recombination remain to be clarified.

A second important point of this study is that the recovery of the induced absorption decay at 720 nm remains incomplete. During the first 100 ps after the femtosecond ionization of water molecules, the fast recombination represents around 50% of the early signal. This percentage is higher than the value that has been obtained in the nanosecond range with picosecond pulse radiolysis of pure water.^{2,3} The authors have observed that from 200 ps to 3 ns the hydrated electron decays to 15% its initial value.³ This apparent discrepancy between photolysis and radiolysis experiments can be caused by the difference in the observation time range, the injection modes of excess electrons which differ by the residual energy, and the initial spatial distribution of electronradical pair.

Our femtosecond investigations suggest that a fraction of excess electrons may have trapping and solvation distances greater than the Onsager radius ($r_c = e^2/4\pi\epsilon kt = 7$ Å in water) and escape far from the geminate primary radicals H_3O^+ or OH. From the available data in the literature, the assumed thermalization length of electrons in liquid water is in the range 20-50 Å.¹⁵⁻¹⁷ Indeed the electrons that are not hydrated in the vicinity of H_3O^+ or OH have a low probability of undergoing a fast geminate recombination process because the long-range Coulomb-type interactions remain negligible.

Further experiments are in progress to determine whether the percentage of geminate recombination of electron-radical pair at early times is dependent on the kinetic energy of excess electrons and on the initial distribution of hydrated electrons near the counterion H_3O^+ or the hydroxyl radical OH.

These femtosecond investigations on geminate pair recombination provide fundamental information about the behavior of photoejected epithermal electrons (E = 1.5 eV) in pure aqueous media and permit a direct estimate of the rate of reactivity of hydrated electron with primary radicals. We are comparing the time-resolved femtosecond data with transient solutions of the Smoluchowski equation governing diffusive geminate charge pair recombination in a Coulombic well and which takes into account a radial distribution function of the charge pair separation.^{18,19} Moreover, the analysis of the femtosecond reactions in the framework of molecular dynamics simulation and computed stochastic models^{4,6,7,20,21} would permit an assessment of the importance of the initial spatial distribution of ionized species, the proton jump, high-frequency fluctuations of the electrostatic potential, or local dynamical molecular structure of the surrounding fluid in the fast radical reactions, including geminate electron-ion pair or electron-radical recombinations.

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Stabilization of Unstable States in the Bistable Iodate-Arsenous Acid Reaction in a **Continuous Flow Stirred Tank Reactor**

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In this paper, we present an algorithm through which unstable states can be stabilized in bistable chemical systems. The control algorithm is designed to be easy to implement through microcomputer control of the bifurcation parameter. As a test case and example, we consider the unstable branch of the bistable iodate-arsenous acid reaction in a continuous flow stirred tank reactor.

Introduction

This paper is concerned with the stabilization of unstable states in bistable chemical systems. The problem is of interest from both the applied and the fundamental point of view. On the practical side, the deliberate operation of chemical reactors near or at an unstable steady state often allows for optimum yield and/or selectivity.¹ It is therefore no surprise that most of the early work on this problem has been reported mainly in the chemical engineering literature.¹⁻⁶ The use of feedback controls to stabilize

unstable states was first explored by Aris and Amundson² and later by many others.³⁻⁶ An alternative approach through which unstable states can be stabilized by appropriate periodic operation of the input flow rates has recently been suggested by Meerkov and collaborators.^{1,7} In a recent series of experiments, Ross et al. used a delayed feedback loop to stabilize and map the unstable branch in two different illuminated thermochemical systems.⁸ The technique used is elegant and yields spectacular results. Unfortunately, the requirement that the dynamical equations remain unchanged by the feedback mechanism makes this technique difficult to apply in the case of more complicated systems. From

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the fundamental point of view, very little is known of these unstable states as they usually are not accessible experimentally. Yet, the accurate determination of the unstable branch is a key element in many fundamental problems related to instabilities in chemical systems. Examples of such problems are (1) understanding the mechanism through which transitions are triggered in multistable systems, $^{8,9}(2)$ the theory of transition rates in bistable systems driven by external noise,¹⁰ and (3) the study of the relaxation of unstable states in chemical systems.^{11,12}

In this paper, we suggest an algorithm through which unstable states can, in principle, be stabilized ad infinitum. Our approach is based on the use of a feedback control loop. The key parameters of the control loop are the relaxation rate and a parameter that we define as the "action threshold parameter". Our approach is not entirely new, and its seeds can be found in a variety of papers on feedback control of unstable states.¹⁻⁶ We believe, however, that our method has the merit of being easier to implement than previous ones¹⁻⁶ and could, therefore, be used in the many systems that are of current interest in nonlinear chemical dynamics.¹³ As a test case, we consider the bistable iodate-arsenous acid reaction in a continuous flow stirred tank reactor (CSTR).

Experimental Section

Our experiments were carried out in a CSTR, the design of which was described elsewhere.¹² Reactants were fed separately to the reactor by means of two ISCO high-pressure liquid chromatography pumps equipped with Hastelloy C-276 inert heads. Flow rates of each reactant were kept identical at all times. All tubings were made of Teflon. The pumps were microcomputer controlled via a Keithley DAS 500 data acquisition and control system. An iodide selective electrode (Orion Model 94-53A) was used to monitor the iodide concentration in the reactor. Fresh reactant solutions were prepared daily and buffered at pH 2.15 with a Na_2SO_4/H_2SO_4 buffer. The flow rate resolution of the pumps was ± 0.05 mL/min.

Results

The autocatalytic oxidation of arsenous acid in a CSTR is known to be bistable over a wide range of control parameters.^{14,15} In excess arsenous acid, the stoichiometric reaction is given by

$$IO_3^- + 3H_3AsO_3 \Rightarrow I^- + 3H_3AsO_4$$

where the iodide concentration $X = [I^{-}]$ satisfies a rate law of the form

$$dX/dt = pX^3 + qX^2 + rX + s = f(X)$$
(1)

with p, q, r, and s given by

$$p = k_0 k_2' \tag{2a}$$

$$q = k_0 [k_1' - k_2' (B_0 + X_0)]$$
(2b)

$$r = k_0 [1 - k_{k1}' (B_0 + X_0)]$$
 (2c)

$$s = -k_0^2 X_0 \tag{2d}$$

In the expressions above, we use Showalter's notation and values for k_1 and k_2 , i.e.^{14,15}

$$k_1' = k_1 [H^+]^2 = 4.5 \times 10^3 [H^+]^2 M^{-3} s^{-1}$$
 (3a)

$$k_{2}' = k_{2}[H^{+}]^{2} = 4.5 \times 10^{8}[H^{+}]^{2} M^{-4} s^{-1}$$
 (3b)

$$B_0 = [IO_3^-]_0$$
 (3c)

$$X_0 = [I^-]_0 \tag{3d}$$



Figure 1. Steady-state iodide concentration X, calculated from eq 1 $[(dX/dt)_{X_1} = 0]$ for $[H_3AsO_3]_0 = 3.00 \times 10^{-3}$ M, $[IO_3^-] = 7.2 \times 10^{-4}$ M, $[I^-]_0 = 3.2 \times 10^{-5}$ M, and $[H^+]_0 = 1.12 \times 10^{-2}$ M. Solid lines represent stable steady states whereas the dotted line represents the unstable branch of steady states.



Figure 2. Schematic representation of potential V(X) as a function of the iodide concentration X and the total reactant flow rate ($\propto k_0$). V(X)was calculated from eq 5 for 20 equidistant values of k_0 between points A and B in Figure 1. Other conditions are as per Figure 1. See text for comments.

where $[]_0$ refers to the concentration of the mixed reactant stream before any reaction takes place. k_0 is the reciprocal residence time in the reactor and is proportional to the total reactant flow rate. The polynomial f(X) is cubic and, therefore, may possess, for a range of parameters, three positive roots corresponding to three distinct steady states. In these cases, two of the steady states are stable and one is unstable^{14,15} (Figure 1). In order to illustrate our approach, let us consider f(x) as deriving from a potential V(X) such that

$$f(X) = -\frac{\partial V}{\delta X} \tag{4}$$

with

$$V(X) = aX^4 + bX^3 + cX^2 - sX$$
 (5)

and a = -p/4, b = -q/3, and c = -r/2.¹⁶ A schematic representation of potential V(X) is given in Figure 2 for a set of points between A and B in Figure 1. For convenience here, the total reactant flow rate ($\propto k_0$) is used as our bifurcation parameter. In this figure, stable steady states correspond to potential minima, while the unstable states correspond to maxima. The latter are the ones in which we are interested. Let us now assume that the system is first prepared in a stable state corresponding to point A (Figures 1 and 2). Next, assume the flow rate is suddenly

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Figure 3. Real-time traces showing the use of control algorithm (6) in the stabilization of an unstable state: (a) the iodide versus reference electrode potential plotted against time; (b) the corresponding trace of flow rate versus time for the same experiment. Experimental conditions are as per Figure 1. Initially, the system is first brought to a stable steady state and the reactant flow stopped at point 1. As seen in (a), the system then starts its transition to the upper branch of stable steady states. At a preset EMF value (point 2), the feedback control (6) is triggered. The system then gradually evolves to a stationary unstable state (point 3) after a brief overshoot. In this example, the initial flow rate guess used as a starting point at (2) was intentionally taken as being far from the approximate location of the unstable state at that flow rate. The time to stabilize the unstable state was therefore much longer than usual ($\simeq 15$ min). For that particular experiment, we used $\Delta X_c = 0.5$ mV and $\Delta f =$ 0.5 mL/min.

brought to a point corresponding to B. As seen in Figures 1 and 2, the upper branch of steady states is no longer stable and, as a result, the system gradually undergoes its transition to the lower branch of stable states. The idea behind our control loop is to continuously monitor the relaxation of the system and, according to its "direction", increase or decrease the flow rate in such a way as to gradually move the system over the ridge. In our example, the system at point B would spontaneously tend to relax to the lower (right-hand) steady state, thereby forcing a decrease in the flow rate. A few iterations of the control loop would eventually yield a path similar to BC (Figure 2). At point C, the sign of the relaxation function changes and the flow rate would be increased. As a result, the system gets closer and closer to path EF which eventually becomes a more or less periodic function of time. The unstable state corresponding to the moving average of path EF would then be stabilized. Assuming a continuous monitoring of X (small Δt), the algorithm through which this strategy is implemented can be written as

$$f(t+\Delta t) = f(t) + (\Delta f)[\delta(\Delta X - \Delta X_c)][\text{sign } (dX/dt)] \quad (6)$$

where f(t) and $f(t+\Delta t)$ are respectively the flow rates at time t and $(t + \Delta t)$, and $\Delta X = X(t+\Delta t) - X(t_t)$, t_t being the time at which the last flow rate correction was made. Δf is the flow rate increment, and ΔX_c is a parameter that we define as the action threshold parameter. This parameter, along with its associated delta function, is here introduced more for practical than fundamental reasons. However, this parameter is essential to the proper implementation of our control algorithm. Its significance is as follows. In any experiment, noise is always present to some extent in the monitoring process. For example, the continuous monitoring of $X = [I^-]$ at a stationary state would reveal that dX/dt is continuously and randomly changing sign as a function



Figure 4. Iodate-arsenous acid bistability showing the experimental stable steady states (solid symbol) and unstable states (open symbol), as determined using control algorithm (6). Experimental conditions were as per Figure 1.

of time. In the control algorithm (6), the delta function $\delta(\Delta X - \Delta X_c)$ ensures that the monitored variable changes by a minimum preset amount ΔX_c before any change in flow rate occurs. Taking ΔX_c larger than the average noise deviation ensures a smooth path toward an unstable state.

Figures 3 and 4 illustrate experimental results obtained upon implementation of control algorithm (6) for the iodate-arsenous acid reaction. The results of Figure 4 were obtained in a set of runs that were done over a period of 1 week. The unstable states were found to be amazingly consistent and, as seen in Figure 4, fit nicely between the two branches of stable states. No attempt was made to compare the experimental unstable states with simulation results, as the latter are only qualitatively correct.¹⁴ Our assessment of algorithm (6) can be summarized as follows. (a) Control algorithm (6) is fairly robust and "moderately" independent of the choice of Δf . Small values of Δf usually yield more accurate values of the unstable-steady-state location. However, multiple overshoots are then common,⁶ and the time required to reach an unstable state is longer. (b) In its present form, algorithm (6) does not allow one to "target" an unstable state and to reach it. The state reached depends on the operational parameters. However, a few tries are usually enough to pinpoint a region and to map it. Moreover, algorithm (6) could easily be improved to accommodate a target option. (c) One nice feature of our algorithm is that it does not change the stability properties of the stationary states.⁵ Once an unstable state is reached, flow rate corrections occur only occasionally (Figure 3). The system then spends most of its time in an unstable equilibrium in a narrow region on the potential ridge, obeying its deterministic kinetics. We have also verified that the algorithm does not change the location and stability properties of the stable steady states. The steady states obtained with and without feedback were the same, within our experimental uncertainty. Whether or not algorithm (6) would create spurious states in more complicated situations (e.g., close proximity of more than two states with different stabilities) still remains to be verified. (d) Although our algorithm does not impose any limits on the time for which an unstable state can be stabilized, it is difficult in practice to stabilize an unstable state for an extended period of time. This is especially true for those states that are close to the marginal stability points. In this case, the relaxation is very slow in one direction and fast in the other. The system then has a tendency to drift toward the nearby stable state or to an unstable state further away from the hysteresis limit. (e) An interesting point raised by one of the referees is how the availability of more degrees of freedom might affect the technique. First, let us emphasize that the arsenous acid system was deliberately chosen for this initial study because of its simplicity. In excess arsenous acid, its one-dimensional structure allows the definition and calculation of a unique global potential describing the relative dynamic stabilities of the steady states. This potential ensures that the only attractors in the vicinity of the unstable branch are two sets of stable nodes. In multidimensional systems, this is not necessarily the case. A variety of attractors of different topology can exist in the phase space in the vicinity of the separatrix considered. The mapping of a given unstable branch by our technique would then be more delicate but nevertheless possible, provided the attractors are not too close. In multidimensional systems, a more direct initial approach of the unstable branch (e.g., through sudden injections of reagents¹⁷)

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might however be preferable to the initial "free fall" technique used in this paper.

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Intramolecular Energy Transfer by an Electron/Energy Transfer "Cascade"

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In the ligand-bridged complex $[(bpy)(CO)_3Re^{I}(4,4'-bpy)Re^{I}(CO)_3(4,4'-(CO_2Et)_2bpy)]^{2+}$ (bpy is 2,2'-bipyridine; 4,4'-bpy is 4,4'-bipyridine; 4,4'-(CO₂Et)₂bpy is 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine) Re^T \rightarrow bpy excitation is followed by rapid, $k(CH_3CN,295 \text{ K}) > 2 \times 10^8 \text{ s}^{-1}$, intramolecular energy transfer to give [(bpy)(CO)₃Re^I(4,4'-bpy)Re^{II}(CO)₃(4,4'-bip)(CO)₃(4 (CO₂Et)₂bpy^{*-})]^{2+*}. Energy transfer appears to occur by an electron/energy transfer "cascade" involving the bridging ligand.

A theme in our work has been the construction of designed molecular structures in which the occurrence and directionality of intramolecular light-induced electron or energy transfer can be controlled.^{1,2} We report here an example where intramolecular energy transfer can be controlled in a ligand-bridged complex by changing the acceptor properties of the bridging ligand.

Our studies have been based on the series of complexes $[(4,4'-(X)_2bpy)(CO)_3Re^{I}(4,4'-bpy)Re^{I}(CO)_3(4,4'-(X')_2bpy)]^{2+}$ with (I) $X = X' = CO_2Et$, (II) $X = X' = NH_2$, (III) X = X' =H, and (IV) X = H and $X' = CO_2Et$. The ligand abbreviations are b or bpy for 2,2'-bipyridine, 4,4'-bpy for 4,4'-bipyridine, and $4,4'-(X)_2$ bpy for $4,4'-(X)_2-2,2'$ -bipyridine (X = H, NH₂, or CO_2Et).³



Shown below is a schematic representation of the structure which

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illustrates the facial geometry at the individual Re(I) sites in the ligand-bridged complexes.4



Following $d\pi(Re) \rightarrow \pi^*(bpy;4,4'-bpy)$ metal to ligand charge transfer (MLCT) excitation of the ligand bridged complexes, the final electron acceptor site can be controlled by varying the substituents, X and X'.⁵ In $[(b(CO_2Et)_2)(CO)_3Re^{I}(4,4'-bpy) Re^{I}(CO)_{3}(b(CO_{2}Et)_{2})]^{2+}$ cyclic voltammetric measurements show that the first ligand-based reduction occurs at $E_{1/2} = -0.82$ V vs SSCE.⁶ Because of the electron-withdrawing ester substituents, the reduction is localized at the $(bpy(CO_2Et)_2)$ ligands. In CH₃CN at 295 \pm 2 K, laser flash excitation⁷ at 390 nm into the $d\pi(\text{Re}) \rightarrow \pi^*(b(\text{CO}_2\text{Et})_2; 4, 4'$ -bpy) MLCT manifold leads to an emission ($\lambda_{max} = 650 \text{ nm}$) which decays with $\tau = 118 \pm 3 \text{ ns}$. The transient absorbance spectrum⁸ in Figure 1A, which was acquired

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⁽³⁾ The symmetrical complexes were obtained in refluxing THF by the (a,4'-(X)₂-bpy)(CO)₃Re¹(CF₃SO₃)]. The unsymmetrical complexes were synthesized from [(bpy)(CO)₃Re¹(L)]⁺ (L = 4,4'-bpy or 3,3'-(CH₃)₂-4,4'-bpy) and an excess of [(4,4'-(CO₂Et)₂-bpy)(CO)₃Re¹(CF₃SO₃)]. The product salts precipitated spontaneously or were precipitated by the addition of ethyl ether. Purifications were achieved by chromatography on silica gel (75–230 mesh) by using a 1:2 (v:v) CH_3CN/CH_2Cl_2 solvent mixture. After the solids were collected by evaporation, they were rechromatographed, if necessary, by starting with the same solvent mixture and ending with 10:1 acetone/water containing $\sim 5 \times 10^{-2}$ M [NH₄](PF₆) as eluent. The product was dried, redissolved in CH₃CN, and reprecipitated by the addition of ether. Satisfactory elemental analyses were obtained in all cases. ¹H NMR (CD₃CN, 200 MHz) spectra were consistent with the proposed formula. Complete experimental procedures will be described in a subsequent paper.

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⁽⁶⁾ All cyclic voltamogramms were obtained in argon deaerated 0.1 M $[N(n-C_4H_9)_4](PF_6)$ CH₃CN solutions vs SSCE by using a platinum disk as the working electrode at scan rates of 0.1 V/s.

⁽⁷⁾ Emission lifetime measurements were obtained by using a PRA LN 1000/LN 102 nitrogen laser/dye laser combination for sample excitation. Emission was monitored at a right angle to the excitation by using a PRA B204-3 monochromator and a cooled, 10-stage, Hamamatsu R928 PMT coupled to either a LeCroy 9400 or a LeCroy 8013 digital oscilloscope in-terfaced to an IBM PC. The absorbance (in 1-cm cuvettes) of the different solutions was ~ 0.1 at the excitation wavelength. Solutions were deoxygenated by Ar bubbling.

⁽⁸⁾ Transient absorbance measurements were performed by using the third harmonic of a Quanta Ray DCR-2A Nd:YAG laser. The excitation beam was coincident to an Applied Photophysics laser kinetic spectrometer including a 250-W pulsed Xe arc probe source, a f/3.4 grating monochromator, and a 5-stage PMT. The output was coupled to a Tektronix 7912 digital oscilloscope interfaced to an IBM PC. Electronic control and synchronization of laser, probe, and digital oscilloscope was achieved by electronics of our own design.