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Critical Slowing Down in the Bistable Iodate-Arsenic(III) Reaction

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Relaxation kinetics in the bistable iodate oxidation of arsenic(III) have been investigated. Evidence for "critical slowing down" has been found as the bistability hysteresis limits are approached. The relaxation behavior is accounted for with a simple two variable model.

In the past few years, a number of autocatalytic reactions have been found to exhibit multiple steady states in continuous flow stirred tank reactors (CSTR).[1-7] These reactions exhibit two or more steady states over a range of a particular system constraint, such as reactor residence time or a reactant concentration in the feed. The relaxation of a perturbed multistable system to a particular steady state is of special interest because the phenomenon of "critical slowing down" may be exhibited. Nitzan et al.[8] and Heinrichs and Schneider[9] have shown with model systems that, at a hysteresis limit or critical point, relaxation times diverge to become infinitely long.[10] We report in this Letter the first quantitative study of critical slowing down in a bistable chemical system.

The autocatalytic iodate oxidation of arsenous acid can be conveniently described in terms of the iodate oxidation of iodide (process A) and the arsenic(III) reduction of iodine (process B). These processes with their corre-

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (A)$$

$$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2I^- + 2H^+ \qquad (B)$$

sponding empirical rate laws generate near quantitative descriptions of the bistability[3] and chemical wave[11] behavior of the reaction.

In reaction mixtures containing excess arsenous acid, a very simple empirical rate law model may be developed. Process A is rate determining for the overall reaction ((A) + 3(B) or (I)); therefore, the rate of iodide autocatalysis

$$IO_3^- + 3H_3AsO_3 = I^- + 3H_3AsO_4 \qquad (I)$$

$$R_\alpha = -d[IO_3^-]/dt = (k_1 + k_2[I^-])[I^-][IO_3^-][H^+]^2 \qquad (\alpha)$$

is governed by the empirical rate law for process A,[12] eq α. The rate of the reaction depends only on [I$^-$] and [IO$_3^-$] since hydrogen ion concentration is maintained constant by buffering the reaction mixture. Rate eq N1 and N2 for

$$d[I^-]/dt = R_\alpha + k_0([I^-]_0 - [I^-]) \qquad (N1)$$

$$d[IO_3^-]/dt = -R_\alpha + k_0([IO_3^-]_0 - [IO_3^-]) \qquad (N2)$$

these two variables are generated from net reaction I and rate law α, where k_0 is the reciprocal residence time of the reactor and $[I^-]_0$ and $[IO_3^-]_0$ are the feed concentrations. Because I$^-$ and IO$_3^-$ are the only stoichiometrically significant iodine containing species, their concentrations are related by $[IO_3^-]_0 + [I^-]_0 = [IO_3^-] + [I^-]$. The steady-state concentrations of iodide as a function of k_0, shown in Figure 1a, are obtained by combining this stoichiometric relation with (N1) or (N2) to yield a cubic equation in $[I^-]_s$.

$$0 = (k_1 + k_2[I^-]_s)([IO_3^-]_0 + [I^-]_0 - [I^-]_s)[I^-]_s[H^+]^2 + k_0([I^-]_0 - [I^-]_s) \qquad (1)$$

The system is bistable for the values of k_0 where branch α and branch β overlap in Figure 1a.

A linear stability analysis[13] of the two variable model (N1)-(N2) generates two eigenvalues for any particular steady state which determine the stability of that steady state. These eigenvalues in terms of reactant concentrations and the steady-state concentration of iodide are given by eq 2. The relaxation rate constants for the decay of

$$\lambda_0 = -k_0$$

$$\lambda_{\alpha,\beta,\gamma} = k_1([I^-]_0 + [IO_3^-]_0 - 2[I^-]_s) + k_2[I^-]_s(2[I^-]_0 + 2[IO_3^-]_0 - 3[I^-]_s) - k_0 \qquad (2)$$

infinitesimal perturbation to a steady state are given by $-\lambda_i$. When one or more eigenvalues are positive, perturbations grow, indicating an unstable steady state. The eigenvalues calculated from eq 2 for branches α, β, and γ are shown in Figure 1b. Eigenvalues λ_α,λ_0 and λ_β,λ_0 are negative for stable branches α and β, respectively, and for the unstable branch γ, λ_γ is positive and λ_0 is negative.

The relaxation time is defined as the time necessary for a perturbation to decay to $1/e$ of its initial amplitude. When the eigenvalues differ sufficiently, the smallest eigenvalue governs the relaxation and the relaxation time is given by $\tau = -1/\lambda_i$. Figure 1b shows that, as the hysteresis limit for branch α is approached, the eigenvalue λ_α rapidly approaches zero. Eigenvalue λ_β similarly approaches zero as the hysteresis limit for branch β is approached. As these limits are approached, relaxation times become very long and critical slowing down is exhibited.

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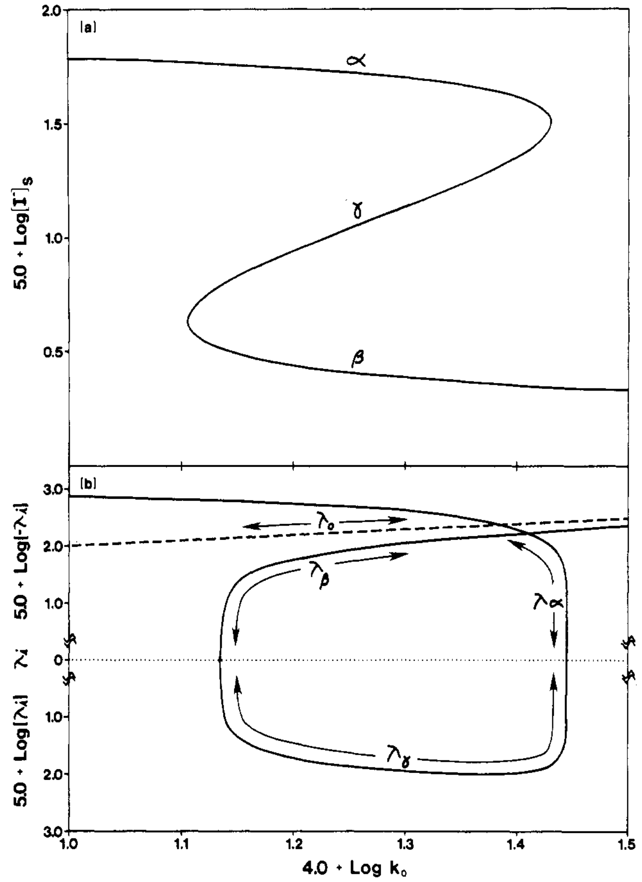

Figure 1. (a) Iodide concentration as a function of k_0 calculated from model (N1)–(N2). Reactant concentrations: $[IO_3^-]_0 = 6.595 \times 10^{-4}$ M, $[I]_0 = 1.85 \times 10^{-5}$ M. Constant concentration: $[H^+] = 6.9 \times 10^{-3}$ M. Rate constants: $k_1 = 4.5 \times 10^3$ M^{-3} s^{-1}, $k_2 = 4.5 \times 10^8$ M^{-4} s^{-1}. (b) Eigenvalues for α branch (λ_α,λ_0), β branch (λ_β,λ_0), and γ branch (λ_γ,λ_0) in (a).

Figure 2 shows reciprocal first-order rate constants as a function of k_0 for the relaxation of perturbations in iodide concentration. In each experiment, the iodide concentration was increased by about 10% above the α branch steady-state concentration by microliter injections of KI reagent. Iodide concentration was measured as a function of time with an iodide-selective electrode and plots of ln $([I^-] - [I^-]_s)$ vs. time were linear. Figure 2 shows that, as the hysteresis limit for branch α at $k_0 = 3.35 \times 10^{-3}$ s^{-1} is approached,[14] the relaxation times become extremely long, just as predicted by the eigenvalue analysis of model (N1)–(N2). Also predicted by the analysis is the shallow minimum in Figure 2, which occurs at the intersection of the eigenvalues λ_α and λ_0 in Figure 1b.

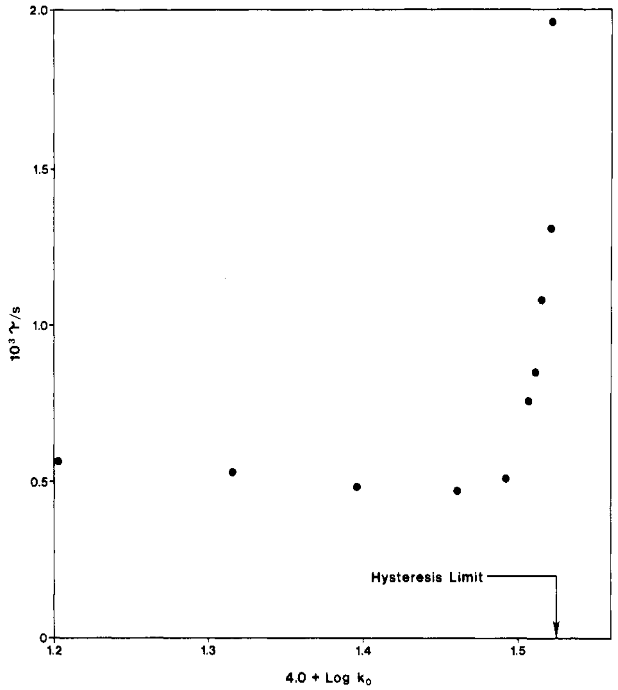

Figure 2. Relaxation times τ as a function of k_0. Solid points show measured reciprocal first-order rate constants. Reactant concentrations: $[IO_3^-]_0 = 6.595 \times 10^{-4}$ M, $[I^-]_0 = 1.85 \times 10^{-5}$ M, $[As(III)]_0 = 1.965 \times 10^{-3}$ M. Acidity ($[H^+] = 6.9 \times 10^{-3}$ M) maintained constant with 0.02 M HSO_4^-/0.04 M SO_4^{2-} buffer. Temperature: 25.0 ± 0.2 °C. Reactor volume: 34.1 mL.

The critical slowing down behavior in bistable chemical systems is suggestive of behavior observed in equilibrium phase transitions. In the system reported here, a transition from the α to β branch (or from the β to α branch) can be considered a first-order nonequilibrium phase transition.[8,15] A detailed investigation of the relaxation behavior in the iodate–arsenic(III) system, including the behavior near the critical point, will be reported in a future paper.

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Registry No. IO_3^-, 15454-31-6; H_3AsO_3, 13464-58-9.

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(14) The hysteresis limit for branch α predicted by model (N1)–(N2) differs slightly from the experimental value. Quantitative agreement between experiment and calculation can be obtained by setting $k_2 = 5.1 \times 10^8$ M^{-4} s^{-1}.

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