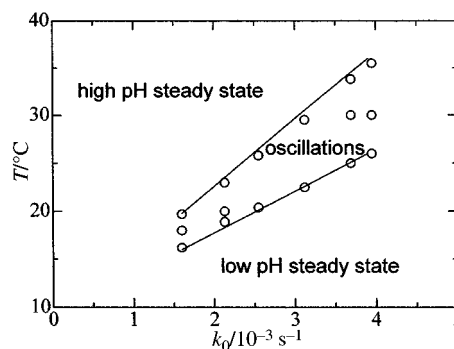


Fig. 1 Measured state diagram in the k_0 – T plane. Input concentrations: $[\text{H}_2\text{O}_2]_0 = 0.0135$, $[\text{S}_2\text{O}_3^{2-}]_0 = 0.0050$, $[\text{SO}_3^{2-}]_0 = 0.0020$, $[\text{H}^+]_0 = 5.0 \times 10^{-4}$ M. k_0 is the reciprocal residence time in the CSTR.

Above and below the oscillatory region a high pH steady state (pH 8–9) and a low pH steady state (pH 4–5.5) exist, respectively. Inside the oscillatory region, the amplitudes were found to decrease gradually with increasing temperature as the upper border was approached. Transition to the low pH steady state with decreasing temperature was sharp. The system behavior became chaotic at low flow rates.¹¹ Here we attempted to avoid such behavior so we kept the flow rate relatively high.

Secondly, we studied the period length of the sustained oscillations as a function of temperature in the disclosed range. An average period length was calculated in minutes for each temperature on the basis of a long run containing at least 20 periods. Reproducibility of the period length was within 6%. As shown in Fig. 2, period length turned out to be remarkably constant throughout the temperature range of oscillations at a fixed flow rate and input concentrations. Some significant deviation from the average period was measured along the borders of the oscillatory region. The pH amplitude and the waveform were altered by temperature changes. The most striking effect was that the high pH stage of a period appeared

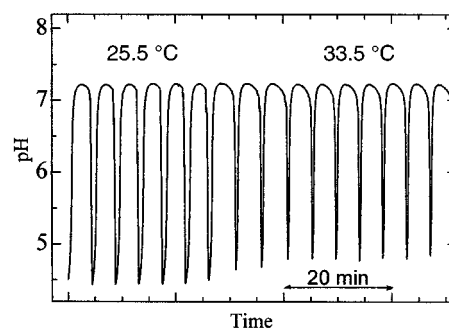


Fig. 2 Measured temperature compensation. Average period lengths at 25.5 and 33.5 °C are 4.45 and 4.41 min, respectively. Input concentrations as in Fig. 1, $k_0 = 3.60 \times 10^{-3} \text{ s}^{-1}$.

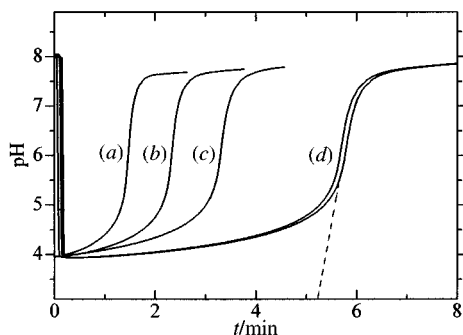
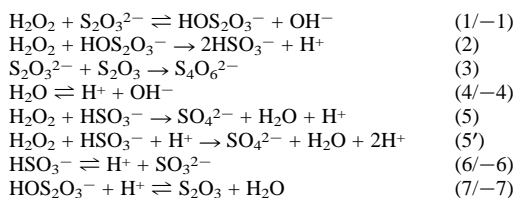


Fig. 3 Measured time-pH traces at (a) 36.0, (b) 30.0 (c) 26.0 and (d) 20.0 °C in a closed system. Double curve (d) shows the reproducibility. Initial concentrations: $[\text{H}_2\text{O}_2]_0 = 0.0135$, $[\text{S}_2\text{O}_3^{2-}]_0 = 0.0050$, $[\text{H}^+]_0 = 5.0 \times 10^{-4}$, $[\text{SO}_3^{2-}]_0 = 0.0020$ M. Dashed line shows how the induction time was determined for the estimation of an apparent activation energy.

to be longer, and the low pH stage become shorter, with increasing temperature. As a result the average period length remained constant (Fig. 2). At $k_0 = 3.90 \times 10^{-3} \text{ s}^{-1}$, we measured the following average periods at different temperatures: 3.52 min (26.0 °C), 3.54 min (28.6 °C), 3.63 min (31.7 °C), and 3.40 min (35.8 °C). We can conclude that in the range 26.0–35.8 °C, complete temperature compensation has been achieved. Similar behavior was measured in the case of other fixed k_0 values inside the oscillatory region, but the period length decreased with increasing flow rate. On the other hand, however, it is surprising that the dynamical behavior exhibited extreme temperature sensitivity under other experimental conditions. For example, at $[\text{H}_2\text{O}_2]_0 = 0.0070$, $[\text{S}_2\text{O}_3^{2-}]_0 = 0.0050$, $[\text{SO}_3^{2-}]_0 = 0.020$, $[\text{H}^+]_0 = 0.0010$ M, and $k_0 = 5.56 \times 10^{-4} \text{ s}^{-1}$ an interesting period doubling route from large amplitude regular oscillations through alternating small and large amplitudes (P2) to chaos could be observed as the temperature gradually changed from 25.0 through 24.0 to 22.0 °C, respectively.

We studied the effect of temperature on the kinetics in a closed reactor where no oscillations take place. Typical pH-time curves are presented in Fig. 3 where a sudden drop followed by an S-shaped increase in the pH is seen. An apparent activation energy, characteristic of the overall reaction rate, $E_a = 67.0 \text{ kJ mol}^{-1}$ could be determined by extrapolating the steepest section of the increasing part of the pH-time curves to the time axis and plotting the logarithm of the reciprocal intercept against $1/T$. Such a value of E_a suggests a usual temperature dependence indicating that the temperature compensation of the oscillatory frequency found in the CSTR does not result from an unusually small temperature sensitivity of the system. A special control mechanism must instead be responsible for the behavior.

We carried out numerical simulations on the basis of the mechanism¹¹ shown in Scheme 1 to see whether it could be responsible for the temperature compensation. Mass action kinetics laws for steps (1)–(7) were taken into account. Two sets of estimated rate constant values were assigned for 26 and 36 °C (Table 1) and were used to simulate oscillations with a semi-implicit Runge Kutta method. Activation energies of the composite reactions were chosen to fall into a chemically reasonable range (25–92 kJ mol). The calculated periods are



Scheme 1

Table 1 Estimated activation energies and rate constants for 26 and 36 °C

Step	$E_i/\text{kJ mol}^{-1}$	k_i^{26}	k_i^{36}	Units
(1)	56.8	0.030	0.063	$\text{M}^{-1} \text{ s}^{-1}$
(-1)	36.0	5.0×10^3	8.0×10^3	$\text{M}^{-1} \text{ s}^{-1}$
(2)	92.2	0.015	0.05	$\text{M}^{-1} \text{ s}^{-1}$
(3)	61.2	9.0	20.0	$\text{M}^{-1} \text{ s}^{-1}$
(4)	31.0	8×10^{-4}	1.2×10^{-3}	$k_4 [\text{H}_2\text{O}] \text{ M s}^{-1}$
(-4)	31.0	8×10^{10}	1.2×10^{11}	$\text{M}^{-1} \text{ s}^{-1}$
(5)	31.0	8.0	12.0	$\text{M}^{-1} \text{ s}^{-1}$
(5')	34.2	1.6×10^7	2.5×10^7	$\text{M}^{-2} \text{ s}^{-1}$
(6)	75.1	3.0×10^3	8.0×10^3	s^{-1}
(-6)	25.8	5.0×10^{10}	7.0×10^{10}	$\text{M}^{-1} \text{ s}^{-1}$
(7)	25.8	1.5×10^3	2.1×10^3	$\text{M}^{-1} \text{ s}^{-1}$
(-7)	67.1	0.025	0.060	s^{-1}

almost the same for both sets of rate constants. Calculated oscillations at °C are preceded by an hour long induction period. Calculations were carried out with $k_0 = 3.9 \times 10^{-3} \text{ s}^{-1}$. Both the calculated amplitudes and waveforms resemble their experimental counterparts. Low and high pH steady states could also be reproduced with simulations.

Differences in activation energies of the composite reactions seem to be important for temperature compensation by this mechanism. The length of the neutral region (pH ca. 7) of a period is determined by the time required for the consumption of SO_3^{2-} , since SO_3^{2-} is produced in steps (2) (92.2 kJ mol⁻¹) and (6) (75.1 kJ mol⁻¹) with high activation energies and consumed in steps (-6) (25.8 kJ mol⁻¹), (5) (31.0 kJ mol⁻¹) and (5') (34.2 kJ mol⁻¹) with low activation energies, its production rate increases more rapidly with temperature than its consumption rate, causing an increase in its average lifetime. As a result, the length of the neutral stage increases with temperature. At the same time, the length of the low pH stage decreases with increasing temperature, as expected from the curves in Fig. 3. The two opposite changes compensate each other under certain conditions leading to constant periods at different temperatures.

In conclusion, a simple chemical system is presented which exhibits temperature compensation in its oscillatory frequency in a CSTR. We found that a mechanism proposed earlier¹¹ can account for such behavior. We suspect that temperature compensation may be found in other pH oscillators with similar mechanism. It remains to be seen whether pH oscillators with such behavior can provide any reasonable guide to the control mechanism of biological clocks. However, the reversibility of some composite processes may be a common feature of chemical and biological temperature compensation.

Financial support was obtained from the Hungarian Science Foundation (OTKA 25076) and from the Japan Society for Promotion of Science.

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