\[
  k_2 = \frac{-1}{[\text{OH}][\text{OCS}]} \frac{d[\text{OH}]}{dt} = \frac{k_a(k_b + k_c[M])}{k_a + k_b + k_c[M]}
\]

de which, if \(k_c[M] << k_b\) becomes
\[
  k_2 = \frac{k_c k_b}{k_a + k_b}
\]

This scheme is consistent with the observed second-order rate law and with the absence of any pressure dependence for \(k_2\).

If \(k_a >> k_b\), then \(k_2 = k_a k_b / k_a\) with the experimental activation energy given by \(E_a = E_b - E_a + E_b\). As explained (p 111 (case (a)(i)) in the analysis by Golden, the \(E_a - E_b\) may be positive or negative so that this scheme is consistent with a positive \(E_b\).

Alternatively, if \(k_a << k_b\), then \(k_2 = k_a / E_a\). According to Benson the addition of a radical to a stable unsaturated species generally requires a small positive activation energy so that this alternative is also consistent with our observation.

To check the feasibility of the assumption that \(k_c[M] << k_b\), we can assign to \(k_b\) a collision frequency value of about \(5 \times 10^{-10} \text{cm}^3 \text{s}^{-1}\) so that at 10 torr \(k_c[M] = 1.6 \times 10^8 \text{ s}^{-1}\). To establish the required inequality \(k_b\) would need to be greater than about \(10^9 \text{ or } 10^{10} \text{ s}^{-1}\) which is not unreasonable for the decomposition of an excited species. This would be consistent with our failure to observe the adduct OC(S)OH with the mass spectrometer.

It is also interesting to compare the observed \(A\) factor \((1.3 \times 10^{-12} \text{ cm}^3 \text{s}^{-1})\) for \(k_2\) with that obtained by transition-state theory. The \(A\) factor may be estimated by using statistical mechanics to obtain the standard entropy of the transition state, \(S^\ddagger\). This gives \(A = (e^R T / h) \exp(\Delta S^\ddagger / R) = 6.4 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}\) for the open ring O-C(OH)=S complex, which is about a factor of 5 greater than the experimental value. Going from this structure to a four-member ring it loses one OH free rotor but adds one out-of-plane bend of this ring. In a bending frequency of about 300 cm\(^{-1}\) is assumed, ring closure lowers \(S^\ddagger\) by \(~3.2\) eu. Consequently, \(A\) factor decreases to \(1.3 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}\) which is consistent with our measurement.

Finally, our value for \(k_2\) implies that the reaction of OH with OCS is virtually insignificant in atmospheric chemistry though a full discussion of this matter is best left to others better qualified than us.

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**Bistability in the Iodate Oxidation of Arsenous Acid**

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Kinetic bistability is exhibited in a tank reactor pumped with iodate and arsenous acid solutions. For a range of flow rates, the system may exist in either a high [I\(^{-}\)], high [I\(_2\)] stationary state or a low [I\(^{-}\)], low [I\(_2\)] stationary state. Iodide and hydrogen ion concentrations were measured as a function of flow rate in the bistable region. Transitions from one steady state to the other were induced by perturbations in [I\(^{-}\)] of a critical magnitude. A simple mechanism autocatalytic in iodide is proposed. Numerical integration of the rate equations yields behavior in good agreement with experiment.

**Introduction**

Examples of pumped isothermal chemical systems which exhibit multiple stationary states are few. Steady-state multiplicity has been actively investigated with theoretical models, but little information is available on experimental systems. Investigation of a number of multistable systems, preferably with somewhat different kinetic features, will be necessary for the development of a general theory for the phenomenon. Kinetic multistability is of practical importance in chemical manufacturing processes which utilize pumped tank reactors and may also be significant in biological systems as a mechanism for on/off switching.

The only bistable system understood in terms of elementary chemical reactions is the acidic bromate oxidation of cerium(III). Geiseler and Föllmer discovered that the system in a continuously stirred tank reactor (CSTR) may display two very different steady states over a range of flow rates. These states are stable to infinitesimal perturbation; however, transitions from one state to another may be induced by finite perturbations of a critical magnitude. Bar-Eli and Noyes have modeled the bistability behavior almost quantitatively by using the bromate chemistry of the Field–Köröös–Noyes (FKN) mechanism for the Be-
Transitions from one state to the other may be induced by perturbations in iodide concentration. Subcritical and supercritical perturbations were determined for a range of reactor residence times (reador volume divided by flow rate) when two distinct stationary states may be exhibited at particular flow rates. A number of heterogeneous and/or nonisothermal systems exhibit multiple stationary states. Steady-state multiplicity in various types of open chemical systems has been reviewed by Schmitz.12

In this paper, we report on the discovery and investigation of kinetic bistability in the iodate oxidation of arsenuous acid. De Kepper, Epstein, and Kustin13 have also discovered and investigated bistability in this reaction. Two distinct stationary states exist for a range of reactor residence times (reactor volume divided by flow rate) when two reactant solutions, one containing KI03 and the other arsenous acid, are fed into an isothermal CSTR. Transitions from one state to the other may be induced by perturbations in iodide concentration. Subcritical and supercritical perturbations were determined for a range of flow rates. In addition, we present a simple mechanism which is used to numerically simulate our experimental observations.

Chemical Reaction

The iodate oxidation of arsenite has been studied for over 60 yr.14 The closely related iodate oxidation of sulfite was first studied by Landolt15 in 1886, and both reactions are often referred to as “Landolt reactions”. In batch reaction a long induction period, characterized by a colorless solution, is followed by a sudden coloration due to the formation of I2. A variety of substances catalyze the reaction causing the induction period to be shortened. Bognár and Sárosi16 developed an analytical method for trace iodide by determining the induction period as a function of initial [I-]. In reaction mixtures containing starch, the colorless solution suddenly “blinks” black, making the reaction a particularly dramatic lecture demonstration (the “iodine clock”).

The reaction can be expressed as the sum of two basic processes:

\[ 5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \] (A)
\[ I_2 + H_3AsO_3 + H_2O = 2I^- + H_2AsO_4 + 2H^+ \] (B)

Process A is the Dushman reaction17 and process B is the Bar-Eli reaction.18 When iodate is in stoichiometric excess to arsenous acid, the net reaction is (A) + (B) or reaction I. Before arsenous acid is consumed, or if it is

\[ 5H_3AsO_3 + 2IO_3^- + 2H^+ = 5H_2AsO_4 + I_2 + H_2O \] (I)

in stoichiometric excess, the overall reaction is (A) + (B) or reaction II. In reaction mixtures containing excess IO3-, the reaction is

\[ 3H_3AsO_3 + IO_3^- = 3H_2AsO_4 + I^- \] (II)

iodide accumulates as H2AsO4 is oxidized; when H2AsO4 is consumed, the I- is rapidly oxidized to I2 in process A.

Although a variety of mechanisms for reaction II originally proposed by Roebuck18 has been challenged, and alternative explanations have appeared.20 Because the rate of process A is at least first order in iodide and its iodine product is converted to iodide by the more rapid process B, the overall reaction is autocatalytic in iodide. That the reaction is autocatalytic was shown in the early studies14 and was later used by Bognár and Sárosi16 to explain their analytical method for determining iodide.

Experimental Section

Materials and Equipment. Solutions were prepared with doubly distilled water and reagent-grade chemicals. Arsenous acid and potassium iodate solutions used to feed the CSTR were prepared in 20-L volumes. Arsenous acid solution was prepared with NaAsO2 and H2SO4 in a 1:1 mole ratio. The As(III) concentration was determined by titration with iodine using a standard procedure.21 The solution acidity calculated from the incomplete dissociation of HSO3- agreed with that determined by pH measurements. Iodate concentration was determined by reducing titration with iodine using a standard procedure.21 The reaction can be expressed as the sum of two basic processes:

\[ 5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \] (A)
\[ I_2 + H_3AsO_3 + H_2O = 2I^- + H_2AsO_4 + 2H^+ \] (B)
concentrations of $\text{H}_3\text{AsO}_3$, $\text{KIO}_3$, and $\text{H}^+$ are given in Figure 1. One experiment utilized a reaction mixture buffered with 0.03 M $\text{NaHSO}_4$ and 0.53 M $\text{Na}_2\text{SO}_4$. A $\text{KI}$ solution was prepared for the iodide perturbation experiments (see Procedure). Iodide concentration was determined by oxidizing the $\Gamma$ with $\text{IO}_3^-$ in acidic solution and titrating the solution buffered to pH 7 with $\text{Na}_2\text{SO}_4$ according to a standard procedure. All solutions were filtered through 40-$\mu$m fritted glass filters.

The tank reactor was constructed of three pieces (base, midsection, and top) machined from Plexiglas. A number of different sized midsections allowed variation of the tank volume. In all experiments reported here, the tank volume was 30.8 cm$^3$. Machined O-ring grooves allowed the three sections to be tightly sandwiched together. Reactant solutions were input through two capillary holes in the base section which were fitted with Teflon tubing connectors. Small-diameter holes prevented chemical reaction from back up in the input streams even at low flow rates. The top section was designed to accommodate a reference and an iodide selective electrode sealed into ports with O-rings. This section also includes a port with a Teflon septum for injections of solution with a microliter syringe. The interior of the top section is conical with an opening at the apex for the stirring impeller shaft. The opening was drilled slightly oversize to permit outflow of material between the shaft and the walls of the opening.

The arsenous acid and iodate solutions were pumped from 200-mL reservoirs through Teflon tubing to the CSTR with a Gilson Minipuls peristaltic pump. The CSTR, the reservoirs, and most of the feed tubing were submerged in a constant-temperature water bath. The thermostated reservoirs were continuously fed from two 20-L carboys. The outflow solution was continuously drained from a small reservoir at the impeller shaft opening by a water pump.

The solution within the CSTR was maintained homogeneous with a glass impeller turning at 1500 rpm, powered by a Fisher Stedi-Speed stirrer. The stirring rate was reproducible to better than 5%. The concentration of iodide was monitored with an iodide selective electrode and a double junction reference electrode connected to an Orion 901 Ionalyzer. Concentration as a function of time was recorded with an Orion 951 printer and a strip chart recorder.

Procedure. The CSTR experiments were carried out by first calibrating the instrument with standard iodide solutions. The flow rate of each channel was then calibrated at the maximum pumping capacity by measuring the time required to pump a known volume of distilled water. The flow rate was also monitored by using in-line flowmeters. An actual experiment began by pumping iodate and arsenous acid feed solutions at the maximum pumping capacity (reciprocal residence time $k_0 = 0.409$ min$^{-1}$) for 120 min. Iodide concentration was monitored as a function of time as the reagents displaced distilled water in the tank. After a monotonic increase in concentration, the system stabilized and the steadystate was defined from this start-up procedure was characterized by a low iodide concentration ($4.4 \times 10^{-5}$ M) and a colorless solution.

The flow rate was decreased in successive steps, each equal to 5% of the maximum flow rate. Establishment of the steady state was slow, requiring up to 90 min for the system to stabilize. At each flow rate, the system was monitored for 30 min after stabilization to ensure no further change. At $k_0 < 0.164$ min$^{-1}$, the [$\Gamma$] abruptly increased and the reaction mixture turned a brown color characteristic of $\text{I}_2/\text{I}^-$. At values of $k_0 < 0.164$ min$^{-1}$, the steady state was established almost immediately; therefore, [$\Gamma$] was monitored for only 50 min at each flow rate. Successive flow-rate decrements were continued until the flow rate was 2.5% of the maximum flow rate. The flow rate was then increased in successive steps to the maximum pumping capacity. All of these steady states were characterized by high [$\Gamma$] and the brown $\text{I}_2/\text{I}^-$ color. Experiments were also carried out to determine [$\text{H}^+$] as a function of $k_0$ and to determine the hysteresis limits for a buffered reaction mixture. An identical procedure was used in these experiments.

Experiments were conducted to investigate the stability of the low [$\Gamma$] steady state to finite perturbations in [$\Gamma$]. The system was allowed to stabilize in the low [$\Gamma$] state at a particular flow rate. A perturbation experiment was carried out by injecting a known volume of 0.03 M KI into the CSTR by using a microliter syringe. After an injection, [$\Gamma$] was monitored until the system stabilized. If the perturbation was insufficient to effect a transition from the low [$\Gamma$] steady state to the high [$\Gamma$] steady state, a slightly greater volume of KI solution was injected. This procedure was repeated until an injection was sufficient to cause a transition. Subcritical and supercritical [$\Gamma$] perturbations were determined for six different flow rates. The injected volumes ranged from 15 to 80 $\mu$L; a simple calculation demonstrated that the dilution effect was insignificant. Other experiments were carried out to ensure that the high [$\Gamma$] steady state at $k_0 = 0.409$ min$^{-1}$ was locally stable. After the system had stabilized, subcritical injections of 0.32 M AgNO$_3$ were made by using a microliter syringe.

Batch experiments were carried out by pipetting equal volumes of KIO$_3$ and $\text{H}_3\text{AsO}_3$ stock solutions into a thermostated beaker. Iodate solution was added last by rapid delivery pipet, and complete delivery was defined as time zero. Iodide concentration was monitored as a function of time using an iodide selective electrode and a double junction reference electrode. Reactant concentrations for the batch experiments are given in Figure 4.

Results

Steady-State Iodide Concentration vs. Flow Rate. Steady-state iodide concentrations as a function of reciprocal residence time are shown in Figure 1 (solid circles). The concentrations of $\text{H}_3\text{AsO}_3$, KIO$_3$, and $\text{H}^+$ given in the figure caption correspond to the concentrations that would result in the absence of any chemical reaction. A unique steady state, characterized by high [$\Gamma$] and a brown solution is exhibited for $k_0$ between 0.164 and 0.409 min$^{-1}$. The high [$\Gamma$] states are subsequently referred to as $\alpha$ states. For $k_0 \geq 0.164$ min$^{-1}$ the $\alpha$ states continue to exist, but another steady state is exhibited, characterized by low [$\Gamma$] and a colorless solution. These states are subsequently referred to as $\beta$ states. For each value of $k_0$ between 0.164 and 0.409 min$^{-1}$, the system may exist in either an $\alpha$ or a $\beta$ steady state. The reciprocal residence time $k_0 = 0.409$ min$^{-1}$ corresponds to the maximum pumping capacity. The iodide concentrations in states $\alpha$ and $\beta$ differ by factors of 16 and 72 for $k_0$ values of 0.164 and 0.409 min$^{-1}$, respectively. An experiment was carried out with a buffered reaction mixture. Reactant concentrations were similar to those for Figure 1 ($\text{KIO}_3 = 2.925 \times 10^{-3}$ M, $\text{H}_3\text{AsO}_3 = 4.355 \times 10^{-3}$ M, and $\text{H}^+ = 2.9 \times 10^{-4}$ M), except the reaction mixture also contained 0.03 M NaHSO$_4$ and 0.53 M Na$_2$SO$_4$. The $\alpha$- and $\beta$-state iodide concentrations were similar to those in Figure 1; however, the lower hysteresis limit occurred at $k_0 = 0.022$ min$^{-1}$. Both steady states were
exhibited for \( 0.022 \leq k_0 \leq 0.409 \) min\(^{-1}\).

Steady-State Hydrogen Ion Concentration vs. Flow Rate. Steady-state hydrogen ion concentrations as a function of \( k_0 \) are shown in Figure 2. The bistability region is essentially the same as in Figure 1. An increase in \( k_0 \) results in an increased [H\(^{+}\)] in the \( \beta \) states. The [H\(^{+}\)] in the \( \beta \) states appears to be insensitive to increases in \( k_0 \). Hydrogen ion concentration in the \( \alpha \) steady state at \( k_0 = 0.164 \) min\(^{-1}\) is \( \sim 22\% \) greater than in the corresponding \( \beta \) steady state. The difference increases to \( \sim 31\% \) at \( k_0 = 0.409 \) min\(^{-1}\).

Iodide-Perturbation Experiments. Experiments were carried out to investigate the stability of the \( \beta \) states to finite perturbations in [I\(^{-}\)]. The results of experiments at \( k_0 = 0.170 \) min\(^{-1}\) are shown in Figure 3. Discontinuous increases in [I\(^{-}\)] resulting from injections of \( 1.54 \times 10^{-5}, 3.08 \times 10^{-5}, \) and \( 4.62 \times 10^{-5} \) mol of KI decayed back to the \( \beta \) steady state. The lower curve in Figure 3 shows the decay of the third perturbation. The injection increased iodide concentration to \( \sim 2.72 \times 10^{-5} \) M, determined by adding the [I\(^{-}\)] resulting from the injection to the steady-state [I\(^{-}\)].

The curves in Figure 3 represent subcritical and supercritical perturbations. The larger perturbation resulted in a transition from the \( \beta \) state to the \( \alpha \) state. The peculiar maximum in [I\(^{-}\)] following the supercritical perturbation resembles the behavior exhibited in batch reaction (see Batch Experiments). Subcritical (\( \bigcirc \)) and supercritical (\( \Delta \)) iodide perturbations are shown in Figure 1 for six different flow rates. As the value of \( k_0 \) increases from the lower hysteresis limit, the iodide perturbation necessary to induce a \( \beta \rightarrow \alpha \) transition increases. The subcritical and supercritical perturbations as a function of \( k_0 \) are given in Table I.

Other experiments were carried out to ensure that the \( \alpha \) state at \( k_0 = 0.406 \) min\(^{-1}\) was locally stable. Discontinuous decreases in [I\(^{-}\)] resulting from injections of \( 3.21 \times 10^{-6}, 8.01 \times 10^{-6}, \) and \( 1.60 \times 10^{-5} \) mol of AgNO\(_3\) decayed back to the \( \alpha \) steady state.

Batch Experiments. Equal volumes of iodate and arsenous acid stock solutions used in the CSTR experiments were mixed in a thermostated beaker. Iodide concentration as a function of time is shown in Figure 4. The reaction mixture remained colorless as [I\(^{-}\)] increased and then suddenly “blinked” brown at the maximum. The ratio of the iodide concentration at the maximum to the initial H\(_2\)AsO\(_3\) concentration is 1.00:2.81, in reasonable agreement with that predicted by the stoichiometry of reaction II. The maximum in [I\(^{-}\)] therefore corresponds to the stoichiometric point for the consumption of H\(_2\)AsO\(_3\). The iodide concentration at the maximum in Figure 4 is the same, within experimental error, as the maximum concentration following the supercritical perturbation in Figure 3.

Discussion

Conservation of mass dictates a unique atomic composition within a reactor continuously pumped with chemical reactants. The concentrations of the chemical species, however, are determined by the kinetics of the chemical reaction, arising ultimately from the detailed chemical reaction mechanism. In a closed system, a single stationary state is established, defined by a unique set of species concentrations: the state of thermodynamic equilibrium. In an open pumped system, a reaction with the appropriate kinetics may exhibit more than one stationary state. An open system exhibiting kinetic bistability exists at a par-

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**TABLE I.**

<table>
<thead>
<tr>
<th>( k_0/\text{min}^{-1} )</th>
<th>subcritical ([\text{I}^{-}])/M</th>
<th>supercritical ([\text{I}^{-}])/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.170</td>
<td>( 2.72 \times 10^{-5} )</td>
<td>( 3.22 \times 10^{-5} )</td>
</tr>
<tr>
<td>0.234</td>
<td>( 4.79 \times 10^{-5} )</td>
<td>( 5.29 \times 10^{-5} )</td>
</tr>
<tr>
<td>0.269</td>
<td>( 5.16 \times 10^{-5} )</td>
<td>( 6.66 \times 10^{-5} )</td>
</tr>
<tr>
<td>0.300</td>
<td>( 5.06 \times 10^{-5} )</td>
<td>( 5.56 \times 10^{-5} )</td>
</tr>
<tr>
<td>0.370</td>
<td>( 6.98 \times 10^{-5} )</td>
<td>( 7.48 \times 10^{-5} )</td>
</tr>
<tr>
<td>0.403</td>
<td>( 7.95 \times 10^{-5} )</td>
<td>( 8.45 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

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**Figure 2.** Hydrogen ion concentration as a function of \( k_0 \). Reactant concentrations and temperature same as Figure 1.

**Figure 3.** Subcritical (lower curve) and supercritical (upper curve) perturbations in iodide concentration from \( \beta \) stationary state at \( k_0 = 0.170 \) min\(^{-1}\). See Table I for concentration perturbations. Reactant concentrations and temperature same as Figure 1.

**Figure 4.** Iodide concentration as a function of time in batch reaction. Initial reactant concentrations: \([\text{KIO}_3]\) = \( 2.295 \times 10^{-4} \) M, \([\text{H}_2\text{AsO}_3]\) = \( 4.450 \times 10^{-5} \) M, \([\text{H}^{+}]\) = 3.5 \( \times \) \( 10^{-5} \) M. Temperature: 25.0 \( \pm \) 0.2 °C.
ticular pumping rate in either of two stationary states, and concentrations of the intermediate species may differ by orders of magnitude in each of the states. Reactant and product concentrations may also differ in each of the stationary states, but usually to a smaller degree than the intermediates. Different product concentrations in one stationary state vs. another may be of considerable practical importance in chemical manufacturing processes utilizing pumped tank reactors.

Iodide Autocatalysis. The iodate–arsenous acid reaction is autocatalytic in iodide.14,16 Bromous acid autocatalysis in the bromate–cerium(III) system is an essential kinetic feature for its bistability behavior.2,3 and the iodide autocatalysis is certain to be of key importance in the iodate–arsenous acid bistability.

Chemical reactions that exhibit bistability in pumped reactors contain the kinetic features necessary for chemical wave behavior in an unstirred distributed system. The initiation and propagation of chemical waves in a bromate–ferroin system has been recently studied.22 A propagating front partitions the reaction mixture into two regions representing different kinetic states.

The Russian workers Epic and Shub23 reported some 25 yr ago that propagating chemical waves may appear in an unstirred reaction mixture containing iodate and arsenous acid. A wave spontaneously initiates at the surface of a solution contained in a test tube and propagates downward. In solutions containing excess iodate, the wave converts the colorless solution to a brown color characteristic of I2/1-. If arsenous acid is in stoichiometric excess, a brown ring propagates down the tube. An addition of KI or I2 solution to the reaction mixture immediately initiates a wave. We have reexamined and confirmed these findings and have developed an electrochemical method for initiating waves in a thin film of solution.24 Wave initiation occurs at a local region containing iodide or iodine in greater concentration than in the bulk solution. Any I2 is rapidly reduced in process B, and an elevated I- concentration results in an acceleration of process A. Iodide concentration in the local region grows autocatalytically and begins to diffuse into surrounding regions. Iodide autocatalysis is promoted in these regions, and the result is a chemical wave triggering its own propagation. The visible brown iodine color represents the region in the wave where the reaction has reached the arsenous acid stoichiometric point. The visible wave therefore represents the trailing edge; the leading edge is a colorless gradient of I-.

A Simple Reaction Mechanism. The iodate–arsenous acid reaction has traditionally been explained as a combination of process A and process B. No mechanism in terms of elementary steps is available, although a variety of mechanisms for process A, the Dushman reaction, and process B, the Roebuck reaction, have been proposed. Liebhafsky and Roe18 have summarized the rate laws reported for the Dushman reaction. Most contain two terms, one first and the other second order in iodide. The most recent study of the Roebuck reaction reports a three-term rate law accounting for various degrees of protonation of As(III).20b

We have combined the most plausible schemes for the Dushman and Roebuck reactions in order to model the bistability exhibited by the iodate–arsenous acid system.

Iodide is reduced by a sequence of oxygen atom transfers in steps R1–R6. This scheme for the Dushman reaction, proposed by Liebhafsky and Roe,19 accounts for the two-term rate law. The intermediate I2O4 (or H2I2O4) either decomposes in reaction R2 or is attacked by iodide in reaction R3. The experimentally observed first-order dependence in iodide at [I-] less than ~10^-7 M and second-order dependence at higher [I-] is explained by this mechanism. When reactions R1 and R2 are combined and reactions R3 and R4 omitted, the sequence R1–R6 is analogous to the reduction of Br2O3 by two equivalent oxygen atom transfers in the Belousov–Zhabotinsky reaction.4

The reduction of HOI by As(III) in reaction R7 was originally proposed by Roebuck18 in his mechanism for the reduction of iodine. Liebhafsky20a showed that the Roebuck mechanism requires a value of k7 somewhat larger than the diffusion limit for a bimolecular reaction and that reaction R7 must have a negative activation energy. Pendlebury and Smith20b pointed out that the activation energy is only slightly negative when more recent values of AHo are used for the hydrolysis of I2 and the formation of I3-. When one uses Pendlebury and Smith's rate constants for the Roebuck reaction and recently determined equilibrium constants25 for I2 hydrolysis and I3- formation, the value of k7 becomes reasonably near the diffusion limit. We therefore include the mechanism originally proposed by Roebuck18 in scheme R1–R7 to account for the regeneration of I-.

No direct reaction of IO3- with H2AsO4 for the initial generation of I- has been included in the mechanism. There is little evidence for the direct reaction, and, because iodate reagent inevitably contains iodide, it is not needed for the initiation of iodide autocatalysis. No reaction for the formation of IO3- has been included in the mechanism. Triiodide is certainly present when the system is in an a steady state; however, the equilibrium is probably not kinetically important. The increased acidity of As(V) over As(III) is accounted for by assuming complete dissociation of H3AsO4 to H2AsO4-

Two parallel reactions, one first and the other second order in iodide, are generated by reactions R1–R7. Both pathways generate the net reaction given by eq Ia. Net

The mechanism was designed to be as simple as possible and still contain the kinetic features necessary to account for the bistability behavior. The mechanism is given by reactions R1–R7:

\begin{align*}
I0_3^- + I^- + 2H^+ & = I_2O_4^- + H_2O \\
I_2O_4^- + H_2O & = HOI + HIO_2 \\
I_2O_4^- + I^- + H_2O & = 2HOI + IO_3^- \\
IO_3^- + H^+ & = HOI \\
I^- + HIO_2 + H^+ & = 2HOI \\
I^- + HOI + H^+ & = I_2 + H_2O \\
H_3AsO_3 + HOI & = H_2AsO_4^- + I^- + 2H^+ 
\end{align*}

first-order pathway and by \([2(R1) + (R3) + (R4)] + (R6) + 5(R7)\) for the second-order pathway. Before the arsenous acid stoichiometric point, the overall reaction for the first- and second-order pathways is given by \([(R1) + (R2)] + (R5) + 3(R7)\) and \([(R1) + (R3) + (R4)] + 3(R7)\), respectively, which is the same as reaction II except that three \(H^+\) ions appear on the product side from the dissociation of \(H_3AsO_4\). When \(I^\prime\) is left on both sides of the equation, the overall reaction becomes reaction IIa. When \(I^\prime\) is not cancelled in eq II, five and six \(I^\prime\) ions appear, respectively, on the reactant and product sides. As long as the product \(I^\prime\) exceeds the reactant \(I^\prime\) by one, the actual number of uncancelled \(I^\prime\) ions is arbitrary.

Autocatalytic generation of \(I^\prime\) is predicted by reactions R1–R7 provided that the consumption of iodide by the Dushman reaction is rate-determining. In batch reaction (see Figure 4), \(I^\prime\) accumulates to its maximum concentration according to the stoichiometry of reaction IIa. When \(H_3AsO_4\) is consumed, the accumulated \(I^\prime\) is rapidly oxidized to \(I_2\) in process A.

**Comparison with Experiment.** The rate equations generated by reactions R1–R7 were numerically integrated to model the CSTR experiment. Iodide concentration was assumed to be constant and was absorbed into the rate constant for reaction RL. Reaction R7 was regarded as irreversible, and therefore the rate equations did not include any As(V) species. Reactions R3 and R4 were combined so that three HOI's are generated in reaction R3 and \(H^+\) is consumed at a rate given by reaction R3. Therefore, the rate equations did not include the species IO\(^-\). All other species were treated as variables, and seven differential equations were necessary to describe the system. A term to describe the outflow of material, \(k_0C_i\), was added to each differential equation, where \(k_0\) is the reciprocal residence time and \(C_i\) is the concentration of species \(i\). The inflow of material was accounted for by including the term \(k_0C_i\) to the rate equations for \(H_3AsO_3\), \(\Gamma^\prime\), and \(H^+\). The term \(C_{io}\) represents the concentration of each species that would be established in the absence of any chemical reaction. The rate constants for reactions R1–R3 are similar to those used by Liebhafsky and Roe\(^{13}\) for the Dushman reaction. The value of \(k_{R2}\) generates a rate constant for the first-order term near that used by Noyes et al.\(^{26}\) for the Bray–Liebhafsky reaction. The value of \(k_{R3}\) generates a rate constant for the second-order term near that obtained by Schildrcourt and Fortunato.\(^{26}\) The rate constants for reactions R5–R6 are the same as those used by Noyes et al.\(^{26}\) The rate of reaction R7 was assumed to be near the diffusion-controlled limit. The rate constants are given in Table II.

The dashed lines in Figure 1 show the computed steady-state concentrations of \(I^\prime\) as a function of \(k_0\). The concentrations of reactants in the calculation were nearly the same as in the experiment (see figure caption). The concentration of \(H^+\) in the input stream matched the experimental value determined by pH measurements. Iodide concentration in the input stream is about that expected from the impurity in iodate reagent.

The calculated \(\alpha\) state (high \([I^\prime]\), high \([I_2]\)) and \(\beta\) state (low \([I^\prime]\), low \([I_2]\)) iodide concentrations in Figure 1 are reasonably near the experimental points. The lower hysteresis limit for the calculated curve at \(k_0 = 0.126 \text{ min}^{-1}\) compares to the experimental value of \(k_0 = 0.164 \text{ min}^{-1}\). Figure 5 shows computed steady-state iodide concentrations as a function of \(k_0\) for the complete hysteresis loop. The calculated upper hysteresis limit \((k_0 = 3.60 \text{ min}^{-1})\) was experimentally inaccessible because of pumping capacity limitations. Figure 5 suggests that only a small part of the hysteresis loop was accessible to the experimental study; however, the computed upper hysteresis limit may be shifted by small changes in certain rate constants (see Refinement of the Mechanism). The experimental data in Figure 1 establish only that the upper hysteresis limit occurs at \(k_0 > 0.409 \text{ min}^{-1}\).

The calculated \(H^+\) concentrations as a function of \(k_0\) are shown in Figure 6. The qualitative features are in good agreement with the experimental values in Figure 2. The \(\beta\) states in the calculated curve are close to the experimental values. The calculated curve for the \(\alpha\) states is somewhat higher than the experimental values, but the difference is less than a factor of 2.

The computed concentrations of \(I_2\) and \(H_3AsO_4\) as a function of \(k_0\) are shown in Figures 7 and 8, respectively. Figure 7 shows that \([I_2]\) is high in the \(\alpha\) states and low in the \(\beta\) states, in agreement with the qualitative experimental observations. Figure 8 shows that the \(\alpha\)-state

**Table II: Rate Constants for Reactions R1–R7**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>(4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>R2</td>
<td>(1.55 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>R3</td>
<td>(7.65 \times 10^3 \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>R4</td>
<td>(2.10 \text{ s}^{-1})</td>
</tr>
<tr>
<td>R5</td>
<td>(8.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
</tbody>
</table>

**Figure 5. Iodide concentration as a function of \(k_0\) computed from reactions R1–R7.** Reactant concentrations same as Figure 5. See Table II for rate constants.

**Figure 6. Hydrogen ion concentration as a function of \(k_0\) computed from reactions R1–R7.** Reactant concentrations same as Figure 5. See Table II for rate constants.

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Iodate Oxidation of Arsenous Acid

Table reactions R1-R7. Reactant concentrations same as Figure 5. See Figure 7. Iodine concentration as a function of $\text{As}^{\text{III}}$ should become zero due to the irreversibility of reaction R7. The $\alpha$-state $[\text{H}_3\text{AsO}_3]$ is only slightly less than the concentration expected in the absence of any chemical from reactions R1-R7. Reactant concentrations same as Figure 5. is -0.1% above its input concentration. A slight extent. The $\beta$-state hydrogen ion concentration when the system is in a $\beta$ state. That the extent of reaction $\text{As}(\text{III})$ is consumed less than 0.1%. At the same times $[\text{H}_3\text{AsO}_3]$, the concentration expected in the absence of any chemical reaction.

Figures 5–8 show that little chemical reaction occurs when the system is in a $\beta$ state. That the extent of reaction is slight can be seen by comparing the input reactant concentrations, $C_{\text{in}}$, to the steady-state concentrations, $C_{\text{ss}}$. Of course as $k_0 \to \infty$, the solution composition must approach that of the feed streams diluted by a factor of 2, with concentrations given by the values of $C_{\text{in}}$. At $k_0 = 0.30 \text{ min}^{-1}$, $[\text{H}_3\text{AsO}_3]_{\text{ss}} = 4.5566 \times 10^{-3} \text{ M}$ compared to the input value $[\text{H}_3\text{AsO}_3]_{\text{in}} = 4.5600 \times 10^{-3} \text{ M}$. At this $\beta$ state, near the middle of the bistable region in Figure 1, arsenous acid is consumed less than 0.1%. At the same $k_0$, $[\Gamma]_{\text{ss}}$ is 1.33 times $[\Gamma]_{\text{in}}$, indicating that iodide autocatalysis occurs to a slight extent. The $\beta$-state hydrogen ion concentration is $\sim 0.1\%$ above its input concentration.

The extent of reaction in the $\alpha$ states is in sharp contrast to that in the $\beta$ states. At $k_0 = 0.30 \text{ min}^{-1}$, $[\text{H}_3\text{AsO}_3]_{\text{ss}} = 9.92 \times 10^{-6} \text{ M}$, indicating that 99.8% of the As(III) from the input stream is consumed. At the same $k_0$, $[\Gamma]_{\text{ss}} = 2.25 \times 10^{-4} \text{ M}$, which is greater than $[\Gamma]_{\text{in}}$ by a factor of 75.0. The $\alpha$-state hydrogen ion concentration is 2.26 times $[\text{H}^+]_{\text{in}}$.

The results of reaction in the $\alpha$ and $\beta$ states and indicate that, when the system is in a $\beta$ state, removal of $\Gamma$ from the reactor by flow prevents iodide autocatalysis from accelerating. In the $\alpha$ states, $\text{H}_3\text{AsO}_3$ is almost consumed by iodide autocatalysis and much of the $\Gamma$ generated has been oxidized to $\text{I}_2$ in process A ($[\text{I}_2] = 7.57 \times 10^{-4} \text{ M at } k_0 = 0.30 \text{ min}^{-1}$). Figure 7 shows that, as $k_0$ approaches zero, $[\Gamma]_{\text{ss}}$ approaches the value $[\Gamma]_{\text{in}}$ predicted by the stoichiometry of reaction I. As $k_0 \to 0$, $[\Gamma]_{\text{ss}}$ should become zero according to reaction I. Figure 5 shows a sharp decrease in $[\Gamma]_{\text{ss}}$ at low values of $k_0$, and calculations at $k_0 < 0.012 \text{ min}^{-1}$ indicate that $[\Gamma]_{\text{ss}}$ indeed approaches zero at zero flow.

Role of $H^+$. Net reaction I predicts a lower $[\text{H}^+]$ upon complete reaction, indicating that the $\alpha$ states should be less acidic than the $\beta$ states. The greater acidity of the $\alpha$ states compared to the $\beta$ states, shown in Figure 2, can be accounted for only by the greater acidity of $\text{H}_3\text{AsO}_4$ compared to $\text{H}_2\text{AsO}_3$. This feature was included in mechanism R1–R7 by assuming complete dissociation of $\text{H}_3\text{AsO}_4$ in reaction R7. Of course, $\text{H}_3\text{AsO}_4$ is a relatively weak acid ($K_a = 5.62 \times 10^{-9}$), but to facilitate integration of the rate equations 100% dissociation was assumed.

The Dushman reaction is rate determining for iodide autocatalysis and, because it is second order in $H^+$, reaction IIa predicts that the iodate–arsenous acid reaction is also autocatalytic in $H^+$. When the incomplete dissociation of $\text{H}_3\text{AsO}_4$ is taken into account, the hydrogen ion autocatalysis is only slightly diminished. A simple calculation using the first dissociation constant for $\text{H}_3\text{AsO}_4$ shows that the $3\text{H}^+$ in reaction IIa is replaced by $1.96\text{H}^+$ when $[\text{As(V)}]$ is given by the initial $[\text{As(III)}]$ in our experiments. The increase in acidity upon complete reaction is also accounted for when the incomplete dissociation is taken into account. A similar calculation shows that the $3\text{H}^+$ in net reaction Ia is replaced by $1.27\text{H}^+$ when $[\text{As(V)}]$ is equal to the initial $[\text{As(III)}]$.

The effect of the $H^+$ autocatalysis on the bistability behavior was investigated by repeating the calculations for Figures 5–8 with no contribution of $H^+$ from As(V). Therefore, only one $H^+$ is produced in reaction R7, and the overall reactions I and II describe the system. The lower hysteresis limit was unchanged by the modification ($k_0 = 0.126 \text{ min}^{-1}$), but the upper hysteresis limit was shifted to $k_0 = 2.16 \text{ min}^{-1}$, corresponding to a lower flow rate. The calculations were also repeated with hydrogen ion concentration held constant at the value of $[\text{H}^+]_{\text{in}}$. This calculation again generated the same value of $k_0$ for the lower hysteresis limit, but now the upper hysteresis limit was shifted to $k_0 = 4.20 \text{ min}^{-1}$, corresponding to a higher flow rate.

When the CSTR experiment was repeated with a buffered reaction mixture, the bistability was similar to that in the unbuffered system, although the lower hysteresis limit was shifted to $k_0 = 0.022 \text{ min}^{-1}$. This shift may have been due to a lower value of $[\Gamma]_{\text{in}}$, indicated by the lower $\beta$-state iodide concentrations at high flow rates.

The calculations and the buffer experiment indicate that the hydrogen ion autocatalysis is of secondary importance. Our initial attempts to model the bistability behavior utilized a mechanism like reactions R1–R7, but reactions R1 and R2 were combined and reactions R3 and R4 were deleted. Therefore, the model did not contain the intermediate $\text{I}_2$ and there was no second-order dependence in iodide. This mechanism modeled the experimental behavior almost as well as the current mechanism. However, De Kepper, Epstein, and Kustin showed that the bistability can be accounted for with empirical rate laws containing no provision for the dissociation of As(V). They also showed that the second-order iodide term in the rate law for the Dushman reaction is essential for the bistability behavior. Their work and the buffer experiment convinced us that hydrogen ion autocatalysis is not essential for the
bistability, and we therefore revised our mechanism to include the intermediate I$_2$O$_5$ in order to obtain a second-order dependence in iodide. We now believe that our initial mechanism reproduced the experimental behavior because the second-order H$^+$ dependence of the Dushman reaction mimicked the second-order iodide dependence.

**Subcritical and Supercritical Perturbations in Iodide Concentration.** Mechanism R1–R7 was used to investigate the perturbation-induced transitions from a β state to an α state. Figure 9 shows the results of two calculations where [I$^-$] was discontinuously increased from its steady-state concentration in the β state. The flow rate ($k_f = 0.17$ min$^{-1}$) corresponds to that in the perturbation experiments shown in Figure 3. When iodide concentration was increased to $4.5 \times 10^{-5}$ M, the system decayed back to the β state. The lower curve in Figure 9 shows the time evolution of the subcritical perturbation. When [I$^-$] was increased to $5.0 \times 10^{-5}$ M, a transition to the α state was induced. The upper curve in Figure 9 shows the evolution of the supercritical perturbation. The qualitative features of Figure 3 are reasonably reproduced by the calculated behavior in Figure 9. The iodide maximum in the supercritical perturbation is very similar to the experimental curve. The major difference between the calculation and experiment is the time required for the steady state to be established. The calculated evolution of the supercritical perturbation is similar to the experimental behavior, but the calculated time for reestablishment of the β steady state in the subcritical perturbation is about 3 times longer than in the experiment.

**Conclusion**

**Comparison to the Bromate–Ceium(III) System.** The kinetic behavior of the iodate–arsenous acid reaction is substantially different from that exhibited by the bromate–cerium(III) reaction. Bromous acid autocatalysis is inhibited by the consumable reactant Br$^-$ in the bromate–cerium(III) reaction. Thus, the batch reaction is nonautocatalytic until Br$^-$ is consumed to a critical concentration; it then becomes autocatalytic. In the iodate–arsenous acid system, the consumable reactant H$_2$AsO$_3$ is necessary for iodide autocatalysis. Thus, the batch reaction is autocatalytic until H$_2$AsO$_3$ is consumed; it then becomes nonautocatalytic.

The bromate–cerium(III) reaction is best explained in terms of a nonradical process and a radical autocatalytic process. The iodate–arsenous acid reaction also involves two processes, but both are accounted for by the nonradical reactions R1–R7.

**Refinement of the Mechanism.** Reactions R1–R7 reproduce the qualitative features of the experimental behavior reasonably well; however, better quantitative agreement would be desirable. The assumption that H$_2$AsO$_4$ completely dissociates is certainly responsible for some of the discrepancy between calculation and experiment. Calculations were also carried out with the actual dissociation and association reactions included in the model. The association reaction was assumed to be diffusion controlled; the dissociation rate constant was obtained from the equilibrium constant and the association rate constant. Introduction of the opposing reactions, each with large rate constants, caused the coupled differential equations to become very stiff. Because computational times were increased by more than 10-fold, this model was not pursued.

The assumption that reaction R7 is irreversible may also be responsible for some discrepancy between calculation and experiment. When [As(V)] is large, consumption of the critical species I$^-$ and H$^+$ by the reverse reaction may have a significant effect on the behavior. In order to reduce the total number of variables, we did not include the reverse reaction; however, it should be included in a refined model.

The hysteresis limits and the iodide concentrations in the α and β states were sensitive to small changes in some of the rate constants. We did not carry out a systematic variation of the rate constants; the values in Table II generated the best reproduction of the experimental behavior out of a few initial attempts. However, we did observe that the lower and upper hysteresis limits were shifted by small changes in the values of $k_R$ and $k_R^*$, respectively. The sensitivity of the bistability behavior to reactions R1–R3 suggests that this system is ideal for developing a better understanding of the Dushman reaction. The hysteresis limits were also sensitive to the values of [I$^-$] and $k_R^*$. The β steady state [I$^-$] must approach [I$^-$]$_0$ in the limit of high flow rate, and therefore the experimental value of [I$^-$]$_0$ can be established fairly accurately. (The value of [I$^-$]$_0$ used for Figures 5–9 was based on the β-state iodide concentration at the maximum pumping capacity in Figure 1.)

**Iodine Autocatalysis.** Steps R2 and R5 must be rate determining for iodide autocatalysis. An intriguing aspect of the iodate–arsenous acid reaction is that autocatalysis in I$_2$ is expected if process B is rate determining. The reduction of I$_2$ by As(III) might become rate determining in a reaction mixture containing high [IO$_3^-$], high [H$^+$], and low [H$_2$AsO$_3$]. A negative hydrogen-ion dependence would be expected in such a system according to the Roebuck$^{16}$ and other$^{20}$ mechanisms. A system with the reactant concentrations adjusted such that the reduction of I$_2$ by I$^-$ and the reduction of I$_2$ by As(III) are about equally rate determining should generate interesting (oscillatory?) behavior in a CSTR.

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