A General Model for pH Oscillators[1]

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Abstract: A four-variable, five-reaction model is proposed for the family of pH oscillators. All major characteristics of these systems, both those observed in experiments and those found in mechanistic studies, are well represented by the model. The model can be further reduced to two smaller versions. In addition to the characteristic pH oscillation, a broad range of bistability is found in one of the reduced versions. The most important feature, which is common to the three versions, but distinct from other oscillatory models, is the role of the fast protonation–deprotonation equilibrium in generating oscillation. This step plays a role both in the autocatalysis and in the negative feedback. Nine pH oscillators are discussed and explained on the basis of these models.

Introduction

The family of pH oscillators[3] consists of those oscillating chemical reactions in which there is a large amplitude change in the pH and in which the pH change is an important driving force rather than merely a consequence or an indicator of the oscillation. Oscillation in a pH oscillator is suppressed when the system is buffered. Other systems that display small-amplitude pH oscillation when buffered or unbuffered are not true pH oscillators.

The first pH oscillator, the reaction of hydrogen peroxide and sulfide ion,[4] was discovered only 5 years ago, but the number of pH oscillators has grown rapidly.[3] Several pH oscillators have been characterized mechanistically,[5-9] with the mixed Landolt or EOE reaction of iodate, sulfite, and ferrocyanide[5] and its bromate analogue[6] being the most thoroughly studied. In a recent attempt to develop a mechanistically based classification of chemical oscillators,[10] these latter systems played a major role in the analysis.

In analyzing mechanisms for the mixed Landolt system, we pointed out[10] that H^+ plays the role of driving force in the following way. On the one hand, H^+ participates in a protonation–deprotonation equilibrium of one of the input species. The protonated (or hydroxylated) form of that species then takes part in a subsequent positive feedback process, in which H^+ is autocatalytically produced. The equilibrium constitutes a supplementary autocatalysis: the production of H^+ shifts the equilibrium in the direction (toward HSO_3^- in the mixed Landolt system, for example) that favors further H^+ production. On the other hand, after the positive feedback has run its course and most of the input species have been consumed, the replenishment of the input in its nonreactive form (SO_3^{2-} in the mixed Landolt system) returns $[H^+]$ to its initial low level through the same equilibrium. This drastic fall of $[H^+]$ provides the delay essential to oscillation by retarding the next pulse of positive feedback until all the components are fully replenished. Thus, the equilibrium also provides a source of negative feedback.

On the basis of this analysis,[10] we extracted a skeleton model consisting of four variables and five reactions from the detailed mechanism proposed for the BrO_3^-–SO_3^{2-}–$Fe(CN)_6^{4-}$ reaction. To supplement that qualitative study, extensive calculations are carried out here. The results show that the model, with all parameters taken from the full mechanism, does oscillate with all major features of the real system retained. We discuss further simplifications that demonstrate more clearly that the negative feedback supplied by the protonation equilibrium is sufficient to generate oscillatory behavior. Our analysis shows why all IO_3^- (BrO_3^-)–SO_3^{2-}-reductant systems require a second reductant to consume H^+ in order to oscillate. The model can be reduced further to a simpler version containing only three variables and three reactions. Even in this simplest form, the model remains a valid representation of several actual pH oscillators.

Table I. Mechanism for the Bromate–Sulfite–Ferrocyanide Oscillator[6]

$BrO_3^- + HSO_3^-$	→	$HBrO_2 + SO_4^{2-}$	(B1)
$HBrO_2 + Br^- + H^+$	→	$2HOBr$	(B2)
$HOBr + Br^- + H^+$	→	$Br_2 + H_2O$	(B3)
$Br_2 + H_2O$	→	$HOBr + Br^- + H^+$	(B4)
$2HBrO_2$	→	$BrO_3^- + HOBr + H^+$	(B5)
$Br_2 + HSO_3^- + H_2O$	→	$2Br^- + SO_4^{2-} + 3H^+$	(B6)
$H^+ + SO_3^{2-}$	→	HSO_3^-	(B7)
HSO_3^-	→	$H^+ + SO_3^{2-}$	(B8)
$BrO_3^- + 2Fe(CN)_6^{4-} + 3H^+$	→	$HBrO_2 + 2Fe(CN)_6^{3-}$	(B9)

The Model

Both the oscillatory behavior and the bistability found in the bromate–sulfite–ferrocyanide oscillator are well described by the mechanism[6] (B1–B9) shown in Table I. From this mechanism, we abstracted a four-variable skeleton model[10] to account for the major dynamical features of the system:[11]

$$X + H \rightleftarrows HX \tag{E1}$$

$$A + HX + H \rightarrow Y \tag{E2}$$

$$HX + Y \rightarrow 3H \tag{E3}$$

$$Y \rightarrow P \tag{E4}$$

$$B + H \rightarrow Q \tag{E5}$$

Here, H corresponds to H^+, X to SO_3^{2-}, and HX to the more reactive form HSO_3^-. Step E1 represents the sulfite protonation equilibrium, i.e., reactions B7 and B8 of the full mechanism. The next two equations, E2 and E3, depict the autocatalysis. We may view them as a summary of (B1–B6), with A as BrO_3^- and Y as one or more of the intermediates, such as $HBrO_2$, HOBr, or Br_2. The presence of H in (E2) reflects the participation of H^+ in the termolecular steps (B2) and (B3). The stoichiometric factor of 3 in (E3) is not simply adopted from (B6), but rather constitutes a minimum number of H^+ ions required to be formed for autocatalysis, since two H's are consumed in the prior steps (E1) and (E2). Reaction E4 serves to deplete the intermediate Y faster

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[1] Systematic Design of Chemical Oscillators. 69. Part 68: Doona, C. J.; Kustin, K. Submitted for publication.

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[3] Rābai, Gy.; Orbān, M.; Epstein, I. R. *Acc. Chem. Res.* **1990**, *23*, 258.

[4] Orbān, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1985**, *107*, 2302.

[5] Edblom, E. C.; Orbān, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 2826.

[6] Edblom, E. C.; Luo, Y.; Orbān, M.; Kustin, K.; Epstein, I. R. *J. Phys. Chem.* **1989**, *93*, 2722.

[7] Edblom, E. C.; Györgyi, L.; Orbān, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 4876.

[8] Gāspār, V.; Showalter, K. *J. Am. Chem. Soc.* **1987**, *109*, 4869.

[9] Luo, Y.; Epstein, I. R. *J. Phys. Chem.* **1989**, *93*, 1398.

[10] Luo, Y.; Epstein, I. R. *Adv. Chem. Phys.* **1990**, *79*, 269. Note the change in notation between the model as presented in that work and here.

[11] A similar four-variable reduced model has been developed from an empirical rate law model for the related iodate–sulfite–ferrocyanide reaction by: Gāspār, V.; Showalter, K. *J. Phys. Chem.* **1990**, *94*, 4973.

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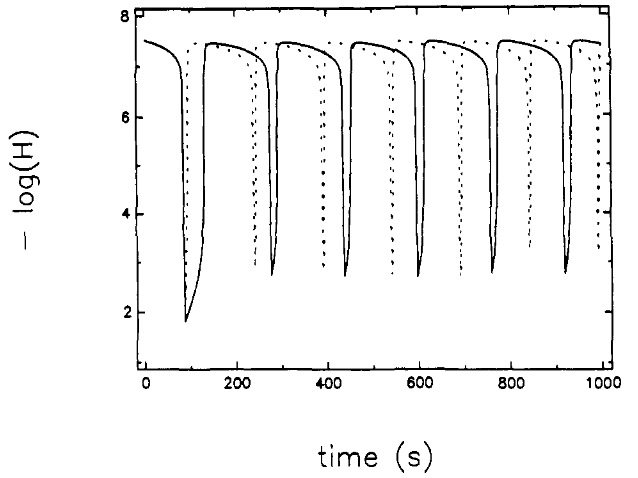

Figure 1. Oscillation with model E1–E5. Conditions: $[X]_0 = 6 \times 10^{-2}$ M; $[HX]_0 = 0.0$ M; $[H]_0 = 2 \times 10^{-2}$ M; $[Y]_0 = 0.0$ M; $[A] = 6.5 \times 10^{-2}$ M; $[B] = 2.0 \times 10^{-2}$ M; $k_0 = 10^{-3}$ s^{-1}; $k_{E1} = 5 \times 10^{10}$ M^{-1} s^{-1}; $k_{-E1} = 3 \times 10^3$ s^{-1}; $k_{E2} = 3.077 \times 10^6$ M^{-2} s^{-1}; $k_{E3} = 10^6$ M^{-1} s^{-1}; $k_{E4} = 11$ s^{-1}; $k_{E5} = 2.5$ M^{-1} s^{-1} (solid line), 30 M^{-1} s^{-1} (dotted line).

than by the simple flow, a role played by (B4) in the full mechanism if we identify Y primarily with Br_2. The last equation, E5, corresponds to (B9), with B as $2Fe(CN)_6^{4-}$ and Q as $2Fe(CN)_6^{3-}$.

The numerical calculations presented in the following text show that the high consumption of H^+ in (B9), which increases the power of the negative feedback, is not essential. We find that in some circumstances (E5) can even be eliminated, allowing us to reduce the model still further.

Results of Calculations

Rate equations for the four variables H, X, HX, and Y were constructed by applying the law of mass action to the skeleton model (E1–E5) with the reactant concentrations A and B held fixed. These equations were solved numerically by use of the GEAR package.[12] In analogy to the actual system, only X and H have nonzero inflow, while all the variables are allowed to flow out of the reactor. Values for the six rate constants, all initial and input concentrations, and the inverse residence time were extracted from experiments and/or from the full mechanism for the bromate–sulfite–ferrocyanide reaction wherever a clear correspondence could be made. Only minor modifications proved to be necessary for generating oscillatory behavior. For example, k_{B1} (divided by an estimate of $[H^+]$ during the relevant time interval—the induction period of the batch reaction) in the bromate–sulfite–ferrocyanide mechanism served as the starting point for k_{E2} in the model, since (B1) is the rate-determining step in the autocatalytic process (B1–B6).[6]

In Figure 1, we show a set of calculated oscillations whose waveform resembles those obtained with the full bromate–sulfite–ferrocyanide mechanism (B1–B9), though the four-variable model gives a much shorter period. By increasing k_{E5} ~1 order of magnitude, to 30 M^{-1} s^{-1}, we obtain oscillations with very sharp spikes (dashed line in Figure 1) similar to the behavior of the iodate–sulfite–ferrocyanide oscillator.[5] Thus, step E5, while not essential for oscillation, as we discuss further in the following text, plays a key role in determining the character of the oscillation.

Additional numerical experiments lead to the following general conclusions:

(1) The equilibrium constant for (E1) determines the value of [H] in the high flow rate steady state. When oscillation takes place, this value usually constitutes one of the boundaries of the oscillation in H.

(2) The lengths of the batch induction period and the oscillation period vary inversely with k_{E2}.

(3) In reaction E3, the species reacting with Y need not be HX. If HX is replaced by a reagent or intermediate whose formation is not accompanied by consumption of H, the number of H generated in (E3) can be lowered from 3 to 2, e.g.

$$C + Y \rightarrow 2H \qquad (E3')$$

(4) At a fixed k_{E4} in the oscillatory range, k_{E5} determines the width (sharpness) of the peaks, as demonstrated in Figure 1.

(5) Step E5 is not necessary for oscillatory behavior. It can be omitted when k_{E4} is sufficiently large (see the following text).

(6) As we show in the following reaction, when k_{E5} is large enough, the variable Y is no longer essential and can be eliminated by merging (E2), (E3), and (E4) into a single reaction.

$$A + HX + H \rightarrow nH \qquad n \geq 2 \qquad (E2')$$

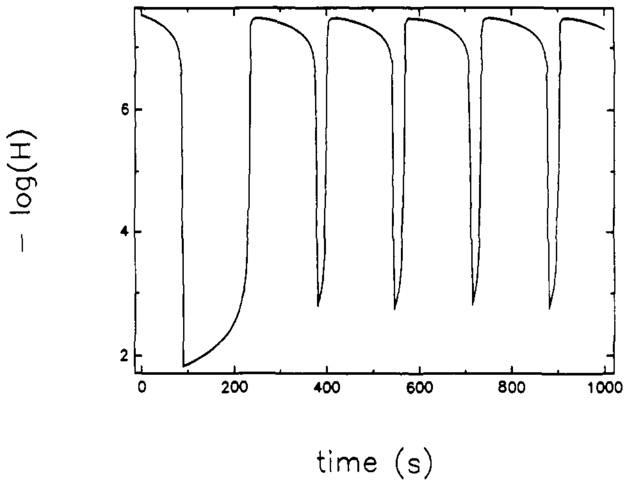

Figure 2. Oscillation with model E1–E4. Other conditions as in Figure 1. The first oscillation differs significantly from the subsequent cycles because the initial (feedstream) concentration differ from those found at the beginning of an oscillatory cycle. This effect is present, but less pronounced in Figures 1 and 4 as well.

Under batch conditions, the model behaves like a clock reaction, with an induction period that terminates in a sudden jump of several orders of magnitude in H followed by exponential decrease of H from its maximum. In the experimental bromate–sulfite–ferrocyanide system, the state corresponding to the batch maximum in H can be maintained as a stable steady state in a range of flow rates in a CSTR. Bistability occurs between this state and a low-H state that corresponds to the initial state of the batch reaction. In the model, the high-H steady state does not exist at any value of the flow rate. The reason is that B in (E5) has been treated as a constant, while in the actual system the corresponding species (ferrocyanide in the bromate–sulfite–ferrocyanide reaction) is consumed to a very low level when H is at or near its maximum. In one of the further simplified models treated in the next section, this problem does not arise, since (E5) has been eliminated. Bistability between high- and low-H steady states is then readily observed.

Further Simplifications

Elimination of (E5). If k_{E4} is sufficiently large, then, as shown in Figure 2, reaction E5 can be deleted with little effect on the oscillatory behavior. The smallest value of k_{E4} for which oscillations persist with the other parameters as in Figure 2 is 4.7 s^{-1}.

With this modification, it becomes possible for the high-H steady state to be stable at low flow rates. A typical hysteresis curve showing bistability between this new state and the high-flow, low-H state is shown in Figure 3.

The fact that the model oscillates without step E5 and species B suggests that the simple Landolt systems,[13] IO_3^-–SO_3^{2-} and BrO_3^-–SO_3^{2-}, might be able to oscillate as well as show bistability even in the absence of added $Fe(CN)_6^{4-}$. The reason why these systems are not oscillatory[5] appears to be that the products of the reactions corresponding to (E4) are not inert end products, but active intermediates in the positive-feedback process. Examples

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[12] Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice-Hall: Englewood Cliffs, NJ, 1971.

[13] Landolt, H. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 1317.

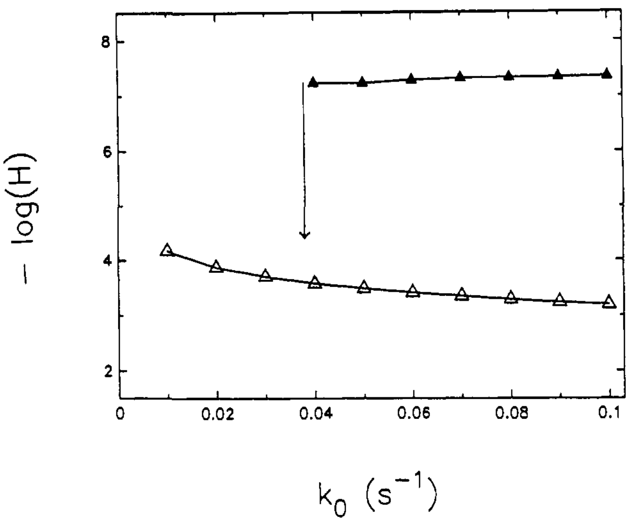

Figure 3. Bistability between steady states of low and high [H] with model E1–E4: $[X]_0 = 5 \times 10^{-2}$ M. Other conditions as in Figure 2. Vertical arrow indicates spontaneous transition from high-pH to low-pH steady state. Reverse transition occurs at $k_0 > 0.1$ s^{-1}.

of such products are HOBr (or Br^-) in step B4 (Table I) of the mechanism for the bromate–sulfite–ferrocyanide system and HOI (or I^-) in step M6 of the mechanism for the iodate–sulfite–ferrocyanide reaction[9] if we identify Y primarily with Br_2 and I_2 in the two systems, respectively.

$$I_2 + H_2O \rightarrow HOI + I^- + H^+ \qquad (M6)$$

Other systems may also be described by this reduced version of the model. One candidate is the sulfide–hydrogen peroxide reaction,[4] the first pH oscillator discovered in 1985. Although a mechanism has not yet been established, the proposed stoichiometric processes,[4] eqs 1–3, already contain the most important features of the simplified model.

$$S^{2-} + H^+ \rightleftharpoons HS^- \qquad (1)$$

$$HS^- + H_2O_2 + H^+ \rightarrow {}^1\!/_8S_8 + 2H_2O \qquad (2)$$

$${}^1\!/_8S_8 + 3H_2O_2 \rightarrow SO_4^{2-} + 2H^+ + 2H_2O \qquad (3)$$

If we identify S^{2-} with X, HS^- in HX, and ${}^1/_8S_8$ with Y, then eqs 1–3 are equivalent to eqs E1, E2, and E3′. The model suggests that the only other building block needed to make this system oscillate is a pathway that consumes S_8 without producing either H^+ or HS^-. One possibility is the formation of $S_2O_3^{2-}$ by the reaction between S_8 and HSO_3^-; bisulfite ion is an intermediate in the oxidation of elemental sulfur to sulfate ion.[4]

The mechanism of Edblom et al.[7] for the iodate–sulfite–ferrocyanide oscillator provides another example of a system describable by eqs E1–E4. Reactions R10–R13 of that mechanism yield the following stoichiometry

$$2Fe(CN)_6^{4-} + I_2 \rightleftharpoons 2Fe(CN)_6^{3-} + 2I^-$$

which can be viewed as a modified (E4)

$$B + Y \rightarrow P \qquad (E4')$$

No direct H^+-consuming (E5-type) step is invoked in that mechanism.

Elimination of the Variable Y. Numerical experimentation reveals that the four-variable model derived from the bromate (iodate)–sulfite–ferrocyanide mechanisms can be further reduced to a three-variable, three-reaction version, (E1), (E2′), and (E5), that preserves the major features of the oscillatory behavior of the mixed Landolt systems. Figure 4 shows oscillations calculated for this reduced model with the stoichiometric factor *n* in (E2′) taken to be 2 or 3. Since B is still held constant in (E5), the high-H steady state cannot be achieved.

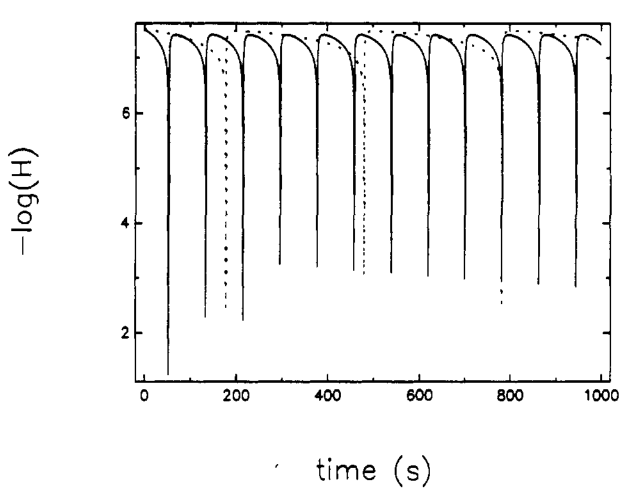

Figure 4. Oscillation with the simplified model (E1), (E2′), and (E5). Feed concentrations and flow rate as in Figure 1. Conditions: $k_{E1} = 5 \times 10^{10}$ M^{-1} s^{-1}, $k_{-E1} = 3 \times 10^3$ s^{-1}, $k_{E2} = 3.077 \times 10^8$ M^{-2} s^{-1}, $k_{E5} = 2.5 \times 10^2$ M^{-1} s^{-1}. *n* in (E2′) is 3 (solid line) and 2 (dotted line).

This version of the model not only facilitates dynamical analysis by reducing the number of variables but also provides a realistic characterization of at least one known oscillator, the H_2O_2–SO_3^{2-}–$Fe(CN)_6^{4-}$ reaction,[14] a derivative of the mixed Landolt system with H_2O_2 substituted for IO_3^- or BrO_3^-. The system is well described by the set of reactions 4–6.[14] The correspondence between eqs 4–6 and eqs E1, E2′, and E5 is established by identifying SO_3^{2-} with X, HSO_3^- with HX, H_2O_2 with A, and $2Fe(CN)_6^{4-}$ with B.

$$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^- \qquad (4)$$

$$H^+ + H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H_2O + 2H^+ \qquad (5)$$

$$2Fe(CN)_6^{4-} + H_2O_2 + 2H^+ \rightarrow 2Fe(CN)_6^{3-} + 2H_2O \qquad (6)$$

Individual Oscillators

We have shown that the two reduced versions of the pH oscillator model, eqs E1–E5, can describe several actual chemical oscillators. We now return to the full set of equations and demonstrate that it can elucidate the majority of the pH oscillator family, with minor variations necessary in some cases to account for special features.

Iodate–Sulfite–Thiourea.[15] Steps E1–E4 are the same as in the analogous Landolt system, with iodate and sulfite reactions accomplishing the positive-feedback process in which H^+ is produced autocatalytically. The reactive form of the reductant is again HSO_3^-. Thiourea plays the role of B, consuming H^+ either directly as in (E5) or indirectly by providing a non-H^+-producing reaction route for I_2 similar to that provided by ferrocyanide in the iodate–sulfite–ferrocyanide mechanism.[7] The latter route appears to be more likely, leading to the modified model (E1–E4) + (E4′).

Iodate–Sulfite–Thiosulfate. Again, the reactions of iodate and sulfite play the roles of (E1–E4). They are followed by the oxidation of thiosulfate, which consumes H^+ and is obviously of type (E5):[16]

$$IO_3^- + 6S_2O_3^{2-} + 6H^+ \rightarrow I^- + 3S_4O_6^{2-} + 3H_2O \qquad (7)$$

The treatment just presented gives only a partial description of this reaction, since this system shows damped oscillation in batch conditions. We discuss the necessary modification to account for this behavior in the following text.

Rābai and Beck[16b] suggested a simplified model, eqs 8–10, to represent their proposed mechanism, with IO_3^- as A, $S_2O_3^{2-}$ and B, and HSO_3^- as HX.

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(14) Rābai, Gy.; Kustin, K.; Epstein, I. R. *J. Am. Chem. Soc.* **1989**, *111*, 3870.

(15) Rābai, Gy.; Nagy, Zs.; Beck, M. T. *React. Kinet. Catal. Lett.* **1987**, *33*, 23.

(16) (a) Rābai, Gy.; Beck, M. T. *J. Phys. Chem.* **1988**, *92*, 2804. (b) Rābai, Gy.; Beck, M. T. *Ibid.* 4831.

$$A + B \rightarrow HX \tag{8}$$

$$A + B + H \rightarrow P_1 \tag{9}$$

$$A + HX + H \rightarrow 2H + P_2 \tag{10}$$

Equation 8 corresponds to the stoichiometric process (11)

$$2IO_3^- + 3S_2O_3^{2-} + 3H_2O \rightarrow 2I^- + 6HSO_3^- \tag{11}$$

The model neglects a key feature of the full mechanism: HX in eqs 8–10 has only reaction 8 as its source. Thus, only the consumption of HX, not its formation, is affected by [H]. In contrast, HX's counterpart in the mechanism, HSO_3^-, derives primarily from the fast protonation of SO_3^{2-}, a continuously input reagent, and its rate of formation is therefore strongly affected by the autocatalytic species H^+.

Although we take issue with the choice of a skeleton model for this system, we do not question the plausibility of reaction 11. This additional production of HSO_3^- undoubtedly accelerates the positive-feedback process and makes the batch reaction more complex than a typical clock reaction like the subsystem IO_3^-–SO_3^{2-}. It plays a crucial role in generating the damped batch oscillations, given an appropriate molar ratio of the inputs,[16] by providing a means to replenish HSO_3^- after its consumption in the autocatalytic process. Equations E1–E5 and 8 should reproduce the nonmonotonic batch behavior with an appropriate choice of k_8.

Periodate–Thiosulfate.[17] The composition of this system suggests that it has little relation to the systems discussed previously. However, if we focus on the dynamics, a clear connection to the bromate–sulfite–reductant systems via the model (E1–E5) can be recognized. The initial products of the reaction (12)

$$2IO_4^- + S_2O_3^{2-} + H_2O \rightarrow 2IO_3^- + 2SO_3^{2-} + 2H^+ \tag{12}$$

between the input species are mainly IO_3^- and SO_3^{2-} (in equilibrium with HSO_3^- depending on pH). When these products accumulate to a sufficient level, the autocatalytic production of H^+ by the iodate–bisulfite reaction becomes the dominant process. Two processes were proposed[17] to account for the direct H^+ consumption (i.e., step E5) that leads to the final products at sufficiently low pH:

$$IO_4^- + 8S_2O_3^{2-} + 8H^+ \rightarrow 4S_4O_6^{2-} + I^- + 4H_2O \tag{13}$$

$$IO_3^- + 6S_2O_3^{2-} + 6H^+ \rightarrow 3S_4O_6^{2-} + I^- + 3H_2O \tag{14}$$

Since eq 12 may replace the inflow as a continuous source of the reactants for oscillation, the mechanism suggests that this system may be able to exhibit nonmonotonic behavior in batch under appropriate conditions. Such behavior has actually been observed experimentally.[17] To adapt model E1–E5 to fit this system, only a simple reaction that produces X is needed to replace the influx of X in the original model.

Periodate–Hydroxylamine. This system has two distinct modes of oscillation, one with large amplitude and short period and the other with small amplitude but substantially longer period.[18,19] For the former, preliminary calculations[18] using an empirical rate law model show oscillations but do not give a satisfactory description of the shape and the period of the observed pH oscillation. Here, we offer a suggestion of an improved mechanism based on our model. Detailed numerical calculations are in progress.

First, we must distinguish two limiting cases:

(1) NH_2OH is in large excess ($[NH_2OH]_0/[IO_4^-]_0 > 4$). The following reactions are consistent with the observed stoichiometry[18]

$$IO_4^- + NH_3OH^+ \rightarrow IO_3^- + NOH + H_2O + H^+ \tag{15}$$

$$IO_3^- + NH_3OH^+ \rightarrow HIO_2 + NOH + H_2O \tag{16}$$

$$HIO_2 + NH_3OH^+ \rightarrow HOI + NOH + H_2O + H^+ \tag{17}$$

$$HOI + NH_3OH^+ \rightarrow I^- + NOH + H_2O + 2H^+ \tag{18}$$

$$2NOH \rightarrow N_2O + H_2O \tag{19}$$

$$IO_4^- + 4NH_3OH^+ \rightarrow I^- + 2N_2O + 6H_2O + 4H^+ \tag{20}$$

where (20) = (15) + (16) + (17) + (18) + 2(19). No NO_2^-, NO_3^-, or I_2 was detected under these conditions.[18]

(2) IO_4^- is in large excess ($[IO_4^-]_0/[NH_2OH]_0 > 3$). Reactions 21–23 give the observed intermediates and end products as well as the correct stoichiometry[18]

$$IO_4^- + NH_3OH^+ \rightarrow IO_3^- + NOH + H_2O + H^+ \tag{21}$$

$$IO_4^- + NOH \rightarrow IO_3^- + NO_2^- + H^+ \tag{22}$$

$$IO_4^- + NO_2^- \rightarrow IO_3^- + NO_3^- \tag{23}$$

$$3IO_4^- + NH_3OH^+ \rightarrow 3IO_3^- + NO_3^- + H_2O + 2H^+ \tag{24}$$

where (24) = (21) + (22) + (23). No I^-, I_2, or N_2O was found in these circumstances.[18]

In the fast oscillation, $[NH_2OH]_0/[IO_4^-]_0 = 2$–$3$. The stable species I^-, I_2, NO_2^-, and NO_3^- are all detected in the reaction mixture. In addition to eqs 15–24, several cross reactions between intermediates of the two limiting processes must be taken into account. In the following mechanism for the fast oscillation, the stepwise reactions, eqs 15–19 and eqs 21–23, are represented by their stoichiometric eq 20 and 24, respectively. This is clearly an (E1) + (E2′) + (E5) type pH oscillator, with both eqs 20 and 24 corresponding to (E2′).

$$NH_2OH + H^+ \rightleftharpoons NH_3OH^+ \tag{25}$$

$$IO_4^- + 4NH_3OH^+ \rightarrow 2N_2O + I^- + 6H_2O + 4H^+ \tag{20}$$

$$3IO_4^- + NH_3OH^+ \rightarrow NO_3^- + 3IO_3^- + H_2O + 2H^+ \tag{24}$$

$$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O \tag{26}$$

The slow oscillation in this system, with periods of several hours in contrast to a few minutes for the fast mode, occurs when NH_2OH is in even greater excess.[19] This mode of oscillation is very similar to the only oscillatory mode observed in the iodate–hydroxylamine reaction, for which an empirical rate law mechanism gives good agreement with the experimental observations.[19] We analyze this latter system in more detail in the following text, since it is an interesting example that shows how different kinds of driving forces can be mixed together.

Iodate–Hydroxylamine. The proposed mechanism[19] is

$$NH_2OH + H^+ \rightleftharpoons NH_3OH^+ \tag{27}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{28}$$

$$3NH_3OH^+ + IO_3^- \rightarrow 3NOH + I^- + 3H_2O + 3H^+ \tag{29}$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \tag{30}$$

$$NH_3OH^+ + I_2 \rightarrow NOH + 2I^- + 3H^+ \tag{31}$$

$$2NOH \rightarrow N_2O + H_2O \tag{32}$$

$$NH_2OH + NOH \rightarrow N_2 + 2H_2O \tag{33}$$

$$I_2(aq) \rightarrow I_2(gas) \tag{34}$$

These reactions are overall stoichiometric processes rather than elementary steps, and reaction 31 in particular has an unusually complicated rate law,[20] eq 35, showing strong inhibition by I^- and H^+.

$$\text{rate} = \frac{(k + k'/[H^+])[NH_3OH^+][I_2]}{1 + k''[I^-] + Q[I^-]^2 + Q'[IO_3^-] + Q''[I^-][IO_3^-]} \tag{35}$$

Again, the protonated hydroxylamine is the reactive species in most of the reactions, especially in the ones that compose the positive feedback that produces H^+ autocatalytically. Thus, the equilibrium (27) plays a major role in the positive feedback. In fact, if we ignore the complex rate law of eq 31, the whole pos-

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(17) Rābai, Gy.; Beck, M. T.; Kuslin, K.; Epstein, I. R. *J. Phys. Chem.* **1989**, *93*, 2853.

(18) Rābai, Gy.; Epstein, I. R. *J. Phys. Chem.* **1989**, *93*, 7556.

(19) Rābai, Gy.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 6361.

(20) Rābai, Gy.; Beck, M. T. *J. Chem. Soc., Dalton Trans.* **1982**, 573.

itive-feedback sequence, reactions 27 and 29–31, is closely analogous to that in the IO_3^-–SO_3^{2-}–$Fe(CN)_6^{4-}$ mechanism[7] with NH_3OH^+ substituted for HSO_3^-. The negative-feedback pathways of the two systems are quite different, however. Reactions 32 and 33 are necessary to give the correct stoichiometry but contribute little to the dynamics. Reaction 34 can be viewed as an ideal example of step E4 in the model (E1–E5). Iodine, the key intermediate in the autocatalysis, reactions (30) + 3(31), is converted in this step to an inert form.

If there were no further complications, this system would be another (E1–E4)-type pH oscillator. The special feature of the negative feedback in this system, however, lies in the rate law for reaction 31, i.e., eq 35. The strong inhibition by $[I^-]$ after its autocatalytic production, which accompanies that of H^+, is strikingly similar to the "coproduct autocontrol" type of negative feedback found in the Oregonator.[10] Therefore, this system is more than a pure pH oscillator. Nevertheless, as we have seen, the pH oscillator model still serves as a useful starting point in analyzing the mechanism. Both the inhibition by IO_3^- in eq 35 and the volatilization of I_2 in reaction 34 retard the positive feedback and contribute to the unusually lengthy oscillation period.

Discussion

Experimental and theoretical perspectives of this new group of chemical oscillators are summarized in a recent review,[3] where the characteristic behavior that distinguishes the pH oscillators from other systems, i.e., the existence of large-scale pH oscillation and the role of H^+ as the major driving force, is pointed out. The pH oscillators are thus the first family of chemical oscillators that is classified according to common behavior rather than common components.

In that review,[3] an attempt is made to characterize several pH oscillators with an expanded Lotka model. This choice is only partially successful, because it fails to take into account that the fast protonation–deprotonation equilibrium between the reactive and nonreactive species implements part of the positive feedback, in that the more H^+ is produced in the course of the reaction, the more of the reactive, protonated species is available to accelerate the reaction. This equilibrium also serves as the key part of the negative feedback by taking up almost all the H^+ when the nonreactive, deprotonated species flows in, thereby inhibiting the autocatalytic H^+-producing process.

We emphasize that the equilibrium is significant in the negative feedback only when reaction E2 or E2′ contains H on its left-hand side. Otherwise, the decrease in H cannot effectively reduce the rate of the autocatalysis. This inhibition is critical in providing sufficient time delay (phase shift) between the two major processes for the sharp oscillations commonly seen in pH oscillators. If (E2) + (E3) (or (E2′)) is not a self-contained autocatalytic process, i.e., if no H appears on its left-hand side, the system may still be able to oscillate, with the activation of one of the components through the equilibrium being more important in the positive feedback but much less so in the negative feedback. In systems of this type, other reactions, e.g., high-order consumption of H, may be necessary. One such example is the IO_4^-–NH_2OH system,[18] where the shape of the calculated oscillation (dashed line in Figure 3, ref 18) is quite different from that of typical pH oscillators.

The models discussed in this work have successfully described the common features in the mechanisms of nine pH oscillators. Two other systems, hydrogen peroxide–ferrocyanide[21] and hydrogen peroxide–thiosulfate–copper(II),[22] have not been treated here. Because of the involvement of radicals, these systems have their own special behaviors in addition to oscillation in pH, such as the photosensitivity of the H_2O_2–$Fe(CN)_6^{4-}$ reaction[21] and the complex shape of the pH oscillation found in the $S_2O_3^{2-}$–H_2O_2–Cu(II) system.[22] Therefore, their mechanisms are expected to diverge from our basic model for systems in which the pH change serves as the dominant driving force.

In all the examples we have treated, the role of H in the model is played by H^+. However, there is no a priori reason why OH^- cannot serve equally well. Calculated oscillations in pH have been obtained in a hypothetical system[23] based on a mechanism[24] for the reaction between a copper–triglycine complex and ethylenediaminetetraacetate ion, which is known to be autocatalytic in OH^-. Experimental studies are now under way.

Our model (E1–E5), including its various modifications, provides a general view of the family of pH oscillators. This new understanding should benefit both the experimental design of new pH oscillators and the mechanistic study of individual systems. This model and the recent work of Gâspâr and Showalter[11] on the EOE reaction[5] are the first to recognize that in an oscillatory system a fast equilibrium process may be a key part of the driving force. We hope this insight will prove useful in understanding not only chemical but biological oscillators as well. For example, in an early review of oscillatory reactions, Higgins[25] suggested a model for glycolysis in which an equilibrium reaction of a product with an inactive form of an enzyme yields an active form of that enzyme. Such a reaction is formally analogous to our key step (E1).

A similar skeleton model, the Oregonator[26] extracted from the FKN mechanism[27] for the BZ reaction, has played a major role in the development of nonlinear chemical dynamics. Although that simplified three-variable model cannot account for all the observed behavior of the BZ reaction, it has been extremely successful in providing (1) deeper and clearer insight into the nature and structure of the complex FKN mechanism, (2) a powerful tool for intensive dynamic analysis[28,29] using analytical methods that cannot be applied to systems of higher dimension, and (3) a guide in constructing mechanisms for new chemical oscillators.[30] Such skeleton models, including the Oregonator, have served as prototypes in efforts to develop a mechanistically based classification of chemical oscillators.[10,31] We anticipate that the model developed here will prove to have a similar significance for the new family of pH oscillators.

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(21) Rábai, Gy.; Kustin, K.; Epstein, I. R. *J. Am. Chem. Soc.* **1989**, *111*, 8271.
(22) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 101.
(23) Lengyel, I.; Kustin, K.; Epstein, I. R. Unpublished results.
(24) Dukes, G. R.; Pagenkopf, G. K.; Margerum, D. W. *Inorg. Chem.* **1971**, 410, 2419.
(25) Higgins, J. *Ind. Eng. Chem.* **1967**, *59*, 18.
(26) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.
(27) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
(28) Bar-Eli, K.; Noyes, R. M. *J. Chem. Phys.* **1987**, *86*, 1927.
(29) Gâspâr, V.; Showalter, K. *J. Chem. Phys.* **1988**, *88*, 778.
(30) Luo, Y.; Orbán, M.; Kustin, K.; Epstein, I. R. *J. Am. Chem. Soc.* **1989**, *111*, 4541.
(31) Eiswirth, M.; Freund, A.; Ross, J. Submitted for publication.