Concentration-Dependent Regulation of Flow Rate in a Chemical Oscillator

Milos Dolnik,[†] Laurence F. Abbott,[‡,§] and Irving R. Epstein*[,†,§]

Departments of Chemistry and Biology and Center for Complex Systems, Brandeis University, Waltham, Massachusetts 02254-9110

Received: March 24, 1994; In Final Form: June 15, 1994[⊗]

A model of the chlorine dioxide−iodide reaction in a single well-stirred flow-through reactor is analyzed. The model includes a flow regulation mechanism that allows the concentration of iodide in the system to control the flow rate. The control is accomplished through a computer-mediated sigmoidal dependence of the dynamic flow rate on the iodide concentration. The dynamical behavior of this system with slow regulation is investigated by the numerical continuation technique. Oscillatory behavior is obtained for parameter values that produce only steady state behavior in the unregulated system. Chaos and bursting also arise as a result of the control mechanism. Responses of the model to changes in input iodide concentration show the ability of the system to adjust to new conditions. Two different transient patterns of adjustment are observed depending on the direction of the change in iodide input concentration. The control mechanism mimics a similar system thought to control activity in biological neurons and may be of practical value.

Introduction

The introduction of control mechanisms in the study of chemical oscillators has increased the variety of behavior seen in these systems. For example, delayed feedback can produce major changes in the dynamics of biological[1−3] and chemical systems.[4,5] Delayed feedback can stabilize otherwise unstable steady states and unstable periodic solutions.

The stabilization of an unstable steady state was first investigated by Aris and Amundson[6] and later by others in the chemical engineering literature.[6−11] Laplante[12] showed the stabilization of an unstable steady state in the bistable arsenous acid−iodate reaction. Hjelmfelt and Ross[13] described a feedback technique to stabilize unstable steady states in the chlorite−iodide reaction under oscillatory and excitable conditions. To control oscillatory behavior of the minimal bromate oscillator, delayed feedback regulation of the flow rate was used both in a single reactor[14] and in two coupled reactors.[15,16] Recently, several studies have focused on controlling chaotic behavior. The unstable periodical orbit contained in a chaotic attractor can be stabilized by repeated small perturbations[17] or by a continuous small amplitude perturbation.[18] Both techniques have been used to control chaos in the Belousov−Zhabotinsky reaction.[19−21] In addition, control can sometimes result in the emergence of dynamical behavior that is not present in the uncontrolled system. Chevalier et al.[22] observed chaotic states in the minimal bromate oscillator by introducing a nonlinear delayed feedback. Bursting behavior, i.e., regular alternating periods of quiescence and oscillation, was observed in the chlorine dioxide−iodide (CDI) reaction in a single reactor[23] and in two coupled flow reactors[24] in which the flow of a reagent into one reactor was controlled according to reagent concentration(s) in the other reactor.

Oscillating chemical reactions can serve as models for more complex biochemical and biological systems. A number of features of the dynamical behavior observed in neurobiological systems have also been found in relatively simple chemical systems. Neurons often exhibit oscillatory patterns of electrical activity, including complex bursting behavior. They maintain such patterns of activity over extensive time periods despite continual protein turnover and changes in extracellular conditions. Similarly, neurons can adjust their electrical properties appropriately during growth and development and can recover from damage. The ability of nerve cells to maintain stable electrical activity suggests that neurons possess a feedback mechanism that controls their intrinsic electrical characteristics.

LeMasson et al.[25] recently introduced a model of activity-dependent regulation of conductances in neurons. The proposed mechanism allows model neurons to self-assemble and adjust their conductances to produce extremely stable and robust patterns of activity.

We utilize here a control mechanism similar to that of LeMasson et al.[25] This type of control requires feedback from one dynamic variable that is a sensitive indicator of activity to another dynamic variable that can change the activity of the system. To achieve this situation, we introduce a new dynamical variable, the flow rate, into the model of the CDI reaction, and we allow it to depend on the iodide concentration. The average iodide concentration serves as an indicator of dynamic behavior. We analyze the role of the controlling variable and investigate the dependence of the dynamics on the target and input concentrations of iodide. We also investigate the ability of the system to maintain a particular pattern of activity when external conditions change.

Model of Dynamical Regulation

The model of the chlorine dioxide−iodide (CDI) reaction proposed by Lengyel et al.[26] is based on two overall stoichiometric reactions:

$$2ClO_2 + 2I^- \rightarrow 2ClO_2^- + I_2 \qquad (R1)$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O \qquad (R2)$$

For a continuous stirred tank reactor (CSTR) the system of differential equations is

$$dX/dt = -R_1 + k_0(X_0 - X)$$

[†] Department of Chemistry.
[‡] Department of Biology.
[§] Center for Complex Systems.
[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

0022-3654/94/2098-10124$04.50/0

$$dY/dt = -R_1 - 4R_2 + k_0(Y_0 - Y) \quad (1)$$

$$dZ/dt = R_1 - R_2 + k_0(Z_0 - Z)$$

where

$$R_1 = k_1XY \quad (2)$$

$$R_2 = k_{2a}ZYH + k_{2b}ZPY/(u + Y^2)$$

Here $X = [ClO_2]$, $Y = [I^-]$, $Z = [ClO_2^-]$, $P = [I_2]$, $H = [H^+]$, and k_0 is the flow rate (the reciprocal of the residence time). The rate constants and parameters used in the simulations are $k_1 = 6000\ M^{-1}\ s^{-1}$, $k_{2a} = 460\ M^{-2}\ s^{-1}$, $k_{2b} = 2.55 \times 10^{-3}\ s^{-1}$, $u = 10^{-14}M^2$, $H = 0.01$ M, $X_0 = 10^{-4}$ M, and $Z_0 = 0$. Iodine concentration in the CSTR can be determined from the conservation of iodine atoms:

$$P \equiv [I_2] = ([I^-]_0 - [I^-])/2 \quad (3)$$

Normally, the flow rate k_0 would be a fixed parameter of the model. We make it a slowly varying dynamic variable instead. We introduce this regulatory mechanism with the intention of forcing the system to establish a specific average concentration of some species in the reactor. The desired average concentration will correspond to a particular pattern of activity; in this way, control and maintenance of activity are realized. We employ iodide ions as the control species, although other species in the CDI system can be chosen as well. Iodide ions have an inhibitory effect, which is crucial for oscillatory behavior, and their concentration can be measured relatively easily in experiments.

The dynamic flow rate can vary between zero and a maximum value k_{max} according to the concentration of iodide in the system. The flow rate varies as a function of the concentration of iodide according to the equation

$$\tau(dk_0/dt) = f(Y) - k_0 \quad (4)$$

where $f(Y)$ is a sigmoidal function:

$$f(Y) = k_{max}/[1 + (Y/I_T)^n] \quad (5)$$

We call I_T the target value of iodide in the reactor, and n is a parameter that determines the slope of the sigmoidal function. The flow rate relaxes to its asymptotic value $f(Y)$ with a time constant τ. The right side of eq 4 is positive when $Y \ll I_T$, and so k_0 increases and more iodide is delivered into the system. If $Y \gg I_T$ the right side of eq 4 is negative, which results in a decrease of the flow rate k_0, and the iodide concentration in the system also decreases.

The value of τ controls how quickly the flow rate responds to changes in the iodide concentration. Relatively small values of τ result in the rapid establishment of equilibrium, and the system is strongly controlled. If τ is large, then changes in the flow rate are slow and adjustment takes a longer time. The latter situation corresponds to most biological systems such as neurons.[25] We study this domain for the CDI reaction.

Numerical Methods

To analyze the system both with and without control, we used the CONT numerical bifurcation and continuation package.[27] Periodic solutions were obtained by numerically integrating the system of ordinary differential equations (eqs 1–5). The integration used a semi-implicit fourth-order Runge–Kutta method with automatic control of the step size. All simulations were performed on an IBM RISC 6000 powerstation Model 340.

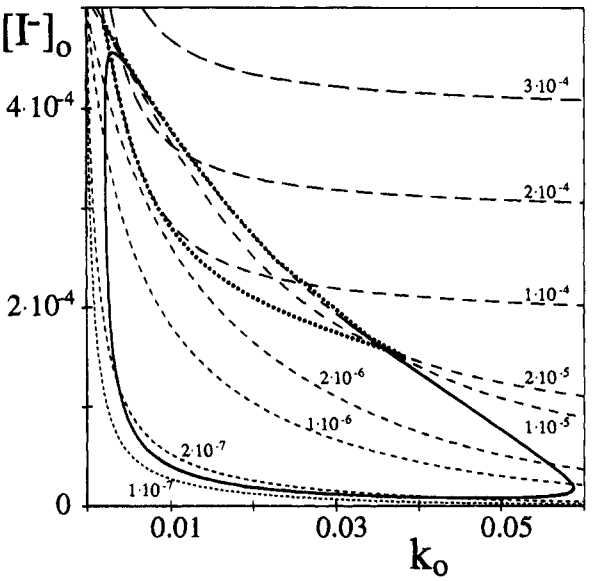

Figure 1. Bifurcation diagram for the model of the CDI reaction: Hopf bifurcation, solid line; saddle-node bifurcation, dotted line. Dashed lines connect points with the same steady state concentration (in M) of iodide. Oscillations occur inside the Hopf curve, and bistability occurs inside the saddle-node curve.

Result of Simulations

Bifurcation Analysis of Control Parameters. The model of the CDI reaction in a well-stirred reactor has been analyzed previously,[23,28] and good agreement with experiment was obtained. The reaction in a CSTR exhibits two different steady states, one with low $[I^-]$ and one with high $[I^-]$, oscillatory behavior, bistability of the two steady states, coexistence of oscillation with a steady state, and excitability and bursting behavior when periodically perturbed. This model also agrees well with the dynamics of the CDI reaction in two coupled CSTRs.[24] The rich dynamical behavior of the uncontrolled system suggests the study of the system with control.

The time-averaged concentrations of ClO_2, ClO_2^-, and I^- correlate with the dynamic pattern of behavior of the reaction. Figure 1 shows the correlation between the steady state value of $[I^-]$ and the pattern of dynamic behavior. In the oscillatory region the value of $[I^-]$ belongs to the unstable steady state and is close to the time average value. Simple (single-period) oscillations exist inside the Hopf bifurcation lines, along which all points are supercritical. The dashed lines connect points with the same steady state value of $[I^-]$. In the bistability region three steady states, one or two unstable, coexist, and dashed lines cross in this region. For k_0 between 0.003 and 0.035 s^{-1} the oscillatory region corresponds to a steady state concentration of $[I^-]$ within the range 2×10^{-7} to 10^{-5} M. If the target concentration of iodide I_T is within this range, oscillations can be stabilized.

CDI Reaction with Control Mechanism. The continuation technique was used to investigate the role of the control parameters I_T, k_{max}, τ, and n. For large enough τ ($\tau \geq 10^4$ s), the flow rate responds slowly to changes in the iodide concentration. Although the control mechanism does not include an explicit time delay, a relatively long time is required to adjust the flow rate if the iodide concentration in the system changes suddenly. For low values of τ, the adjustment of the flow rate is very fast and the dynamics is characterized by stable

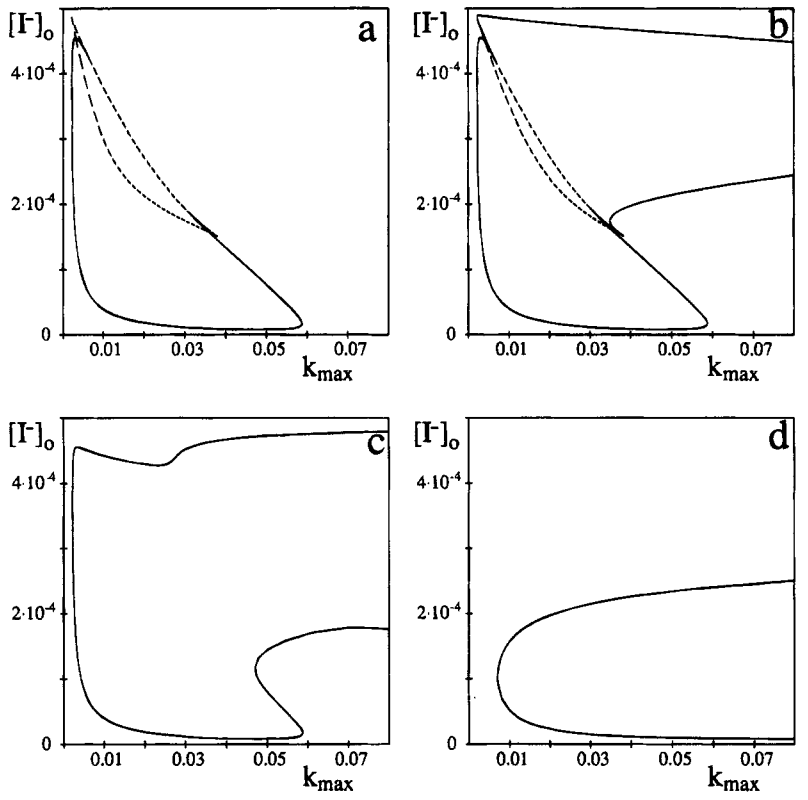

Figure 2. Dynamical control of the CDI reaction. Two-parameter bifurcation diagrams with Hopf (solid) and saddle-node (dashed) bifurcation lines. Oscillations occur inside the Hopf curve, and bistability occurs inside the saddle-node curve. Control parameters are $n = 5$, $\tau = 10\,000$ s, target concentration of iodide ions (a) $I_T = 10^{-4}$ M, (b) $I_T = 5 \times 10^{-5}$ M, (c) $I_T = 1 \times 10^{-5}$ M, (d) $I_T = 2 \times 10^{-7}$ M.

steady states over a wide range of parameters where the uncontrolled system shows oscillatory behavior. In this paper we are interested in the situation where large values of τ allow the system to react slowly to concentration changes. We choose $\tau = 10^4$ s.

The control parameter n affects the steepness of the sigmoidal function in the region where Y is equal or close to I_T. The larger the value of n, the steeper the slope of the sigmoidal function, and the more strongly the system is forced to find dynamics with an iodide concentration closer to the target value. As a convenient value, we choose $n = 5$.

The oscillatory region in the two-parameter $[I^-]_0$–k_0 bifurcation diagram is enclosed by Hopf and saddle-node bifurcation lines for the uncontrolled system (Figure 1). The Hopf and saddle-node bifurcation lines have similar shapes in the controlled system for a target iodide concentration $I_T = 10^{-4}$ M (Figure 2a). However, new Hopf lines appear as the target concentration is decreased to 5×10^{-5} M. The Hopf lines do not terminate in Bogdanov points, as in the previous case. Instead, the Bogdanov points vanish and the Hopf lines enclose an additional region of oscillation for high $[I^-]_0$ and high k_{max}. The saddle-node bifurcation lines which surround the region of bistability disappear when the target concentration I_T is below 4×10^{-5} M. With further decrease of I_T, the distance between the Hopf lines (size of the oscillatory region) at first increases and then decreases until the Hopf lines vanishs. For $k_{max} > 0.08$ s^{-1}, the Hopf lines are nearly parallel with the x-axis. The parameter k_{max} does not play an important role when it is sufficiently high.

The target value I_T is the key parameter that determines what kind of dynamic pattern will be established in the controlled system. Figure 3 shows two-parameter bifurcation diagrams in the $[I^-]_0$–log I_T plane. When k_{max} is large enough ($k_{max} = 0.1$ s^{-1}, Figure 3a), the Hopf line forms a closed curve in the $[I^-]_0$–log I_T plane. In this case, steady state behavior is the only possible solution for any input concentration of iodide for high values of the target concentration ($I_T > 5 \times 10^{-5}$ M, Figure 3a). When the maximum flow rate is decreased ($k_{max} = 0.04$ s^{-1}, Figure 3b), oscillations are possible for large I_T for lower input concentrations $[I^-]_0$. The cusps on the Hopf lines indicate that for specific constant values of $[I^-]_0$ three qualitatively different steady states can be obtained for different target values I_T. For input iodide concentration 4.2×10^{-4} M $< [I^-]_0 < 4.55 \times 10^{-4}$ M, a low iodide steady state is established for $I_T < 2 \times 10^{-6}$ M, a high iodide state is established for $I_T > 5 \times 10^{-5}$ M, and for $I_T \approx 1 \times 10^{-5}$ M, a steady state with an intermediate concentration of iodide is an asymptotic solution (see Figure 3b). Three steady states can also be found for input concentrations $[I^-]_0 \approx 1.7 \times 10^{-4}$ M. When k_{max} is further decreased, the region of bistability is characterized by saddle-node bifurcation lines. The bistability region grows with decreasing k_{max}. When k_{max} decreases to a relatively low value, the oscillatory region shrinks (Figure 3d) and finally the Hopf line disappears.

The region of oscillation can be accurately determined from a one-parameter bifurcation diagram. Figure 4 shows bifurcation diagrams for two different input iodide concentrations. In each case, the Hopf bifurcation points at low I_T are subcritical and, as a result, the stable steady states and the limit cycle oscillations coexist for a wide range of target concentrations I_T. In this region the system will asymptotically approach either steady state or limit cycle oscillations depending on initial conditions. On the contrary, the Hopf bifurcation points for higher I_T are supercritical. Hence, the oscillatory region in the two-parameter bifurcation diagram extends far beyond the Hopf lines for low values of I_T and the borders of the oscillatory region coincide with the Hopf lines for high I_T.

Figure 4b shows the appearance of a stable steady state with intermediate concentration of iodide and two additional supercritical Hopf bifurcation points corresponding to the extrema

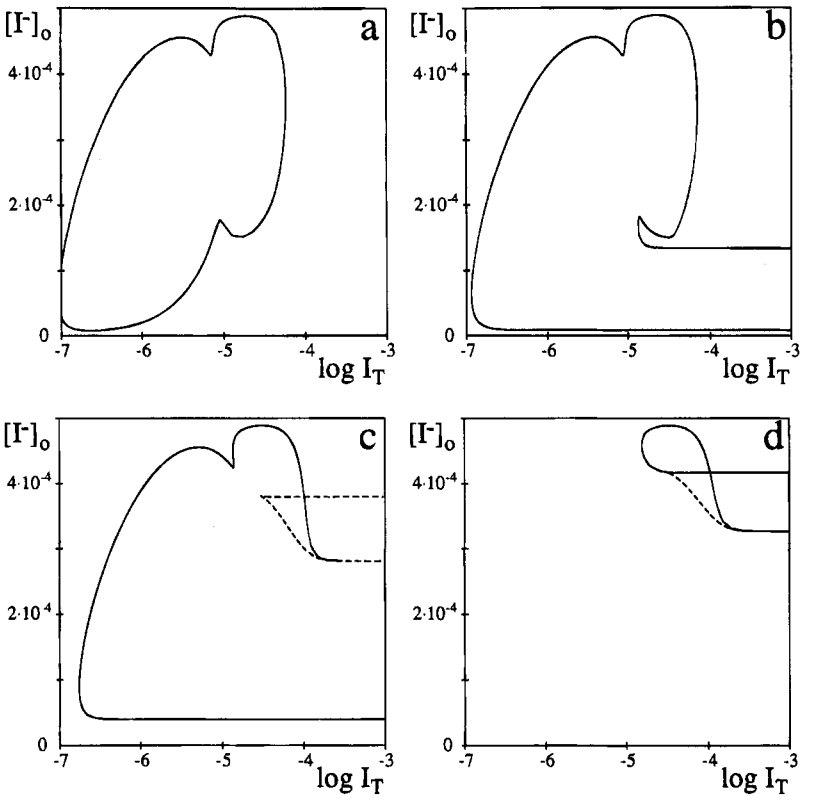

Figure 3. Dynamical control of the CDI reaction. Two-parameter bifurcation diagrams with Hopf (solid) and saddle-node (dashed) bifurcation lines. Oscillations occur inside the Hopf curve, and bistability occurs inside the saddle-node curve. Control parameters are $n = 5$, $\tau = 10\,000$ s, maximal flow rate (a) $k_{max} = 0.1\ s^{-1}$, (b) $k_{max} = 0.04\ s^{-1}$, (c) $k_{max} = 0.01\ s^{-1}$, (d) $k_{max} = 0.007\ s^{-1}$.

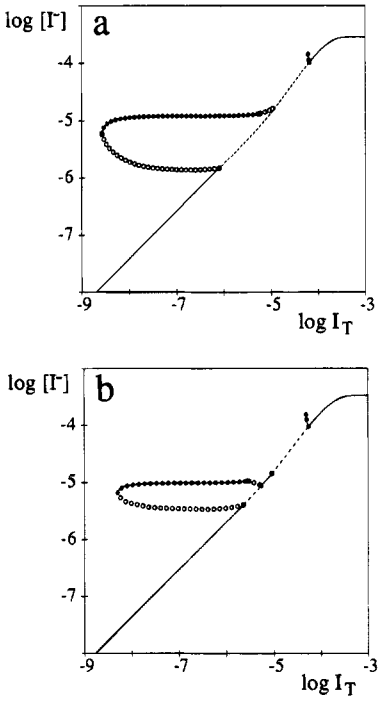

Figure 4. One-parameter bifurcation diagram of the CDI reaction with dynamical control: solid lines, stable steady states; dashed lines, unstable steady states; filled circles, branches of stable periodic solutions; empty circles, branches of unstable periodic solutions. Control parameters are $n = 5$, $\tau = 10\,000$ s, $k_{max} = 0.05\ s^{-1}$. Input iodide concentration (a) $[I^-]_0 = 4 \times 10^{-4}$ M, (b) $[I^-]_0 = 4.5 \times 10^{-4}$ M.

of the Hopf lines in the $[I^-]_0$–log I_T parameter plane for $[I^-]_0 = 4.5 \times 10^{-4}$ M.

Chaos and Bursting. The bifurcation analysis indicates that all branches corresponding to periodic solutions change their stability. However, in some cases at the same time that the periodic solution becomes unstable, the steady state also loses stability, so that the only stable solution is more complex behavior (see Figure 4).

Numerical simulations were carried out in the region of stable and unstable periodic solutions. Simple (single-period) oscillations with relatively large amplitudes of X, Y, and Z oscillations and small amplitude of k_0 oscillations were observed in the region which corresponds to the stable periodic solutions. Figure 5 shows an example of such oscillations. The period of the oscillations is much smaller than τ, and the iodide concentration varies rapidly around the control target concentration I_T. Because of the high value of τ, the change in flow rate is moderate in comparison with the concentration changes. Thus, the amplitude of the oscillations in the flow rate is small. As soon as an unstable periodic branch appears, the single-periodic solutions become unstable, and a period-doubling sequence occurs, leading to chaos and then ultimately to bursting behavior.

Figure 6a shows the period-doubling sequence leading to chaos in the k_0–I_T plane. Figure 6a was obtained from a Poincaré map where the variable k_0 was evaluated at $[I^-] = 10^{-7}$ M, for decreasing $[I^-]$. The projection of the chaotic attractor in the log $[I^-]$–k_0 phase plane is shown in Figure 6b. The dashed line in the figure represents the surface where the Poincaré maps were constructed. Thus, deterministic chaos emerges as an outcome of the control mechanism.

The period-doubling sequence appears when the target concentration I_T is increased. Chaos is replaced by bursting behavior when I_T is increased still further. An example of the bursting dynamics is shown in Figure 7. Bursting behavior exists in a rather wide range of parameter space. The unregulated CDI reaction can exhibit bursting when perturbed.[23,24,29] The regulated flow acts in a similar way. When the concentration of ClO_2 drops below a critical value, fast consumption of the remaining ClO_2 follows. Chlorine dioxide

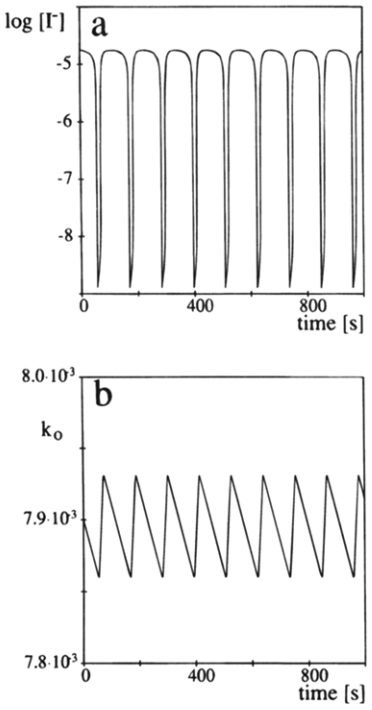

Figure 5. Dynamics of the CDI reaction with control−periodic oscillations. $[I^-]_0 = 4 \times 10^{-4}$ M; $I_T = 10^{-6}$ M. Time courses of iodide concentration (a) and flow rate k_0 (b). Other control parameters as in Figure 4.

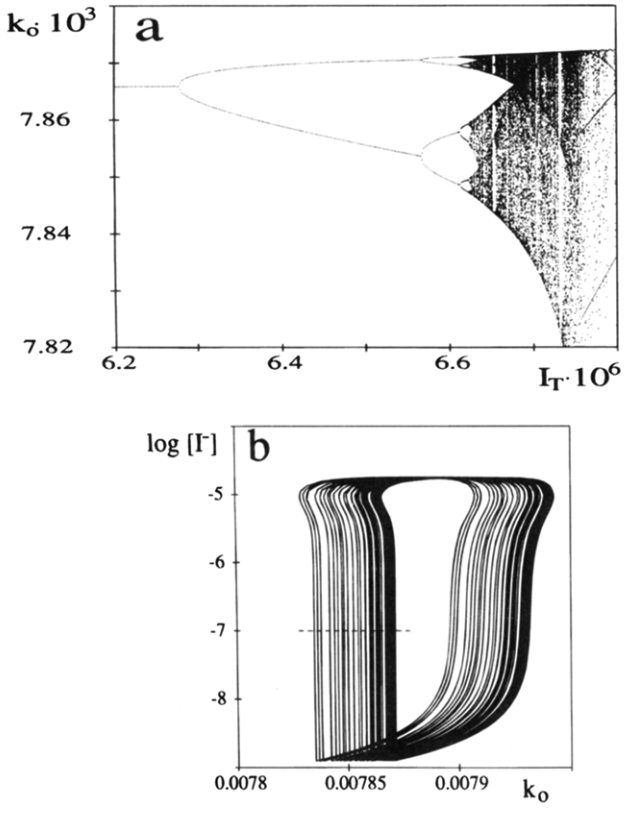

Figure 6. Dynamics of the CDI reaction with control−period-doubling sequence leading to chaos. $[I^-]_0 = 4 \times 10^{-4}$ M. (a) Diagram constructed from Poincare maps. (b) Chaotic attractor for $I_T = 6.7 \times 10^{-6}$ M. For other control parameters see Figure 4.

is not produced by any chemical reaction and can be restored only by inflow of new reagents, which is a relatively slow process. Part of the fresh solution of ClO_2 is immediately consumed by reaction R1, and reestablishment of a higher ClO_2 concentration may take a very long time. Oscillation appears again when the concentration of ClO_2 increases to its maximum value. The control mechanism periodically forces the system to surpass the critical concentration, and periods of quiescence alternate with periods of oscillation.

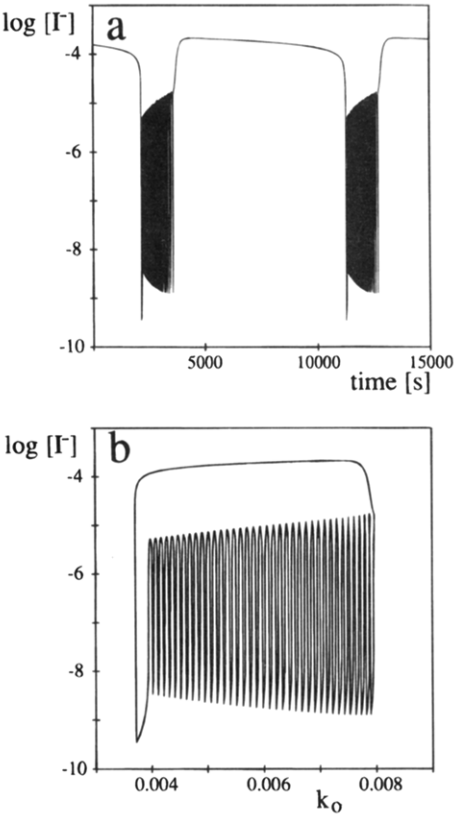

Figure 7. Dynamics of the CDI reaction with control−bursting behavior. $[I^-]_0 = 4 \times 10^{-4}$ M; $I_T = 7 \times 10^{-6}$ M. Time development of iodide concentration (a) and log[I^-]−k_0 phase plane (b). Other control parameters as in Figure 4.

We observe two different patterns of bursting behavior: one where large-amplitude oscillations alternate with periods of quiescence and another with alternation of low- and high-amplitude oscillations. The first pattern has previously been observed in the perturbed CDI reaction system.[23,24]

Response to Perturbations. One important consequence of the regulation scheme is the stabilization of dynamical behavior. When input concentrations are changed, the flow rate automatically adjusts and a dynamic pattern similar to the initial one is restored. In Figure 8 the arrows represent the moment when the input concentration of iodide was changed. Two different types of transient behavior were observed depending on how the change of the input iodide concentration was made. When the input concentration of iodide decreases, the amount of iodide in the system also decreases. The regulation process responds by increasing the flow rate in order to increase the amount of iodide in the system. Depending on how much the input concentration is changed, the transient adjustment of the flow rate can take a relatively short time or can be fairly long. For example, if the decrease in input concentration is less than 2%, the adjustment takes less than one-tenth of the value of τ (Figure 8a,b). If the change is more than 50%, however, the adjustment is very slow and after the transient time the period is somewhat (Figure 8c,d) or substantially (Figure 8e,f) different.

Different transient behavior is observed when the input iodide concentration is suddenly increased. Increase of iodide in the system supports consumption of chlorine dioxide, and $[ClO_2]$ drops below the critical value. The response of the regulation

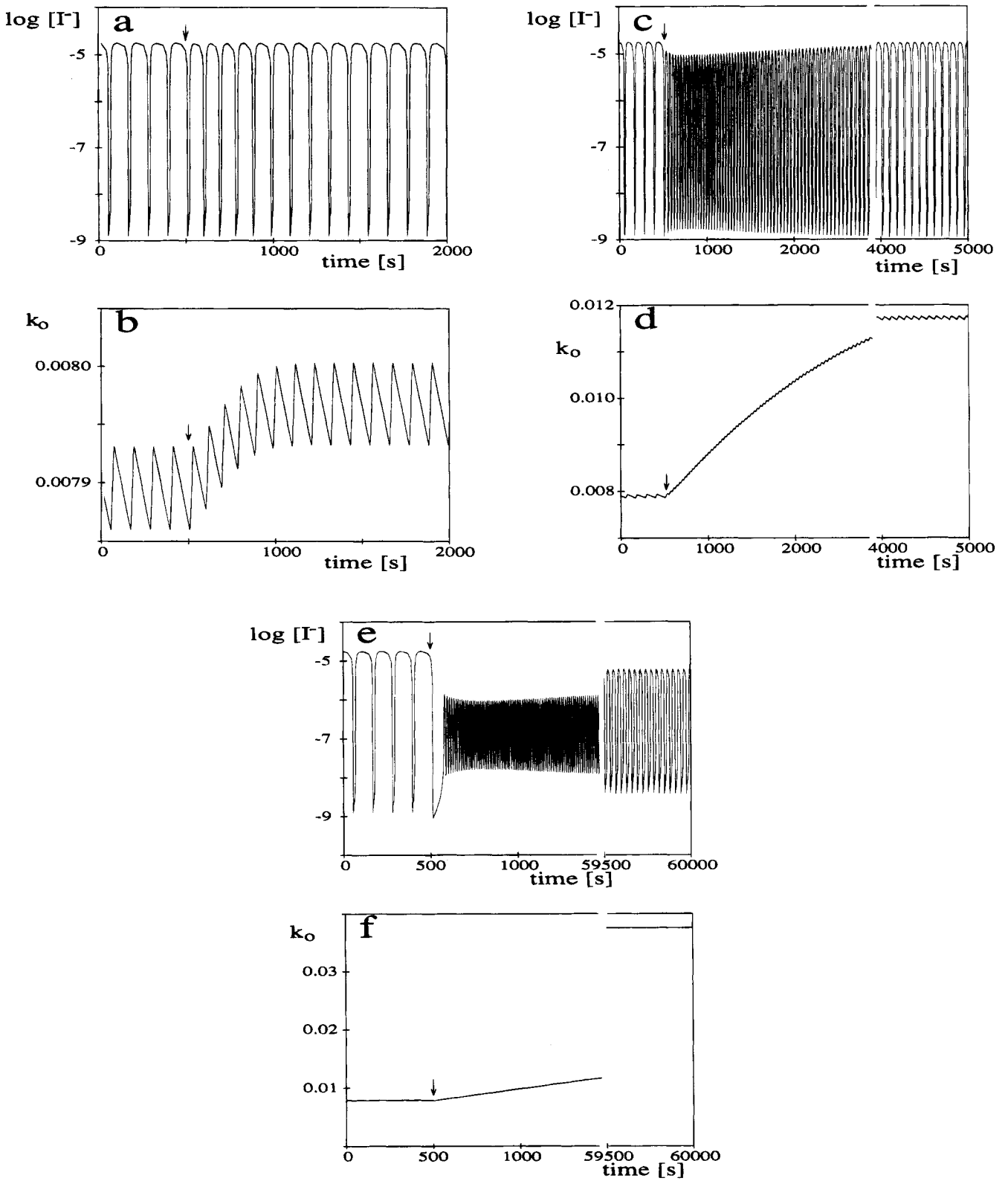

Figure 8. Response of the model of the CDI reaction to changes in input iodide concentration. Arrows indicate time when input iodide concentration was decreased from $[I^-]_0 = 4 \times 10^{-4}$ M to (a, b) $[I^-]_0 = 3.99 \times 10^{-4}$ M, (c, d) $[I^-]_0 = 3.5 \times 10^{-4}$ M, (e, f) $[I^-]_0 = 1.0 \times 10^{-4}$ M. $I_T = 5 \times 10^{-6}$ M. Other control parameters as in Figure 4.

mechanism is to decrease the flow rate, but this has only a modest effect on the iodide concentration in the system. As a result, the flow rate decreases more than is necessary. Only after the iodide concentration drops below the target value I_T and oscillations appear does the flow rate increase and start to adjust to the new conditions. These long adjustment times occur for relatively small iodide increases. Even for changes less than 1% it takes a relatively long time for the flow rate to adjust (Figure 9a,b). The transient period for an increase is approximately equal to τ, and this does not change significantly with the amplitude of the perturbation. If the increase of input iodide concentration is high enough, the regulation mechanism is unable to reestablish single-period oscillatory behavior and bursting occurs as the recovery regime (Figure 9c,d). At still higher values of the input iodide concentration the reaction is unable to oscillate and approaches a steady state.

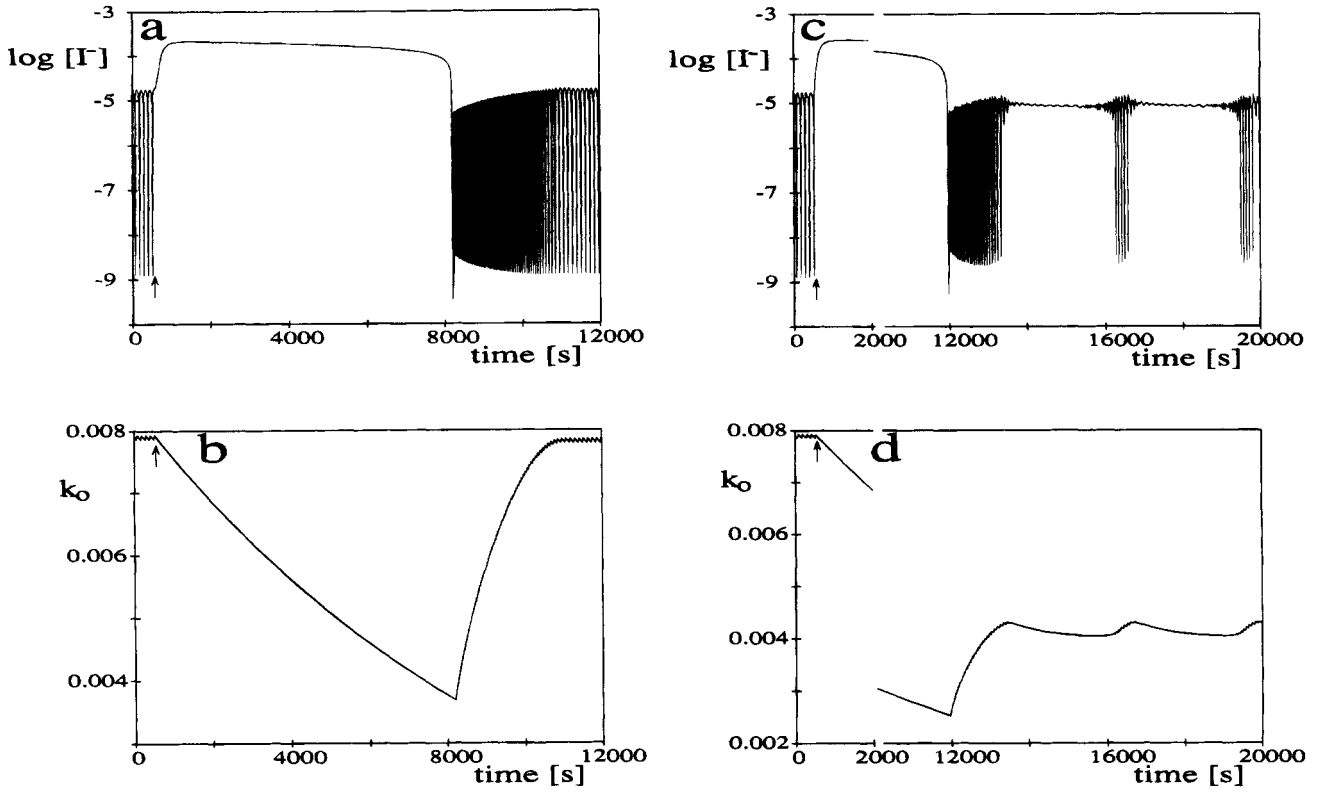

Figure 9. Response of the model of the CDI reaction to changes in input iodide concentration. Arrows indicate time when input iodide concentration was increased from $[I^-]_0 = 4 \times 10^{-4}$ M to (a, b) $[I^-]_0 = 4.01 \times 10^{-4}$ M, (c, d) $[I^-]_0 = 4.5 \times 10^{-4}$ M. For other control parameters see Figure 8.

Conclusions

The concentration of iodide in the CDI reaction correlates with the dynamical behavior of the system, as shown in Figure 1. A regulation mechanism that works like a chemostat and attempts to establish a specific iodide concentration is responsible for interesting dynamical behavior. Depending on how the target concentration is chosen, steady state or oscillatory behavior can be stabilized. Moreover, calculations show that a variety of complicated dynamics appear as an outcome of the control. Period-doubling sequences leading to chaos are probably a generic behavior of oscillatory systems with dynamical control, while bursting behavior seems to be a specific feature of the CDI reaction.

The responses to parameter changes obtained here are qualitatively similar to those reported for a neuron model.[25,30] A chemical oscillatory system may serve as a dynamical model system for a neuron. To mimic the dynamic regulation in a neuronal network, we can continue by studying the dynamic control of chemical oscillators both in single reactors and in networks of coupled reactor cells.

Acknowledgment. This work was supported by the National Science Foundation (Grants DMS-928266 to L.F.A. and CHE-9023294 and BNS-9009251 to I.R.E.) as well as by a U.S.–Czechoslovakia cooperative (INT-8912462) grant.

References and Notes

(1) MacDonald, N. *Time Lags in Biological Models*, Lecture Notes in Biomathematics; Springer-Verlag: New York, 1978; Vol. 27.
(2) Rapp, P. E. In *Mathematical Models in Molecular and Cellular Biology*; Segal, L. A., Ed.; Cambridge University: New York, 1980.
(3) Murray, J. D. *Mathematical Biology*; Springer-Verlag: Berlin, 1989.
(4) Schell, M.; Ross, J. *J. Chem. Phys.* **1986**, *85*, 6489.
(5) Epstein, I. R. *Int. Rev. Phys. Chem.* **1992**, *11*, 135.
(6) Aris, R.; Amundson, N. R. *Chem. Eng. Sci.* **1958**, *7*, 121.
(7) Chang, M.; Smitz, R. A. *Chem. Eng. Sci.* **1975**, *30*, 21.
(8) Chang, M.; Smitz, R. A. *Chem. Eng. Sci.* **1975**, *30*, 837.
(9) Ding, J. S. Y.; Sharma, S.; Luss, D. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 76.
(10) Bruns, D.; Bailey, J. *Chem. Eng. Sci.* **1975**, *30*, 755.
(11) Bruns, D.; Bailey, J. *Chem. Eng. Sci.* **1977**, *32*, 257.
(12) Laplante, J. P. *J. Phys. Chem.* **1989**, *93*, 3882.
(13) Hjelmfelt, A.; Ross, J. *J. Phys. Chem.*, in press.
(14) Weiner, J.; Holz, R.; Schneider, F. W.; Bar-Eli, K. *J. Phys. Chem.* **1989**, *93*, 2704.
(15) Weiner, J.; Schneider, F. W.; Bar-Eli, K. *J. Phys. Chem.* **1992**, *96*, 8915.
(16) Holz, R.; Schneider, F. W. *J. Phys. Chem.* **1993**, *97*, 12239.
(17) Romeiras, F. J.; Grebogi, C.; Ott, E.; Dayawansa, W. P. *Physica* **1992**, *58D*, 165.
(18) Pyragas, K. *Phys. Lett.* **1992**, *A170*, 421.
(19) Peng, B.; Petrov, V.; Showalter, K. *J. Phys. Chem.* **1991**, *95*, 4957.
(20) Petrov, V.; Gáspár, V.; Masere, J.; Showalter, K. *Nature* **1993**, *361*, 240.
(21) Schneider, F. W.; Blittersdorf, R.; Förster, A.; Hauck, T.; Lebender, D.; Müller, J. *J. Phys. Chem.* **1993**, *97*, 12244.
(22) Chevalier, T.; Freund, A.; Ross, J. *J. Chem. Phys.* **1991**, *95*, 308.
(23) Dolnik, M.; Epstein, I. R. *J. Chem. Phys.* **1992**, *97*, 3265.
(24) Dolnik, M.; Epstein, I. R. *J. Chem. Phys.* **1993**, *98*, 1149.
(25) LeMasson, G.; Marder, E.; Abbott, L. F. *Science* **1993**, *259*, 1915.
(26) Lengyel, I.; Rábai, G.; Epstein, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 9104.
(27) Marek, M.; Schreiber, I. *Chaotic Behavior of Deterministic Dissipative Systems*; Cambridge University: Cambridge, 1991.
(28) Lengyel, I.; Li, J.; Epstein, I. R. *J. Phys. Chem.* **1992**, *96*, 7033.
(29) Dolnik, M.; Kosek, J.; Votrubova, V.; Marek, M. *J. Phys. Chem.* **1994**, *98*, 3707.
(30) Abbott, L. F.; LeMasson, G. *Neural Comp.* **1993**, *5*, 823.