

Bistability in the Oxidation of Arsenite by Iodate in a Stirred Flow Reactor¹

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Abstract: The reaction between arsenite and iodate at 25 °C and pH 2.25 in a stirred tank reactor exhibits bistability over a range of flow rates and input arsenite and iodate concentrations. Observed steady-state I⁻ and I₂ concentrations and points of transition between bistable and unstable behavior are in excellent agreement with values calculated from a simple model consisting of three overall component processes: (A) IO₃⁻ + 3H₃AsO₃ = I⁻ + 3H₃AsO₄; (B) IO₃⁻ + 5I⁻ + 6H⁺ = 3I₂ + 3H₂O; (C) I₂ + H₃AsO₃ + H₂O = 2I⁻ + H₃AsO₄ + 2H⁺. Implications for the recently discovered arsenite-iodate-chlorite-oscillating reaction are discussed.

Studies of oscillating chemical reactions and related phenomena are of fundamental and rapidly increasing interest both because of the light they shed on the complexities of dynamic behavior possible for systems far from equilibrium and because they may provide experimentally tractable models for some of the endogenous rhythms observed in living systems. The ability of chemists to develop and test general theories of chemical oscillation has been hindered somewhat by the paucity of examples. In spite of intensive efforts in the last decade to design new oscillators, only two fundamentally different nonbiological, homogeneous oscillating reactions, the Bray-Liebhaftsky³ (B-L) and the Belousov-Zhabotinsky⁴ (B-Z) systems, have been characterized.

The array of known oscillators has been augmented by variations and hybrids of the above two reactions, as well as by systems of biological origin. Since oscillations in the B-L and B-Z systems were discovered serendipitously, it seems fair to summarize the techniques by which chemical oscillators have been found as (a) accident (the B-L and B-Z reactions), (b) variation on a theme (the uncatalyzed B-Z reaction,⁵ the Briggs-Rauscher reaction⁶), and (c) study of biological systems (glycolysis⁷). From the point of view of formulating general approaches to chemical oscillation, technique a is too unreliable, while b is unlikely to yield a sufficient variety of behavior, and the systems of type c tend to be both highly complex and difficult to monitor.

Although no necessary and sufficient set of conditions for the existence of chemical oscillations has been established, several factors are known to be either essential or helpful in producing oscillatory behavior. For example, oscillating chemical systems must be far from equilibrium and must contain an appropriate nonlinear coupling mechanism, the most common example of which is autocatalysis.⁸ It would seem that even such a rudimentary understanding as this might make it possible to construct systematically new chemical oscillators by combining known reactions under appropriate conditions.

In a recent communication (part 2¹), we proposed a systematic approach to the design of chemical oscillators and applied it successfully to generate a new homogeneous oscillating reaction involving arsenite, iodate, and chlorite. This system has since been found to be the prototype of a family of chemical oscillators involving iodate, chlorite, and a reducing agent which produces iodide from iodate and/or from iodine at a suitable rate.⁹

The approach used to generate these new oscillators starts with an autocatalytic reaction in a continuous-flow stirred tank reactor (CSTR). The autocatalysis constitutes the destabilizing nonlinear coupling mechanism, while the CSTR guarantees that the system is maintained far from equilibrium. We then make use of a simple dynamical model developed by Boissonade and De Kepper,¹⁰ which suggests that oscillations can result from the application of an appropriate feedback step to an intrinsically bistable system. The next step in the search for oscillation is to seek a reaction which

perturbs the stability of the two stable branches on a suitable time scale so as to generate oscillation.

The approach outlined above has at least two virtues. The model is sufficiently simple and general that, unlike more detailed models of chemical oscillation,¹¹⁻¹³ it can be applied directly to a wide range of reactions. Secondly, it splits the task of finding new oscillating systems into two more tractable subproblems, the discovery of bistable systems and the design of suitable feedback reactions.

In this paper we report a series of experiments on the behavior of acidic mixtures of arsenite and iodate in a CSTR. The system exhibits bistability over a significant range of input concentrations and flow rates. Similar results have also been obtained by Papsin et al.¹⁴ We show here that calculations with a simple model consisting of three overall reaction steps yield results in excellent agreement with our experiments. In further papers we shall present studies of other bistable systems as well as of the detailed coupling of the arsenite-iodate reaction with the chlorite-iodide system to generate oscillation.

Experimental Section

The apparatus consists of a thermally regulated stirred tank glass (Pyrex) flow reactor¹⁵ connected to a Sage Model 375A peristaltic pump which allows for one to four independent input flows. The constraints or variables controlled by the experimenter in this system are the temperature, which was maintained at 25.0 ± 0.1 °C in this series of experiments, the residence time τ , and the concentrations $[A_i]_0$ that each input species A_i would attain in the tank if no reaction took place. Measurements were made of the potential of an Orion iodide-specific electrode with respect to a mercury-mercurous sulfate reference electrode and of the absorbance at 460 nm, the wavelength of maximum absorbance of I₂. Iodine concentrations are calculated by assuming that I₂ is the only species which absorbs significantly at this wavelength. When nonnegligible concentrations of iodide ion are present, accurate [I₂] values

(1) Part 3 in the series Systematic Design of Chemical Oscillators. Part 2: De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 2133-2134. Part 1: Epstein, I. R.; Kustin, K.; Warshaw, L. *Ibid.* **1980**, *102*, 3751-3798.

(2) To whom correspondence should be addressed.

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(9) Orbán, M.; De Kepper, P.; Epstein, I. R.; Kustin, K. *Nature (London)*, in press.

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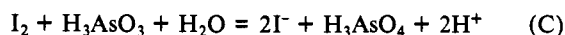
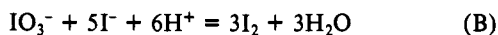
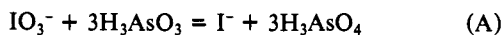
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will require a correction for the triiodide equilibrium.

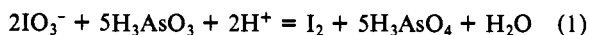
Arsenite and iodate solutions were prepared from the highest purity commercially available grades of As_2O_3 and NaIO_3 in a doubly distilled water buffer containing 0.05 M Na_2SO_4 and 0.008 M H_2SO_4 (pH 2.25 \pm 0.05).

The Arsenite-Iodate Reaction

The acidic oxidation of arsenite by iodate was first shown to be autocatalytic some 60 years ago by Eggert and Scharnow¹⁶ in a classic study of the Landolt reaction and related systems. These authors identified three major component processes in the reaction.¹⁷



Stoichiometrically, process A, which is the net reaction in the presence of excess arsenite ($[\text{H}_3\text{AsO}_3]_0/[\text{IO}_3^-]_0 > 3$), is equivalent to $\text{B} + 3(\text{C})$. Kinetically, however, if the rate of process B is slower than that of process C, then B is rate determining and the rate of production of I^- becomes dependent on the concentration of iodide; the reaction is autocatalytic. Eggert and Scharnow¹⁶ found such an autocatalytic effect of I^- on the reaction rate in the presence of excess arsenite and reported pseudo-first order rate constants for processes A and B. If iodate is in excess, the net stoichiometry is $2(\text{B}) + 5(\text{C})$ or $\text{A} + \text{B} + 2(\text{C})$.



The accelerating effect of iodide on the reaction, which undergoes a dramatic color change at the stoichiometric point owing to the sudden appearance of I_2 , was used by Bognár and Sárosi¹⁸ to construct a chronometric technique for the determination of small amounts of iodide.

Component processes B and C have been the subject of kinetic studies since the early years of this century. Reaction B is the well-known Dushman reaction.¹⁹ Mechanisms which account for the variety of complex rate laws observed for this reaction have been proposed by Liebhafsky and Roe²⁰ and by Morgan, Peard, and Cullis.²¹

Reaction C, the Roebuck reaction,²² played an important role in the development of chemical kinetics, as it provided the first demonstration that the ratio of forward and reverse rates in a multistep reaction equals the equilibrium quotient expression obtained from the law of mass action. Liebhafsky²³ later showed that Roebuck's proposed mechanism, which involved a rate-determining reaction between HOI and arsenite, could not be correct, and he proposed an alternative scheme. Further experimental studies, notably those of Pendlebury and Smith,²⁴ augmented Roebuck's rate law with additional terms.

While the component processes of the arsenite-iodate reaction have been the subject of considerable study, no systematic investigation of the total reaction appears to have been carried out since the work of Eggert and Scharnow¹⁶ in 1921. In this paper we show that analysis of the reaction in terms of the component processes A, B, and C gives a description of the system's behavior in the CSTR in remarkably good agreement with experiment. Our

aim in this work has been to study experimentally the existence of multiple steady states and to see whether and how the interactions of these three component processes give rise to bistability and to transitions between states. No attempt has been made here to develop a complete mechanism in terms of elementary processes.

Model and Method of Calculation

The model we employ for simulating our experiments consists of three irreversible overall processes, A, B, and C.²⁵ The $[\text{H}^+]$ concentration is assumed to be constant at 6×10^{-3} M. Triiodide formation is not taken into consideration; the only iodine-containing species in the model are IO_3^- , I^- , and I_2 .

For process A, we take the rate law, in agreement with Eggert and Scharnow,¹⁶ to be

$$r_A = k_A[\text{IO}_3^-][\text{H}_3\text{AsO}_3] \quad (2)$$

Eggert and Scharnow's assumed rate law for process B consists of a single term proportional to $[\text{I}^-]$ and $[\text{IO}_3^-]$, with an unspecified $[\text{H}^+]$ dependence. Later studies of the Dushman reaction, recently summarized by Liebhafsky and Roe,²⁰ have yielded a variety of rate laws, most of them involving terms of the form

$$r_B = k_{B1}[\text{H}^+]^2[\text{IO}_3^-][\text{I}^-] + k_{B2}[\text{H}^+]^2[\text{IO}_3^-][\text{I}^-]^2 \quad (3)$$

Our calculations show that inclusion of the second term on the right-hand side of eq 3 is essential for bistability.

No discussion of the rate of process C is given by Eggert and Scharnow, other than to note that it must be rapid. We employ the rate law given by Roebuck,²² assuming rapid equilibrium among I_3^- , I_2 , and I^- , so that triiodide may be eliminated from the expression.

$$r_C = k_C \frac{[\text{H}_3\text{AsO}_3][\text{I}_2]}{[\text{H}^+][\text{I}^-]} \quad (4)$$

In addition to the chemical processes A, B, and C, several physical processes must also be taken into consideration. Iodate, arsenite, and iodide flow into the reactor at rates $k_0[\text{IO}_3^-]_0$, $k_0[\text{H}_3\text{AsO}_3]_0$, and $k_0\alpha[\text{IO}_3^-]_0$, respectively, where k_0 is the reciprocal of the residence time τ and α is the fraction of iodide impurity in the iodate.²⁶ Each nonvolatile species X flows out of the reactor at rate $k_0[\text{X}]$, while iodine leaves the reactor not only in the output flow but also by evaporation from the solution. This effect, which depends upon such factors as the stirring and aspiration rates, is by no means insignificant and can be experimentally characterized by monitoring the exponential decay of optical density for an iodine solution in the CSTR at zero flow. We take k_s to be the associated first-order rate constant.

The rate equations for the four independent species in our model are thus

$$d[\text{IO}_3^-]/dt = -r_A - r_B + k_0[\text{IO}_3^-]_0 - k_0[\text{IO}_3^-] \quad (5)$$

$$d[\text{I}^-]/dt = r_A - 5r_B + 2r_C + k_0\alpha[\text{IO}_3^-]_0 - k_0[\text{I}^-] \quad (6)$$

$$d[\text{I}_2]/dt = 3r_B - r_C - k_s[\text{I}_2] - k_0[\text{I}_2] \quad (7)$$

$$d[\text{H}_3\text{AsO}_3]/dt = -3r_A - r_C + k_0[\text{H}_3\text{AsO}_3]_0 - k_0[\text{H}_3\text{AsO}_3] \quad (8)$$

where the rates r_A , r_B , and r_C are given by eq 2-4. Note that inclusion of the evaporation term $-k_s[\text{I}_2]$ in eq 7 makes $[\text{I}_2]$ an independent variable. In the absence of such a term, one could calculate $[\text{I}_2]$ from a knowledge of $[\text{IO}_3^-]$ and $[\text{I}^-]$. The model contains six "free" parameters, k_A , k_{B1} , k_{B2} , k_C , k_s , and α as well as the constraints k_0 , $[\text{IO}_3^-]_0$, $[\text{H}_3\text{AsO}_3]_0$, and $[\text{H}^+]$.²⁷

The experiments were simulated numerically by integrating eq 5-8 with use of the GEAR algorithm²⁸ for coupled sets of stiff

(16) Eggert, J.; Scharnow, B. *Z. Elektrochem. Z.* **1921**, *27*, 455-470.

(17) The pK values for the first dissociation of arsenious and arsenic acid are 9.2 and 3.6, respectively. Since our solutions are buffered at pH 2.25, we shall write both arsenite and arsenate in the fully protonated forms.

(18) Bognár, J.; Sárosi, S. *Anal. Chim. Acta* **1963**, *29*, 406-414.

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(20) Liebhafsky, H. A.; Roe, G. M. *Int. J. Chem. Kinet.* **1979**, *11*, 693-703.

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(23) Liebhafsky, H. A. *J. Am. Chem. Soc.* **1939**, *61*, 3513-3519.

(24) Pendlebury, J. N.; Smith, R. M. *Int. J. Chem. Kinet.* **1974**, *6*, 663-685.

(25) While the equilibrium constants for processes A and B are quite large, process C has an equilibrium constant near unity. However, in most of the experiments discussed here, the species concentrations are such that the reverse of process C may be neglected.

(26) The manufacturer gives an upper limit of 10^{-5} for α , and our experiments described in the Discussion suggest a significantly lower value.

(27) The temperature is also a constraint which is at the disposal of the experimenter. It is included implicitly in the rate constants and is held constant at 25 ± 0.1 °C in all experiments reported here.

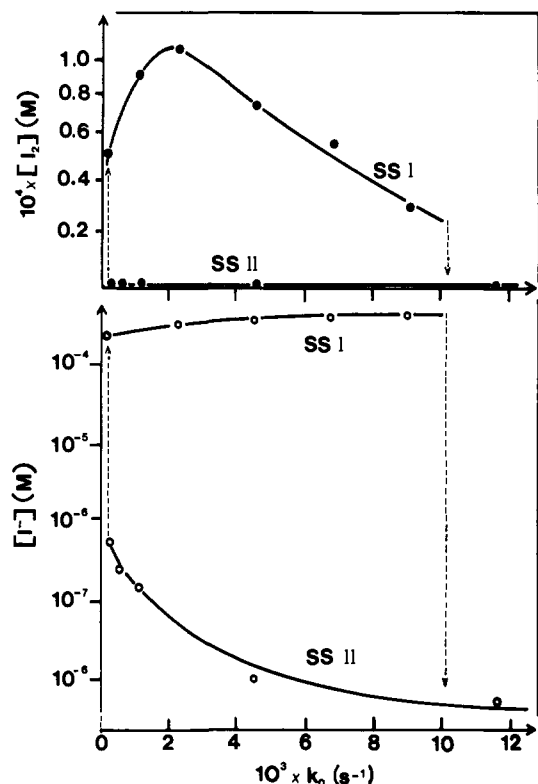


Figure 1. Experimentally determined $[I_2]_{SS}$ and $[I^-]_{SS}$ as a function of flow rate with $[IO_3^-]_0 = 1.33 \times 10^{-3}$ M and $[H_3AsO_3]_0 = 2 \times 10^{-3}$ M. Arrows indicate transitions from one steady state to the other as the flow rate is varied. (At all k_0 $[I_2]_{SSII}$ is too small to measure.)

differential equations. Typically, starting values for $[IO_3^-]$, $[I^-]$, $[I_2]$, and $[H_3AsO_3]$ were taken as $[IO_3^-]_0$, $\alpha[IO_3^-]_0$, 0, and $[H_3AsO_3]_0$, respectively, for the first flow rate at a given set of input flow concentrations, and the initial concentrations for each subsequent flow rate were the final steady-state concentrations at the previous flow rate. This procedure simulates the experimental protocol.

With each set of constraints, the integration was continued until the concentrations of the four independent species showed no significant further change. This procedure yields a set of steady-state concentrations which constitute a stable solution of the set of algebraic equations obtained from eq 5–8 when the left-hand sides of those rate equations are set to zero. For some values of the constraints, different sets of steady-state concentrations may be found depending upon the initial conditions. Such multistability implies that the algebraic equations for the steady state have two or more different stable solutions.²⁹

Results

Bistability. In the CSTR, the arsenite–iodate system may exhibit either of two stable steady states. The first of the states, which we designate SSI, is the continuation of the thermodynamic branch or equilibrium state which appears at zero flow rate. It is distinguished by relatively high values of $[I^-]_{SS}$ ³⁰ as measured by the iodide-selective electrode and high $[I_2]_{SS}$ as given by the absorbance at 460 nm. The other state, SSII, is the extension of the flow branch; i.e., the state which appears in the limit that the flow rate vastly exceeds the chemical reaction rates, so that the steady-state concentrations essentially follow those of the input

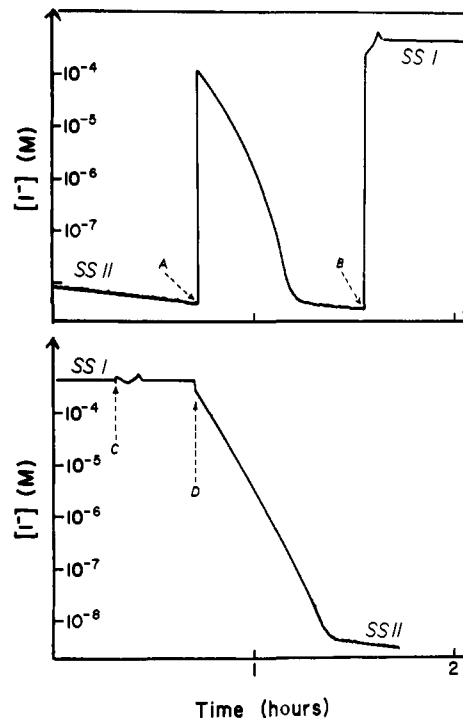


Figure 2. Transition by perturbation between steady states with $[IO_3^-]_0 = 1.33 \times 10^{-3}$ M, $[H_3AsO_3]_0 = 2 \times 10^{-3}$ M, and $k_0 = 1/\tau = 2.2 \times 10^{-3}$ s⁻¹. At points A and B SSII is perturbed by sudden injections of KI into the CSTR to produce initial increases in $[I^-]$ of 1.3×10^{-4} and 3×10^{-4} M, respectively. At points C and D, SSI is perturbed by rapid additions of NaOH inducing sudden increases in $[OH^-]$ of 3×10^{-2} and 12×10^{-2} M, respectively.

flows. This state shows relatively low values of both $[I^-]_{SS}$ and absorbance ($[I_2]_{SS}$).

For certain values of $[IO_3^-]_0$, $[H_3AsO_3]_0$, and k_0 , either state SSI or SSII may exist. Which one is actually observed depends upon the initial conditions of the system. Transitions from one state to the other may be induced by a suitable transient perturbation, e.g., injection into the CSTR of a small amount of some species or a temporary change in the flow rate. *The system is thus bistable.*

In Figure 1, we show the $[I^-]_{SS}$ and $[I_2]_{SS}$ values³¹ as functions of k_0 for the two steady states under conditions for which the region of bistability covers nearly the entire range of flow rates ($0 \leq k_0 \leq 1.1 \times 10^{-2}$ s⁻¹) accessible with our pump. If one starts from the maximum flow rate, the system settles into SSII and remains in that state, with $[I^-]_{SSII}$ increasing continuously as the flow rate is lowered, until k_0 reaches 2.2×10^{-4} s⁻¹ ($\tau = 4440$ s). If the flow rate is lowered further, both $[I^-]_{SS}$ and $[I_2]_{SS}$ undergo discontinuous jumps to the SSI values shown. If the flow rate is then increased, $[I^-]_{SSI}$ and $[I_2]_{SSI}$ vary smoothly until k_0 is changed from 9.0×10^{-3} s⁻¹ to 11×10^{-3} s⁻¹, at which point a transition from SSI back to SSII is observed. *The system exhibits hysteresis.*

Iodine concentrations in SSII are indicated as zero, because the optical density in this state is indistinguishable from that of pure water. Also, because of the solubility of the silver iodide crystal of the iodide-sensitive electrode and the possibility of experimental artifacts such as desorption of I^- from the fritted glass of the reference electrode, values of $[I^-]$ below about 5×10^{-7} M are not quantitatively reproducible and should be considered only as indicators of relative trends as a function of flow rate.

In Figure 2, we show how injection into the CSTR of a quantity of KI exceeding a threshold value induces a transition from SSII to SSI. The stability of SSII is illustrated by the return of the system to that state when smaller iodide perturbations are made. Transition from SSI to SSII may be generated, as shown in the

(28) Gear, C. W. "Numerical Initial Value Problems in Ordinary Differential Equations"; Prentice-Hall: Englewood Cliffs, N.J., 1971; Chapter 11. Hindmarsh, A. C. "Gear: Ordinary Differential Equation Solver", Technical Report No. UCM-30001, Rev. 2, Lawrence Livermore Laboratory, 1972.

(29) Nitzan, A.; Ortoleva, P.; Deutch, J.; Ross, J. *J. Chem. Phys.* **1974**, *61*, 1056–1074.

(30) Concentrations with subscripts SS refer to steady-state concentrations. Where ambiguity may arise, subscripts SSI or SSII will be used.

(31) We take ϵ_{I_2} at 460 nm as 770 cm⁻¹ M⁻¹.

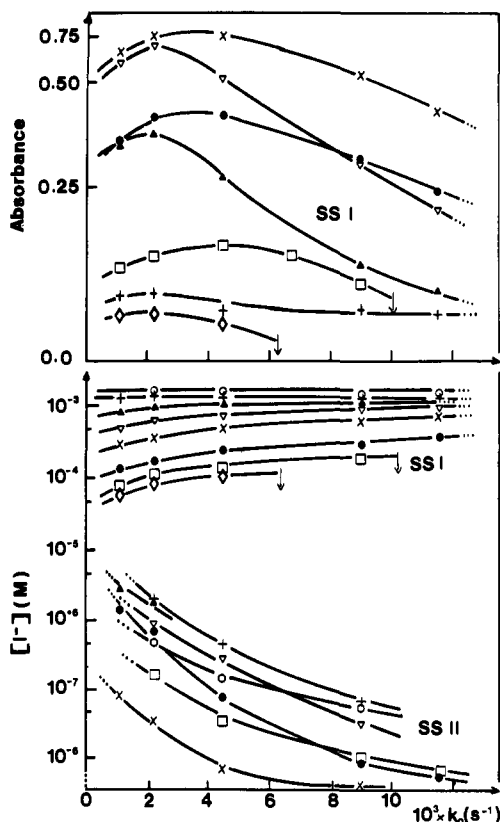


Figure 3. Experimentally determined absorbance in SSI and $[I^-]_{SS}$ as functions of flow rate with $[IO_3^-]_0 = 2 \times 10^{-3}$ M for $[H_3AsO_3]_0$ values given by symbols: $\circ = 12 \times 10^{-3}$ M, $+$ = 6.0×10^{-3} M, $\blacktriangle = 5.5 \times 10^{-3}$ M, $\nabla = 5.0 \times 10^{-3}$ M, $\times = 4.0 \times 10^{-3}$ M, $\bullet = 2.0 \times 10^{-3}$ M, $\square = 1.0 \times 10^{-3}$ M, $\diamond = 0.5 \times 10^{-3}$ M. Absorbance in SSII is too small to measure.

second part of the figure, by addition of NaOH.

More complete summaries of the stability of and concentrations in the two states as functions of k_0 are shown in Figures 3 and 4, which illustrate the behavior of the system as the constraints $[H_3AsO_3]_0$ and $[IO_3^-]_0$, respectively, are varied. As Figure 3 shows, at $[IO_3^-]_0 = 2 \times 10^{-3}$ M, SSII is stable over a wide range of k_0 (though, as in Figure 1, it must yield to the thermodynamic branch SSI at sufficiently low flow rates). Decreasing the input flow of arsenite narrows the region of stability of SSI, presumably because the I^- and I_2 producing processes proceed more slowly and are thus overtaken by the flow at relatively lower values of k_0 . This interpretation is further supported by Figure 4, which shows that SSI also has a narrower region of stability when $[IO_3^-]$ is low. At very high iodate inputs, SSII becomes stable only at relatively high flow rates, because processes A and B produce I^- and I_2 at a rapid rate, and these species must be depleted by the output flow in order for SSII to be stable.

Finally, the experimental and calculated stabilities of the steady states are summarized in the phase diagrams of Figures 5 and 6, which show the $([H_3AsO_3]_0, k_0)$ and $([IO_3^-]_0, k_0)$ constraint planes, respectively. One must bear in mind that for all input concentrations, only SSI can be stable in the limit $k_0 \rightarrow 0$, and only SSII stability can be observed as $k_0 \rightarrow \infty$.

Stoichiometry. Our analysis of the reaction in terms of the three component processes A, B, and C implied that when $[H_3AsO_3]_0/[IO_3^-]_0 < 3$, the net reaction is given by eq 1, with 2 mol of iodate consumed for every 5 mol of arsenite and I_2 as the major product. When arsenite is in excess, process C consumes the remaining I_2 , and the product is I^- , with the stoichiometry being that of process A.

Figures 7 and 8 which show $[I^-]_{SS1}$ and $[I_2]_{SS1}$ as functions of the input concentrations, support this view. In Figure 7, $[I_2]_{SS1}$ is seen to increase to a maximum with increasing $[H_3AsO_3]_0$ until the stoichiometric ratio of eq 1, $[H_3AsO_3]_0/[IO_3^-]_0 = 2.5$, is

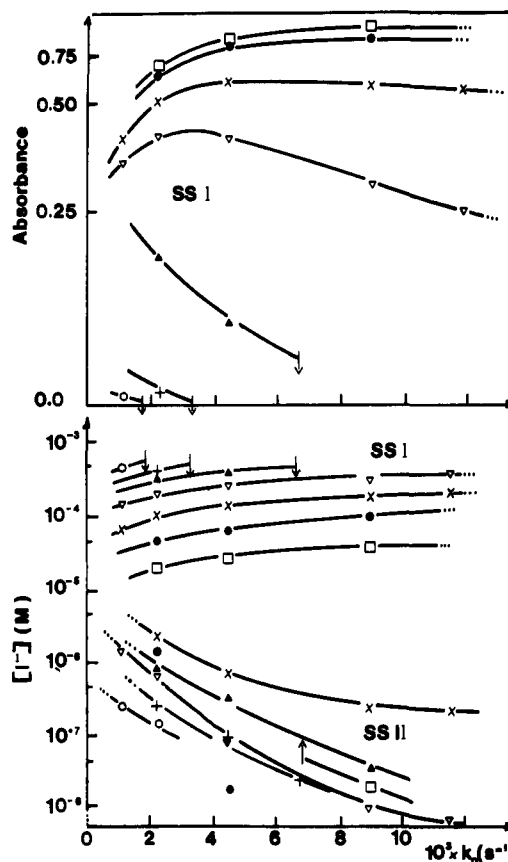


Figure 4. As in Figure 3, but with $[H_3AsO_3]_0 = 2 \times 10^{-3}$ M for $[IO_3^-]_0$ values given by symbols: $\square = 85.3 \times 10^{-3}$ M, $\bullet = 21.3 \times 10^{-3}$ M, $\times = 5.3 \times 10^{-3}$ M, $\nabla = 2.0 \times 10^{-3}$ M, $\blacktriangle = 1.0 \times 10^{-3}$ M, $+$ = 0.67×10^{-3} M, $\circ = 0.33 \times 10^{-3}$ M.

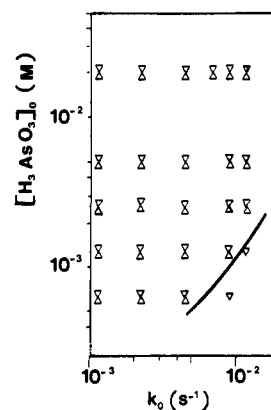


Figure 5. A portion of the phase diagram in the $([H_3AsO_3]_0, k_0)$ constraint plane. Symbols: \blacktriangle , SSI stable; ∇ , SSII stable; \times , bistability SSI/SSII. Solid lines indicate boundaries of the bistable region calculated using the model. All other constraints are kept constant with $[NaIO_3]_0 = 2 \times 10^{-3}$ M.

reached. The steady-state iodine concentration then decreases sharply until, when the limiting arsenite-iodate ratio of 3:1 is reached, $[I_2]_{SS1}$ becomes essentially zero as the stoichiometry becomes that of process A. The figure also shows that $[I^-]_{SS1}$ rises with increasing arsenite until at the 3:1 ratio a limiting value of $[I^-]_{SS1} = [IO_3^-]_0$ is approached.

In Figure 8, we see that as iodate is increased at fixed arsenite, $[I_2]_{SS1}$ approaches a limiting value qualitatively consistent with that given by eq 1 in the case of excess iodate, while $[I^-]$ decreases almost linearly on this log-log plot.

Dynamics. The major part of our investigation has concentrated on the nature and stability of the steady states. This focus has the advantage of yielding reproducible results which are sufficiently

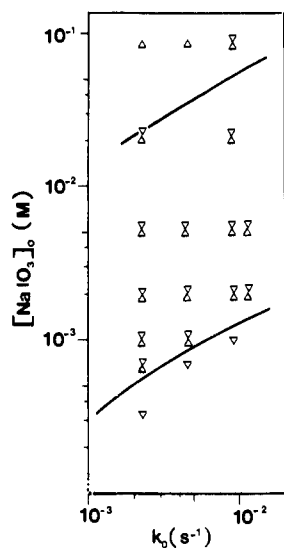


Figure 6. As in Figure 5, but in the $([IO_3^-]_0, k_0)$ constraint plane with $[H_3AsO_3]_0 = 2 \times 10^{-3} M$.

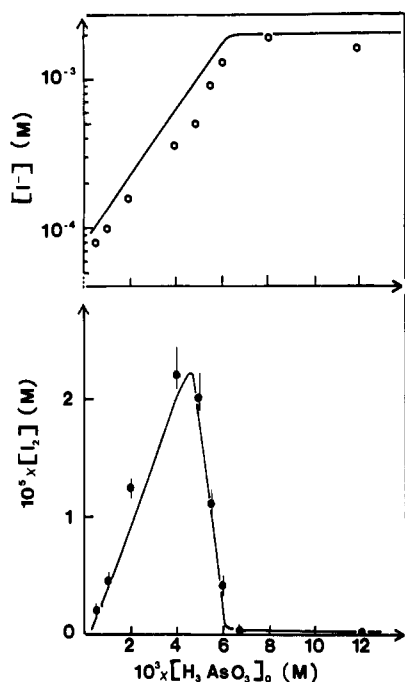


Figure 7. Experimental (points) and calculated (lines) $[I^-]_{SS1}$ and $[I_2]_{SS1}$ vs. $[H_3AsO_3]_0$ with $[IO_3^-]_0 = 2 \times 10^{-3} M$ and $k_0 = 2.2 \times 10^{-3} s^{-1}$.

sensitive and extensive to make possible the testing of proposed models. Nevertheless, both the experiments and our calculations generate a great deal more data in the form of I^- concentrations and absorbance or I_2 concentrations as functions of time.

One interesting dynamic phenomenon which appears in our system and in other reactions in flow systems is the emergence of overshoots and undershoots when the external constraints on the system are changed. In Figure 9, we show the experimental and calculated response of $[I_2]$ to sudden variations in the flow rate. Note the excellent qualitative agreement. Overshoots and undershoots are also observed when stepwise changes are made in $[H_3AsO_3]_0$ at a fixed flow rate. No overshoots and undershoots are observed, however, when $[IO_3^-]_0$ is varied in an analogous manner.

It has also been suggested³² that dynamic data analyzed in terms of the spectrum of relaxation times, when a system in a CSTR

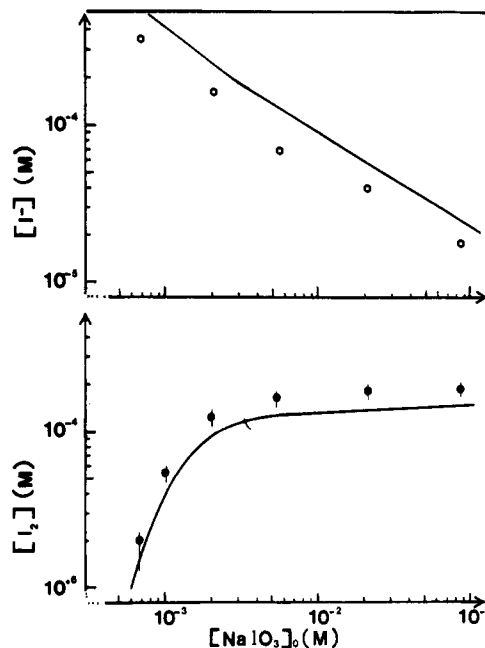


Figure 8. Experimental (points) and calculated (lines) $[I^-]_{SS1}$ and $[I_2]_{SS1}$ vs. $[IO_3^-]_0$ with $[H_3AsO_3]_0 = 2 \times 10^{-3} M$ and $k_0 = 2.2 \times 10^{-3} s^{-1}$.

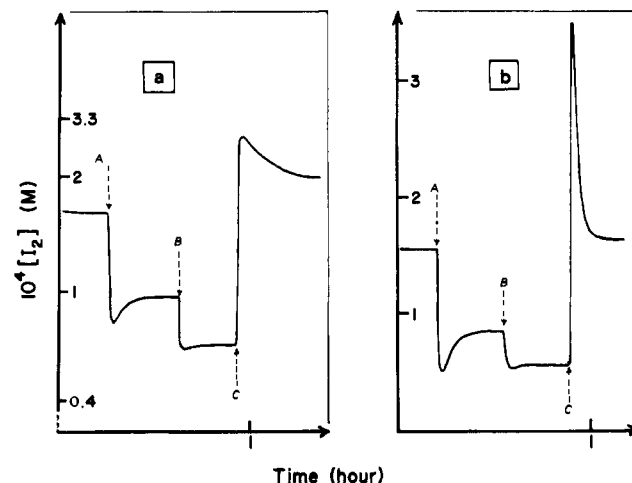


Figure 9. Experimental (a) and calculated (b) response of the system to sudden changes in the flow rate k_0 showing overshoot and undershoot ($[IO_3^-]_0 = 2 \times 10^{-3} M$; $[H_3AsO_3]_0 = 5 \times 10^{-3} M$). The initial value of k_0 is $4.5 \times 10^{-3} s^{-1}$. At A, B, and C, respectively, k_0 is set to 9×10^{-3} , 12×10^{-3} , and $2.3 \times 10^{-3} s^{-1}$.

returns to a steady state after perturbation, can yield useful chemical information. We agree that the dynamic behavior of CSTR systems does indeed contain much information of significance, though more thorough theoretical analyses will probably be required to extract it.

Discussion

The model we have employed for the arsenite-iodate reaction is a crude one in that no attempt is made to dissect the component processes into elementary steps. Nevertheless, the model gives regions of stability of the steady states in almost perfect agreement with experiment and predicts the trends in both sets of steady-state concentrations correctly as well as yielding qualitative values of concentrations in the more easily measurable SSI to surprising accuracy. The model also has the virtues of providing some qualitative understanding of the origin of the bistability and of being sufficiently simple that one can extract the effects of the various free parameters on the system behavior.

We have outlined above the view that bistability results from a balance between the rate of chemical reaction, which tends to stabilize SSI, and the rate of flow in and out of the reactor, which

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Table I. Values of the "Free" Parameters

parameter	value	method of determination
k_A	$1 \times 10^{-11} \text{ M}^{-1} \text{ s}^{-1}$	experimental upper limit from initial rate of I^- formation, calculated effect on SSII stability
k_{B1}	$8 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$	reference 20
k_{B2}	$6 \times 10^8 \text{ M}^{-4} \text{ s}^{-1}$	reference 20, necessary for bistability, calculated effect on SSI stability
k_C	$3.2 \times 10^{-2} \text{ s}^{-1}$	reference 24
k_s	$3.4 \times 10^{-3} \text{ s}^{-1}$	experimentally determined from decay rate of I_2 solution optical density
α	5×10^{-8}	experimental upper limit from effects of initially added I^- , calculated effect on SSII stability

favors SSII. Factors which increase the reaction rate will generally tend to extend the region of stability of SSI to higher flow rates and/or to shift to higher flow rates the lower limit of SSII stability.

In Table I we give the final values arrived at for our six "free" parameters. These values were established by our own direct experimental measurement where possible, augmented by the use of rate constants available in the literature and finally, where necessary, adjustment of parameters to give the best agreement between our calculated and experimental results.

Eggert and Scharnow¹⁶ give a value for k_A of $4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. In our calculations, changing the value of k_A has two principal effects. Increasing k_A raises the value of k_0 below which SSII becomes unstable, i.e., the flow rate above which we have bistability. Also, k_A is the major determinant of $[\text{I}^-]_{\text{SSII}}$, which is almost directly proportional to k_A for a wide range of flow rates. The value of k_A has negligible influence on either the stability of or the I^- and I_2 concentrations in SSI.

Preliminary calculations showed that Eggert and Scharnow's value for k_A caused the model to underestimate significantly the width of the bistable region. We therefore carried out batch experiments in which $[\text{I}^-]$ was monitored as a function of time for given initial iodate and arsenite concentrations. By neglecting process B, we may then obtain an upper limit on k_A from eq 2 taking $\Delta\bar{t}$ as the time required for $[\text{I}^-]$ to reach some specified value $\Delta\bar{c}$, which we chose as 10^{-6} M .

$$k_A \leq (\Delta\bar{c}/\Delta\bar{t})[\text{IO}_3^-]_0^{-1}[\text{H}_3\text{AsO}_3]_0^{-1} \quad (9)$$

The value obtained from eq 9 is $2 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, significantly lower than that found by Eggert and Scharnow. Further calculations showed that obtaining the correct region of bistability requires $k_A \leq 1 \times 10^{-11} \text{ M}^{-1} \text{ s}^{-1}$. Since our calculated values of $[\text{I}^-]_{\text{SSII}}$ are lower than our experimental values, k_A was chosen as this upper limit. However, it is likely that process A could be eliminated completely from our model and increases in $[\text{I}^-]_{\text{SSII}}$ obtained by appropriate modification of the other parameters.

Two reasons can be cited for the sharp disagreement between the k_A reported by Eggert and Scharnow and the value found here. First, Eggert and Scharnow consider process A as the only source of iodide in the reaction. If their iodate contained any I^- impurity, then their reaction time, which they take as the time to the appearance of I_2 , would be decreased, thereby raising their calculated k_A . Secondly, Eggert and Scharnow employ a single term rate law for the Dushman reaction, ignoring the term second order in $[\text{I}^-]$, which is dominant when iodide levels exceed 10^{-4} – 10^{-5} M . If the rate of process B is underestimated in this manner, then k_A must be overestimated in order to give the correct reaction time.

Liebhaufsky and Roe²⁰ summarize a variety of rate studies on the Dushman reaction, process B. They quote values for k_{B1} ranging from $4 \times 10^2 \text{ M}^{-3} \text{ s}^{-1}$ to $3 \times 10^6 \text{ M}^{-3} \text{ s}^{-1}$ and for k_{B2} from $3 \times 10^8 \text{ M}^{-4} \text{ s}^{-1}$ to $2 \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$. Eggert and Scharnow's value for k_{B1} (with $k_{B2} = 0$) is $1.6 \times 10^6 \text{ M}^{-3} \text{ s}^{-1}$. Our calculations failed to produce bistability with any k_{B1} in this range in the absence of the k_{B2} term. This failure is not surprising when one observes that in SSI, $[\text{I}^-]$ is sufficiently high that the k_{B1} term should be small compared with the term second rate order in iodide. The

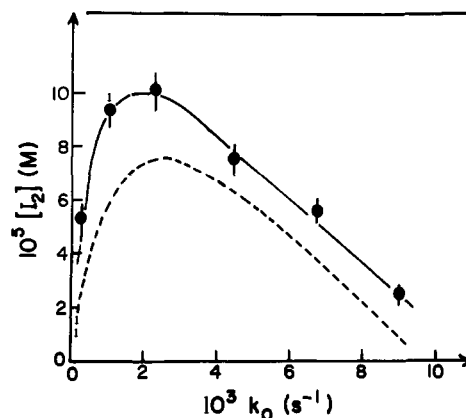


Figure 10. Experimental (solid line) and calculated (dashed line) $[\text{I}_2]_{\text{SSII}}$ showing maximum as a function of flow rate ($[\text{IO}_3^-]_0 = 1.33 \times 10^{-3} \text{ M}$; $[\text{H}_3\text{AsO}_3]_0 = 2 \times 10^{-3} \text{ M}$).

value chosen here for k_{B1} lies between that obtained with classical kinetic techniques by Abel and co-workers^{33,34} and that found by Beran and Bruckenstein³⁵ with electrochemical methods employing rotating disk cathodes. Our k_{B2} value is intermediate between those determined by electrochemical³⁶ and spectrophotometric³⁷ techniques. The value of k_{B2} strongly influences both the flow rate at which SSI becomes unstable, i.e., the upper limit of bistability, and the values of $[\text{I}^-]_{\text{SSII}}$. Thus k_{B2} plays a somewhat complementary role to that of k_A .

The rate constant for the Roebuck reaction k_C has much the same effect as k_{B2} . That is, increasing k_C moves the SSI \rightarrow SSII transition to higher flow rates and increases $[\text{I}^-]_{\text{SSII}}$. We chose for our initial k_C the rate constant for the term in Pendlebury and Smith's experimental rate law corresponding to eq 4.²⁴ Since this value gave results in excellent agreement with our experiments, no further modification of k_C was undertaken. Given the simplicity of our model, no attempt was made to include the detailed hydrogen ion or ionic strength dependence found by Pendlebury and Smith in their stopped flow experiments.

An upper limit on the value of α can be established by batch experiments in which measured amounts of iodide are added to initial reaction mixtures containing excess iodate. Under these conditions a peak is observed in $[\text{I}^-]$ as a function of time and the solution abruptly turns brownish orange owing to I_2 formation; we have a clock reaction.

So long as the added iodide produces a noticeable acceleration of the clock reaction, $\alpha[\text{IO}_3^-]_0$ must be less than or comparable to $[\text{I}^-]_0$. Significant accelerations were observed with $[\text{IO}_3^-]_0 = 4 \times 10^{-2} \text{ M}$ for $[\text{I}^-]_0$ values down to our lowest experimentally practical concentration of 10^{-8} M , thereby establishing an upper limit on α of 2×10^{-7} .

Like k_A , the parameter α exerts its major influence on the stability and concentration of SSII. The largest α value which gave the observed SSII \rightarrow SSI transition correctly was 5×10^{-8} , which was chosen for this study. The parameters k_A and α are strongly coupled, as are k_{B2} and k_C , and changes in one parameter of a pair can be compensated by an opposite change in the other parameter.

The iodine decay rate k_s was determined experimentally by monitoring the decrease in absorbance of an iodine solution in the CSTR at zero flow. As Figures 3 and 4 show, $[\text{I}_2]_{\text{SSII}}$ exhibits a maximum as a function of k_0 for nearly all sets of input concentrations. In an initial set of calculations carried out before we became aware of the effects of iodine evaporation ($k_s = 0$), $[\text{I}_2]_{\text{SSII}}$ was generally about 3 times higher than the results obtained by allowing for evaporation and decreased monotonically with k_0

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at all input concentrations. As Figure 10 illustrates, introduction of this evaporation effect into our model indeed yields the observed maximum in $[I_2]_{SSI}$. Our calculations give a small but systematic underestimate of the experimentally determined $[I_2]_{SSI}$. One reason for this discrepancy may lie in our neglect of triiodide formation. Particularly in SSI, where $[I^-]$ is relatively high, some of the iodine in our model will actually be present as nonvolatile I_3^- . Equation 7 will then yield an overestimate of the rate of loss of I_2 from the system.

The model employed in our calculations ignores many complexities of the full system. The reverse steps of the component processes are omitted; no note is taken of the complex kinetics of the Roebuck reaction; the formation of triiodide and the reactivity of that species are not considered. In spite of these simplifications, remarkably good agreement between our calculations and the experimentally determined steady-state concentrations, phase diagram, stoichiometry, and dynamics have been achieved. It thus appears that the qualitative picture of the reaction suggested by Eggert and Scharnow¹⁶ some 60 years ago is correct, despite major quantitative differences between their analysis and ours.

We have not attempted to develop a mechanism for the arsenite-iodate system consisting of a complete set of elementary steps. Any such mechanism must pass the stringent tests of consistency not only with the experimental results presented here but also with the considerable body of data available from batch experiments on the Dushman²⁰ and Roebuck^{22,24} reactions as well as on the arsenite-iodate reaction¹⁶ itself. Efforts are now under way to construct such a mechanism.

A number of the "free" parameters in our model were either determined experimentally or were taken from other experimental studies in the literature. The remaining constants could be fixed

rather accurately by fitting the observed transition points between the two steady states. We suggest that this procedure of choosing rate constants to reproduce experimentally determined phase diagrams in bistable flow systems may prove a useful addition to the kineticist's array of techniques, particularly when the number of unknown parameters is relatively small.

In addition to forming part of the recently discovered arsenite-iodate-chlorite oscillator, the reaction studied here has been shown to propagate waves of chemical reactivity in an initially homogeneous unstirred solution.³⁸ To date, only three other isothermal, nonbiological homogeneous bistable systems, the Briggs-Rauscher³⁹ reaction, the cerium-bromate system,⁴⁰ and the reaction of bis(trichloromethyl) trisulfide with aniline in methanol,⁴¹ have been treated in the literature. In further papers in this series we shall examine several other cases of bistability in the CSTR, including the chlorite-iodide and the ferrous-nitrate systems. With this considerably expanded range of experimental examples, it may then prove feasible to elucidate some of the actual relations among the phenomena of autocatalysis, bistability, temporal oscillation, and the propagation of spatial waves.

Acknowledgment. This work was supported by Grant CHE 79-05911 from the National Science Foundation. We thank Professors Colin Steel and Paul Dorain for their enthusiastic support and for the loan of several pieces of apparatus used in these studies.

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Synthesis and Characterization of the Major Component of Alamethicin

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Received April 17, 1981

Abstract: Natural alamethicin has been purified on a high-performance liquid chromatography (HPLC) system developed to purify and characterize synthetic peptides corresponding to the proposed structures of alamethicin. Five of the twelve components detectable by UV absorption at 210 nm were isolated in pure form and were characterized for their antibacterial and ionophoric properties. Low-resolution electron-impact mass spectrometry (LREIMS) indicates that the purified major component and a synthetic preparation based on the recently proposed structure are identical in their primary structures. This major component, along with another fraction of the natural alamethicin mixture, closely demonstrates the spectrum of antibiotic activity possessed by the mixture. All fractions are equally potent in producing conductances of 30 $\mu\text{S}/\text{cm}^2$ in lipid bilayers, but the current-voltage curves induced by the different fractions have different slopes. Thus, their potencies at higher conductance levels can be expected to diverge. The synthetic peptide shows a close correspondence to the major component by all criteria examined.

The recently reported primary structure (Figure 1D) of the major component of alamethicin is based on a combination of techniques emphasizing both electron-impact and field-desorption high-resolution mass spectrometry.¹ Alamethicins fall into a special class of peptide antibiotics along with antiameobins, em-

erimicins, and suzukacillin termed as "peptaibophols".²⁻⁵ Peptides of this class have been found to have several aminoisobutyric acid

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