FEATURE ARTICLE

Chlorite–Iodide Reaction: A Versatile System for the Study of Nonlinear Dynamical **Behavior**

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The autocatalytic reaction between chlorite and iodide ions exhibits a remarkable range of dynamical behavior. In a stirred tank reactor it shows bistability between steady states and between a steady and an oscillatory state. It forms the core of a large family of systematically designed chemical oscillators. The chlorite-iodide system has served as the prototype reaction in the discovery and investigation of mixing effects in stirred tank reactors, in studies of coupled oscillators, and in new experimental approaches to spatiotemporal bifurcation behavior. Mechanistic studies of the system have resulted in an eight-step mechanism that gives excellent agreement with nearly all the above observations.

I. Introduction

Until well into the present decade, the study of nonlinear chemical dynamics-oscillating chemical reactions, multistability, traveling waves, and pattern formation-was essentially the study of a single reaction. This system, the Belousov-Zhabotinskii¹ (BZ) reaction, in which an organic substrate (e.g., malonic acid) is oxidized by bromate in a sulfuric acid solution with a metal ion catalyst (e.g., Ce(III)/Ce(IV)), was, prior to 1980, by far the best characterized and most versatile of the handful of known chemical oscillators. In the past decade, thanks to the development of a systematic design procedure² based on a simple mathematical model,³ several dozen new chemical oscillators have been discovered, opening up the possibility of finding new systems that may be more suitable than the BZ reaction for probing certain types of nonlinear dynamical behavior.

In this Feature Article, we discuss one such system, the reaction of chlorite and iodide ions in acidic aqueous solution. The chlorite-iodide reaction exhibits most, if not all, of the dynamical behavior shown by the BZ reaction. These phenomena include periodic oscillation, bistability between steady states and between steady and oscillatory states, chemical waves, and pattern formation. The ClO_2 -I⁻ system has served as the prototype reaction for the study of mixing phenomena in continuous flow stirred tank reactors (CSTR's), for investigations of the properties of coupled chemical oscillators, and for new experimental methods of examining the spatiotemporal behavior of nonlinear chemical reactions in open systems. The reaction constitutes the core or "minimal oscillator"⁴ of a large family of oscillatory reactions derived from it by adding further species. Several members of this family display new and interesting dynamical phenomena.

Finally, unlike the BZ reaction, where it is difficult to unravel the details of processes involving the organic substrate and its derivatives, the purely inorganic chlorite-iodide system lends itself nicely to mechanistic analysis. Many of the elementary steps in this system have been thoroughly studied, and computer simulations with a proposed mechanism⁵ give excellent agreement with a wide range of experimental results.

II. Dynamical Behavior

Batch Behavior. Like many oscillating chemical reactions, the chlorite-iodide reaction behaves when run batchwise, in a closed system, as a "clock reaction" characterized by an initial relatively slow reaction rate (induction period) followed by a sudden evolution to completion.⁶ Such behavior is typical of reactions involving feedback mechanisms such as autocatalysis or substrate inhibition.

The time traces of the iodide and iodine concentrations⁷ shown in Figure 1 illustrate the "clock" behavior of the chlorite-iodide reaction when chlorite is in stoichiometric excess. Note that after an initial slow decrease [I⁻] suddenly drops by 5 orders of magnitude at about the same time that $[I_2]$ reaches a maximum. The stoichiometry and kinetics of the batch reaction have been investigated by several authors.⁸ The reaction is found to be partly inhibited by iodide (the substrate) and catalyzed by iodine, a product of the reaction.

One of the most striking phenomena shown by this clock reaction is that in a narrow range of conditions it behaves stochastically; i.e., the time at which the rapid drop in $[I^-]$ occurs varies irreproducibly in a set of replicate experiments (Figure 2). This behavior, which is also seen in a small number of other reactions,9 has been characterized by Nagypál and Epstein.10 The distribution of reaction times, which is reproducible, is sensitive

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⁽²⁾ Epstein, I. R.; Kustin, K.; De Kepper, P.; Orban, M. Sci. Am. 1983, 248 (3), 112.

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⁽⁵⁾ Citri, O.; Epstein, I. R. J. Phys. Chem. 1987, 91, 6034.

⁽⁶⁾ In some cases the sensitivity of the induction period to impurities has (a) Bognår, J.; Sárosi, S. Anal. Chim. Acta 1963, 29, 406. (b) Bognår, J.; Jellinek, O. Mikrochim. Acta 1969, 2, 318. (c) Wolff, C.-H.; Schwing, J. P. Bull. Soc. Chim. 1975, 5-6, 679.

⁽⁷⁾ Dateo, C. E.; Orbán, M.; De Kepper, P.; Epstein, I. R. J. Am. Chem. Soc. 1982, 104, 504.

^{(8) (}a) Kern, D. M.; Kim, C. H. J. Am. Chem. Soc. 1965, 87, 5309. (b) De Meeus, J.; Sigalla, J. J. Chim. Phys. Phys.-Chim. Biol. 1966, 63, 453.

 ^{(9) (}a) Sickle cell hemoglobin polymerization: Hofrichter, J. J. Mol. Biol.
 1986, 189, 553. (b) ClO₂-S₂O₃²⁻: Nagypál, I.; Epstein, I. R. J. Phys. Chem. 1986, 90, 6285



Figure 1. Batch behavior of the chlorite-iodide reaction at 25 °C and pH 3.3 with initial concentrations $[ClO_2^-] = 2.5 \times 10^{-4}$ M and $[I^-] = 4 \times 10^{-4}$ M: (a) experimental,⁷ (b) calculated.⁵

not only to the reactant concentrations and the stirring rate but also to the *volume* of the solution. This surprising behavior is attributed to amplification of internal fluctuations by the highorder autocatalysis or "supercatalysis".^{9b} It is thought to be related to the ability of the system to produce chemical waves (vide infra).

Flow (CSTR) Dynamics. When the reaction is run in a CSTR with a $[ClO_2^-]_0:[I^-]_0$ ratio in the range 0.25–1.5, bistability is readily observed over a wide range of pH (0-4) and flow rate at room temperature. Figure 3 shows the typical bistability phenomenon, resulting from the overlap of the stability range of a high iodide (low iodine) steady state (HI branch) and a low iodide (high iodine) steady state (LI branch), as a function of $[I^-]_0$, the input concentration of iodide in the total feed stream. The large $[I^-]$ difference, about 5 orders of magnitude, between the two steady-state branches is noteworthy. The LI branch is the continuation of the thermodynamic equilibrium state observed in the limit of zero flow rate, while the HI branch is the continuation



Figure 2. Stochastic behavior under batch conditions.¹⁰ Absorbance traces at 510 nm of 10 replicate experiments in a closed, stirred photometric cuvette. $[Ac^-] = 0.0333$ M, [HAc] = 0.1666 M, $[ClO_2^-] = 0.00666$ M, $[I^-] = 0.0015$ M. Recordings of successive experiments are displaced by 0.02 absorbance unit to avoid complete overlap of the curves.

of the state that would be observed in the limit of infinite flow rate, where no reaction can take place between the input species.

Figure 4, a section of the $[ClO_2^-]_0-[I^-]_0$ plane of the phase diagram, demonstrates that at other values of the control parameters the system displays a small region of sustained oscillation at the high $[ClO_2^-]_0$, high $[I^-]_0$ end of the bistability domain. Figure 5 provides an example of oscillatory pI⁻ and $[I_2]$ traces in this region.

Stirring and Premixing Effects. The investigations described above were all carried out in flow reactors stirred at a constant rate with the major reactants entering the reactor through separate ports. These feed conditions, which are employed in nearly all CSTR studies of nonlinear dynamical behavior in chemical systems, will be referred to as nonpremixed (NPM). In 1983, Roux et al.¹¹ noted that with NPM feeds the range of bistability in the chlorite-iodide reaction can be very sensitive to the stirring rate, especially as a function of flow rate. This surprising behavior occurs even at stirring rates (several hundred rpm) usually considered sufficient to guarantee good macroscopic homogeneity of the bulk of the reactor.

Figure 6 demonstrates the very strong dependence of the LI steady state on stirring rate; a 20% increase in stirring rate can induce a 4-fold increase in the high flow rate value for spontaneous transition to the HI steady state. This observation triggered many new experimental¹² and theoretical investigations¹³ of the role of stirring in the chlorite-iodide reaction and in other bistable or oscillating reactions performed in stirred tank reactors. The sensitivity of the bistability range to stirring was initially thought to result from a spontaneous nucleation-induced transition.¹¹ It was soon recognized, however, that the continuous input of fresh solution constituted a much more relevant perturbation to homogeneity than the spontaneous concentration fluctuations. Further evidence that the reaction depends dramatically on feed mixing imperfections is provided by the observation that the stability of the different states is strongly influenced by the way major reactants are introduced into the reactor.¹⁴ If, in contrast to the original NPM feeding mode, the major reactants are mixed just before they enter the reactor through a single port,¹⁵ a mode

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Figure 3. Bistability under flow conditions as input $[I^-]_0$ is varied: (a) experimental,⁷ (b) calculated.⁵ Residence time 3 min, pH 3.3, $[ClO_2^-]_0 = 2.5 \times 10^{-4}$ M. Dashed arrows indicate spontaneous transitions between states.

referred to as premixed (PM) feed, the stability range of the LI state, at fixed stirring rate, is greatly enhanced. This behavior may be seen in Figure 6 by comparing the PM (dashed curves) and NPM (solid curves) steady-state potentials. Note also that under PM conditions the steady-state values become less sensitive to stirring rate, except at very low stirring rates.

The chlorite-iodide reaction demonstrates that differences in feeding mode and stirring rate of a CSTR can produce not only quantitative modifications in the dynamical behavior of the system but also striking qualitative changes. Figure 7 shows two sections

(15) In the chlorite-iodide system the reaction is initially very slow, so no significant reaction occurs during the transit time (<1 s) for premixing.



Figure 4. Section of the phase diagram in the $[ClO_2^{-}]_0^{-}[I^{-}]_0$ plane with pH = 2 and reciprocal residence time $k_0 = 1.1 \times 10^{-3} \text{ s}^{-1}$: (a) experimental,⁷ (b) calculated;³¹ \blacktriangle , HI state; \bigtriangledown , LI state; \diamondsuit , bistability; O, oscillation. Inset shows same data on a linear scale in neighborhood of cross point P.

of the phase diagram in the $([ClO_2^{-}]_0, T)$ plane, differing only in the feeding mode of the reactor; under PM conditions the system exhibits only a cusp-shaped domain of bistability between the LI and HI steady states, while under NPM conditions the dynamics of the system is much richer. Part of the previous range of bistability is changed into a region of sustained oscillation.

In the same spirit, stirring rate can act as a bifurcation parameter^{12,16} in much the same way as the other chemical and physical constraints such as feed stream concentrations, flow rate, or temperature. In the phase diagram of Figure 8, stirring rate S is one of the variable constraints. Transitions among the two steady states and the oscillatory state can be obtained simply by changing S at appropriate values of the other constraints. Notice that the oscillatory behavior with NPM feeds is observed only over limited ranges of stirring rate. This surprising result has been found in several laboratories^{12,16} and challenges the simple interpretation of the oscillatory behavior in terms of homogeneous kinetics.

⁽¹⁶⁾ Luo, Y.; Epstein, I. R. J. Chem. Phys. 1986, 85, 5733.



Figure 5. Typical oscillations in the chlorite-iodide reaction in a flow system showing behavior of $[I_2]$ (absorbance, note double peak) and $[I^-]$ (measured with iodide-selective electrode): (a) experimental,⁷ (b) calculated.⁵



Figure 6. Stirring rate dependence of the stability limit of the LI branch under PM (dashed lines) and NPM (solid lines) conditions.^{13e,14} One feed stream contains $[NaClO_2]_0 = 1.3 \times 10^{-4}$ M and $[NaOH]_0 = 1 \times 10^{-3}$ M, and the other $[KI]_0 = 5 \times 10^{-4}$ M, $[H_2SO_4]_0 = 5 \times 10^{-3}$ M, and $[Na_2SO_4]_0 = 5 \times 10^{-2}$ M. T = 13 °C.

Stirring and mixing effects in open reactors are not an altogether new phenomenon. Chemical engineers have been concerned for some time with the consequences of nonideal mixing in chemical plant reactors. This is a matter of great economic importance, since the yield of chemical converters may vary considerably with



Figure 7. Section of the phase diagram in the $[ClO_2^{-}]_0$ -temperature (θ) plane in (a) PM and (b) NPM conditions.^{41a} Stirring rate = 1500 rpm, residence time = 400 s, $[KI]_0 = 2.5 \times 10^{-3}$ M, $[H_2SO_4]_0 = 1.2 \times 10^{-2}$ M, $[Na_2SO_4]_0 = 3.0 \times 10^{-3}$ M, and variable chlorite concentration in $[NaOH]_0 = 1 \times 10^{-3}$ M. Δ , LI state; ∇ , HI state; O, oscillation. Pairs of symbols in a region indicate bistability between the corresponding states.



Figure 8. Section of the phase diagram^{41a} in the $[ClO_2^-]_0$ -stirring rate (S) plane in NPM mode at $\theta = 31.1$ °C. All other conditions and symbols as in Figure 7.

the mixing quality. Over the past 30 years chemical engineers have developed a variety of concepts to deal with mixing questions. These are discussed in a number of reviews.¹⁷

In stirred flow reactors one can grossly distinguish two levels of deviations from perfect mixing. First, there are large scale (of the order of the reactor size) inhomogeneities that account for imperfections such as short circuits and dead zones, which alter the ideal residence time distribution of species in the reactor. These imperfections can produce quantitative changes in the yield of even simple first-order reactions. The small scale inhomogeneities

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(of the order of the smallest hydrodynamic turbulent scale) involve the mixing process at the molecular level. The actual physical mechanism for this micromixing process is quite complex.¹⁸ Micromixing effects are manifest even when the reacting medium seems macroscopically homogeneous. They are significant only if the reaction is dominated by nonlinear kinetic terms (second order or higher) that evolve on a time scale shorter than the slowest mixing process. Micromixing processes dominate the actual "set to contact" of chemical species in the reactor; their effect is thus strongly dependent on the feeding mode of the reactor.

It now seems clear that the major cause of the sensitivity of the chlorite-iodide reaction to feeding mode irrespective of the reactor geometry (position of input ports, shape of stirrer, etc.) lies in the micromixing. This point will be discussed further when we consider modeling the reaction.

The experimental observations may be summarized as follows. Feeding mode and stirring rate primarily affect the stability of the low iodide state. Premixing and increasing the stirring rate lead to a lower bulk [I⁻] and stabilize the LI state. Oscillatory behavior is readily found in NPM conditions, while the oscillatory domain is dramatically reduced¹⁶ or even totally suppressed^{12b-d} in PM conditions with reasonably rapid stirring. Under PM conditions there is evidence¹⁶ for a third steady state with intermediate [I⁻] values, which can coexist with either of the other two stable steady states.

Stirring rate sensitivity has also been observed in BZ-type reactions,¹⁹ but most of these experiments were performed in reactors with a liquid-gas interface, so that stirring enhances surface exchange of reactive volatile species either released (Br₂) or dissolved (O_2) by the medium. Studies²⁰ of stirring rate effects in the BZ system in CSTR's without a free surface have only recently received careful attention, reviving a controversy as to the origin of the deterministic chaos observed in the BZ reaction in a CSTR.²¹ Initial efforts to study feeding mode sensitivity in the BZ reaction have been hampered by the fact that in this system premixing can lead to significant initial reaction in the premixer.

Related Systems. During the 1960s and particularly the 1970s, the BZ reaction spawned a large number of "daughter reactions". related systems that also display chemical oscillation. It was found that the cerium ion catalyst could be replaced by a number of other species with similar redox potentials. The organic substrate did not have to be Belousov's citric acid or Zhabotinskii's malonic acid but could be any of a variety of organic molecules with a hydrogen in the α -position with respect to two electron-withdrawing groups; each gave an oscillator with slightly different properties. More significantly, Orban and Körös discovered the uncatalyzed BZ oscillators,²² in which the metal catalyst could be eliminated if certain aniline or phenol derivatives were used as substrates. Noves²³ suggested a mechanistically based classification of this family of bromate-driven oscillators. Later, Orbán et al.²⁴ demonstrated that the catalyzed bromate oscillators could be thought of as derived from a single "minimal" system, the reaction of bromate, bromide, and a metal ion catalyst.

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TABLE I: Chemical Oscillators Derived from the Chlorite-Iodide Reaction

species				
Α	В	С	ref	remarks
I-			7	bistability between oscillatory and stationary states (hard excitation)
I-	10, ⁻		25	,
1-	BrŎ₃ ⁻		25, 26	hard excitation, birhythmicity, compound oscillation
I-	MnO₄⁻		25	•
I-	$Cr_2O_7^-$		25	
I-	malonic acid		27	batch oscillations, spatial waves
[-]-	103	malonic acid	27, 28	batch oscillations
1-	103	H ₃ AsO ₃	25	G
103	H ₃ AsO ₃		29	designed chemical oscillator
IO₃⁻	$Fe(CN)_6^{4-}$		28	
103-	SO ₃ ²⁻		28	
1O ₃ -	S ₂ O ₃ ²⁻		27, 28	batch oscillations
103-	CH ₂ O·SO ₂ ⁻		28	
1O ₃ -	ascorbic acid		28	
1 ₂	$Fe(CN)_6^{+-}$		25	
12	SU ₃ ²⁻		25	
12	S ₂ O ₃ -		25	

Like the BZ reaction, the chlorite-iodide reaction has been a prolific generator of new, related chemical oscillators. Unlike the BZ system, the chlorite-iodide reaction is itself a minimal oscillator,⁴ in that it is an oscillating reaction whose constituents are found or generated in a family of oscillators and from which one cannot remove any component without destroying the oscillatory behavior. The size of the chlorite-iodide family of oscillators is enhanced by the fact that chlorite ion can act either as an oxidant of I⁻, yielding I_2 or IO_3^- , or as a reductant of iodine or iodate to generate I⁻, which can then react with other species.

As Figure 4 shows, the range of conditions under which the chlorite-iodide system shows oscillatory behavior is rather narrow. The major overall processes in the pure chlorite-iodide system may be written as

$$I(V) + 5I^{-} \rightarrow 6I(0) \tag{1}$$

$$4I^{-} + Cl(III) \rightarrow 4I(0) + Cl^{-}$$
⁽²⁾

$$4I(0) + 5CI(III) \rightarrow 4I(V) + 5CI^{-}$$
(3)

where I(0), I(V), and Cl(III) represent $1/2I_2$, IO₃, and ClO₂ or HClO₂, respectively.

If another oxidant, Ox, is added to the input flow in a CSTR, the region of oscillation may broaden dramatically. Suppose for specificity that Ox is a one-electron oxidant with reduced form Red. Then the following processes may occur

$$Ox + I^{-} \rightarrow Red + I(0)$$
 (4)

$$5Ox + I(0) \rightarrow 5Red + I(V)$$
 (5)

$$Ox + Cl(III) \rightarrow Red + Cl(IV)$$
 (6)

$$2Ox + Cl(III) \rightarrow 2Red + Cl(V)$$
 (7)

where Cl(IV) and Cl(V) represent ClO₂• and ClO₃-, respectively. If processes 4 and 5 are fast enough, then oscillation becomes possible in regions of the phase diagram where $[ClO_2^-]_0/[I^-]_0$ is too low to permit oscillation in the minimal system. On the other hand, if processes 6 and 7 are too rapid, chlorite is removed from the system, lessening the ability of the system to oscillate.

Alternatively, one may start from flows of chlorite, either iodate or iodide, and a reductant Red that can participate in the processes

$$I(V) + 6Red \rightarrow l^- + 6Ox$$
 (8)

$$I(0) + \text{Red} \rightarrow l^- + \text{Ox}$$
 (9)

^{(18) (}a) Ottino, J.; Leong, C. W.; Rising, H.; Swanson, P. D. Nature 1988, 333, 419. (b) Ottino, J. M. Sci. Am. 1989, 260 (1), 56.
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Figure 9. Tristability in the chlorite-iodide-arsenite-iodate system.²⁵ $B_{i/j}$ indicates region of bistability between SS_i and SS_j. T indicates region of tristability. Fixed constraints: $[ClO_2^-]_0 = 2.5 \times 10^{-3} \text{ M}, [IO_3^-]_0 = 2.5 \times 10^{-2} \text{ M}, \text{ pH } 3.35, k_0 = 5.35 \times 10^{-3} \text{ s}^{-1}, T = 25 \text{ °C}.$

While the equations are written for a one-electron reductant, either one- or two-electron species can function in this fashion. If reactions 8 and 9 proceed sufficiently rapidly, enough I⁻ is generated to produce oscillation.

Examples of $ClO_2^--l^--Ox$, $ClO_2^--lO_3^--Red$, and $ClO_2^--l_2^--Red$ oscillators are given in Table I. Three systems in particular merit special mention. The chlorite-iodide-malonic acid reaction²⁷ unlike most chlorite oscillators, which function only in an open (flow) system, also shows transient oscillatory behavior in a closed (batch) configuration. Unstirred in a Petri dish, it exhibits spatial pattern formation much like that seen in the BZ reaction. These features have made it a useful system for the study of nonlinear spatiotemporal phenomena, as we discuss below. The chlorite-iodide-iodate-arsenite system²⁵ combines the features of chlorite-iodide-oxidant and chlorite-iodate-reductant oscillators. It exhibits a wide variety of phenomena, not all of which have been fully explored. One of the more interesting, shown in Figure 9, is tristability among three different steady states. A third derived system, the chlorite-iodide-bromate reaction, will be considered in detail when we discuss coupled oscillator systems below.

III. Modeling

Kinetic Aspects. The rich array of dynamical phenomena exhibited by the chlorite-iodide and related systems offers an inviting challenge for mechanistic analysis. The logical place to start is with the minimal $ClO_2^{-}-l^{-}$ reaction under homogeneous conditions. If a satisfactory mechanism can be developed for this system, one can then attempt to expand and adapt it to describe more complex phenomena and systems. While some 15 years passed between the discovery of the BZ oscillator¹ and the proposal of a satisfactory mechanism³⁰ for it, development of a mechanism for the chlorite-iodide system³¹ required only 3 years. The greater speed with which mechanistic studies advanced in the latter system may be attributed to several factors: (a) earlier studies of the other oscillators had improved techniques for, and heightened interest in, the mechanistic analysis of chemical oscillators; (b) more powerful computers and software had become available; (c) more prior kinetics studies had been done on the components of the chlorite-iodide system than on those of the BZ reaction; (d) the inorganic chlorite-iodide reaction does not involve the large number of poorly characterized intermediates generated from the organic substrate of the BZ reaction.

In 1985, Epstein and Kustin³¹ constructed a 13-step mechanism for the chlorite-iodide reaction. The mechanism accounted for

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- 8649.
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TABLE II: An Elementary Step Mechanism for the Chlorite-Iodide Reaction

$Cl(III) + I^- + H^+ \rightarrow HOCl + HOI$
$HOI + I^- + H_2 \rightleftharpoons I_2 + H_2O$
$HClO_2 + HOI \rightarrow HOCl + HIO_2$
$HOCI + I^- \rightarrow HOI + CI^-$
$HIO_2 + I^- + H^+ \Rightarrow 2HOI$
2HIÕ ₂ → HOI + IO ₁ ⁻ + H ⁺
$HIO_{1}^{+} + HOI \rightarrow IO_{1}^{-} + I^{-} + 2H^{+}$
$HIO_{2}^{-} + HOCI \rightarrow IO_{3}^{-} + CI^{-} + 2H^{+}$

the batch "clock" behavior and for the bistability and periodic oscillation observed in a CSTR. It involved no radical intermediates, a significant departure from earlier mechanisms for chemical oscillators, but instead invoked a binuclear singlet intermediate, IClO₂. The construction of the mechanism relied heavily on previous experimental work on three key overall stoichiometric processes.

The stoichiometry of the reaction of Cl(III) with I⁻ was established in the early part of the century by Bray³² as

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2H_2O$$
 (10)

More recent kinetics studies⁸ showed that the reaction has a multiterm autocatalytic rate law:

$$\frac{1}{2} d[\sum I_2] / dt = (k_a[H^+][I^-] + k_b[I_2] / [I^-] + k_c[I_2])[ClO_2^-]$$
(11)

The $k_{\rm b}$ term in eq 11, which is autocatalytic in the product I₂ and inhibited by the reactant I⁻, plays a key role in promoting the oscillations.

The I₂ produced in reaction 10 can be further oxidized to iodate in another reaction whose stoichiometry was determined by Bray.32

$$5CIO_2^- + 2I_2 + 2H_2O \rightarrow 5CI^- + 4IO_3^- + 4H^+$$
 (12)

Grant et al.³³ used stopped-flow methods to establish the following rate law:

$$-\frac{1}{2} d[I_2]/dt = (k_d[ClO_2^-] + k_e[ClO_2^-]/[H^+] + k_f)[I_2]$$
(13)

Finally, the Dushman reaction³⁴

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
 (14)

plays an important role in many iodine-containing oscillators. A large number of studies of its kinetics are best summarized by the two-term rate law³⁵

$$-d[IO_3^-]/dt = k_g[H^+]^2[IO_3^-][I^-] + k_h[H^+]^2[IO_3^-][I^-]^2$$
(15)

By designing their mechanism to be consistent with the rate laws (11), (13), and (15) as well as with the "clock" behavior, Epstein and Kustin were able to construct a mechanism that explained much of the complex dynamics described above.

Just as the FKN mechanism³⁰ for the BZ reaction has undergone a number of revisions and improvements since it was first proposed, the initial chlorite-iodide mechanism³¹ has also been modified so as to improve the agreement with experiment and to reduce the number of steps. Citri and Epstein⁵ showed that a mechanism involving only six principal species and eight elementary steps gives somewhat better agreement with the flow experiments and is able to reproduce the partial regeneration of iodine in the batch experiments, which the earlier mechanism could not.³⁶ This simplified mechanism, shown in Table II, does not invoke either radicals, the intermediate IClO₂, nor ICl, whose formation was proposed by Beck and Rábai³⁶ as a route to regenerating I₂. The quality of the agreement between simulations based on the mechanism and the experimental results is shown in Figures 1 and 3-5.

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Efforts to improve the mechanism of the BZ reaction have resulted in more careful determination of the kinetics of elementary steps.³⁷ Again, a parallel situation exists in the chlorite-iodide system, where Song et al.³⁸ have recently used stopped-flow methods to reinvestigate the kinetics of the initial reaction between Cl(III) and I⁻ at low pH (<1.75) where the autocatalytic pathways in eq 11 are suppressed. They find a complex rate law

 $\frac{1}{2} d[\Sigma I_2]/dt =$ $(k_i[H^+] + k_i[H^+]^2)[Cl(III)][I^-]/([H^+] + K_a)$ (16)

where K_a is the dissociation constant of chlorous acid. These results, which have yet to be incorporated into a full mechanism for the reaction, may improve the pH dependence of the calculated behavior, one of the remaining weak points of the mechanism.

One of the virtues of a simplified mechanism like the one in Table II is that the model can be combined with mechanistic descriptions of other chemical and/or physical processes to treat more complex systems. For example, Citri and Epstein³⁹ have shown that the chlorite-iodide mechanism may be combined with an earlier model⁴⁰ of the bromate-iodide oscillator to yield a good description of the behavior of the chemically coupled bromatechlorite-iodide system. The remarkably complex behavior of this reaction is discussed in some detail below. The same simplified mechanism was used successfully by Boukalouch et al.41 to account for the oscillatory instability induced by mass interchange between two physically coupled steady-state CSTR's, while Sagués et al.⁴² have combined the Citri-Epstein mechanism⁵ with a Langevin equation approach to simulate and analyze the stochastic behavior of the batch reaction.¹⁰ In a similar vein, Weitz and Epstein⁴³ have used a primitive model of the chlorite-iodide kinetics together with a simple treatment of diffusion to simulate chemical wave propagation in the $ClO_2^--l^-$ reaction.

Mixing Effects. Mixing imperfections were initially attributed to macroscopic inhomogeneities arising from stagnation zones^{13c} or from localized composition gradients around the feed ports,13a and stirring effects were modeled by coupled arrays of homogeneous compartments whose relative sizes and exchange rates were treated as expendable parameters. These models implicitly discarded feeding mode sensitivity by assuming instantaneous mixing of feed streams. Though there are certainly macroscopic inhomogeneities in all CSTR experiments, especially around the feed ports, we now believe that the main origin of stirring and feeding mode sensitivity, irrespective of the reactor geometry, in the chlorite-iodide reaction lies in a more fundamental problem: the natural microscopic residual inhomogeneities of the bulk due to the finite time t_m necessary for mixing species at the molecular level. When a chemical reaction possesses several competing reaction paths, as in the chlorite-iodide reaction, the relative contributions of these paths can depend quite sensitively on the instantaneous composition of small eddies and thus on the way in which the chemicals are mixed. Because the reaction steps are fundamentally nonlinear processes, the averaged behavior of a distributed system can differ significantly from that of a homogeneous system with the same overall composition. It is this inherent nonlinearity that leads to micromixing effects.

The determination of the actual physical mechanisms of mixing is a very complex hydrodynamic problem. Nonetheless, several simple approaches have been developed which provide significant insight into the micromixing phenomenon.^{18,44} Several of the

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simplest models divide the contents of the reactor into a large number of elemental fluid parcels (i.e., small scale vortices), which exchange matter among themselves⁴⁵ or with their averaged environment^{44,46} on a time scale characteristic of the mixing time $t_{\rm m}$. In a well, but not ideally, mixed reactor, the residence time distribution of the fluid elements can be characterized by τ , the mean residence time which, in all the above-mentioned experiments, is large compared to t_m . Thus, at all times the fraction of "unmixed" fresh solution droplets, issuing from the feed, is of the order of $t_{\rm m}/\tau$. With such a description, no matter what feeding mode is chosen, an entering droplet always has more chance to interact with fluid elements having the composition of the bulk than with an unmixed droplet coming from another feed stream.

We now develop some crude heuristic arguments to show how feeding mode and stirring rate can change the dynamics of the chlorite-iodide reaction in a CSTR. Under PM conditions, the major reagents enter the reactor at high concentrations in the same fluid droplet and in appropriate stoichiometric ratio for the autocatalytic oxidation path (C3 + C4 + C5) of iodide to HOI. If the bulk composition of the reactor is on the LI branch, [HOI] will be high enough to trigger this autocatalytic reaction as soon as HOI penetrates the incoming droplet. The composition of the droplet will then approach that of the bulk in a short fraction of the time t_m . The PM mode thus favors the positive feedback reaction path, which stabilizes the LI state. Since transitions in the entering droplets occur on a time scale significantly shorter than the mixing time, the stability of the LI branch should not depend sensitively on the stirring rate. This is just what it is observed experimentally.^{14,16} With premixing the increased stability of the LI state enlarges the bistability region even at the expense of the oscillatory region.^{12a,d,16}

Under NPM conditions ClO_2^- and I^- enter the reactor in separate droplets. When the bulk composition is on the LI branch, the bulk $[I^-]$ is very low, and $[ClO_2^-]$ is virtually zero, while intermediate species such as HOI, HOCl, HIO₂, and I₂ are in relatively high concentrations. On mixing with the bulk, most of the iodide from the iodide-rich droplets is oxidized to iodine through the sequences (C5 + C2) and (C4 + C2). In the chlorite-rich droplets, in the absence of iodide, iodine species coming from the bulk are oxidized all the way to iodate through the sequence (C3 + C8). These different sequences of fast steps exhibit no positive feedback, and the rate of depletion of iodide and chlorite is essentially driven by the rate of the dilution (or mixing) processes. Thus, the rates of consumption of iodide and chlorite become strongly dependent on stirring rate. The characteristic lifetime of inhomogeneities is thus t_m , and the contribution of these inhomogeneities to the mean iodide concentration is of order $[I^-]_0 t_m / \tau \approx 10^{-7}$ M, which is significant (see Figure 1). This higher average iodide concentration destabilizes the LI branch and thus reduces the range of bistability. NPM feeds also favor the formation of I_2 and IO_3^- . These are relatively inert species on the time scale of the autocatalytic pathway, which introduces a time lag in the interaction of chlorite and iodide through their most reactive intermediate species. This delayed pathway competes with the autocatalytic pathway and, like any delay mechanism, enhances the potential for oscillatory behavior.

The above analysis is in agreement with the fact that oscillatory dynamics are readily observed with NPM feeds, while they are more difficult to find under PM conditions.^{12b-d,16} In the absence of premixing, increased stirring decreases the relative contribution of the nonautocatalytic reaction paths, and as observed experimentally, oscillatory behavior becomes favored at the expense of bistability.^{12,16} If the bulk composition belongs to the HI branch, the large [I⁻] quenches the autocatalytic processes, and the evolution of the reaction is slow, so that mixing is no longer a limiting factor. The stability of the HI branch thus depends but little on stirring rate and feeding mode, except possibly when the bulk iodide concentration deviates significantly from that of the feeds

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Figure 10. Phase diagram in the reciprocal residence time-[I⁻]₀ plane for the bromate-chlorite-iodide system.²⁶ Fixed constraints: T = 25 °C, [BrO₃⁻]₀ = 2.5 × 10⁻³ M, [ClO₂⁻]₀ = 1.0 × 10⁻⁴ M, [H₂SO₄]₀ = 0.75 M.

and when [I₂] and [HOI] become large enough to stimulate significantly the autocatalytic processes within the bulk. This view is borne out by all the experimental observations.

These heuristic ideas are supported by computational results obtained by modeling the mixing with a coalescence-redispersion method due to Curl^{45a} or with the interaction by exchange with the mean (IEM) model of micromixing.44 Studies employ either overall rate equations^{13a} or a more detailed six-variable reaction scheme based on the Citri-Epstein mechanism.⁵ The calculations clearly show that increased mixing rate or the use of PM feeds stabilizes the LI steady-state branch^{13a,47} and that NPM feeds favor oscillatory behavior.47

IV. Coupled Systems

Because of its multifaceted dynamics and the ease with which it can be combined with other species to yield new oscillators, the chlorite-iodide reaction has been the subject of several investigations of the behavior of coupled systems. We discuss here two types of studies. Those of chemically coupled systems⁴⁸ involve subsystems, each individually capable of oscillatory behavior, which have one or more species (reactant, intermediate, or product) in common and which are combined in a single reactor. Physically coupled systems consist of subsystems that are linked by transport of matter and/or energy. The simplest and most thoroughly studied case consists of an oscillatory reaction in two CSTR's that are coupled by mass interchange.

Chemical Coupling. In addition to their role in the chloriteiodide system, both ClO_2^- and I^- are key components of several other chemical oscillators. It is therefore possible to explore the behavior of chemically coupled systems in which the chloriteiodide reaction plays the role of one subsystem while the other subsystem is an oscillator involving either CIO_2^- or I⁻ and an additional component(s). Such composite systems sometimes display a considerably wider repertoire of dynamical behavior than either of their component subsystems.49

The most thoroughly studied system of this type is the reaction of bromate, chlorite, and iodide ions in a CSTR.²⁶ An indication of the complexity of this system is found in the phase diagram of Figure 10. Among the more interesting modes of behavior found are birhythmicity,²⁶ i.e., bistability between a large- and a small-amplitude oscillatory state, compound oscillation,²⁶ in which the two modes of oscillation appear to merge into a single waveform, and chaos,⁵⁰ or aperiodic oscillation. These phenomena are illustrated in Figure 11. As noted in the section on modeling, much of the dynamics of the bromate-chlorite-iodide system may



Figure 11. Complex dynamical behavior in the bromate-chlorite-iodide system. (a) Birhythmicity.²⁶ Flow rate in each time segment is shown as reciprocal residence time k_0 at top and is changed at each arrow. Oscillatory states A and B are both stable at $k_0 = 7.14 \times 10^{-3} \text{ s}^{-1}$. [I⁻]₀ = 6.5×10^{-4} M. Other constraints as in Figure 10. (b) Compound oscillation C between A and B states as flow rate is varied.²⁶ Fixed constraints as in (a), except $[I^-]_0 = 4.0 \times 10^{-4}$ M. (c) Chaotic oscillation.⁵⁰ $[H_2SO_4]_0 = 0.1$ M, $k_0 = 2.5 \times 10^{-3}$ s⁻¹. Other constraints as in (b).

be understood from consideration of the uncoupled $ClO_2^{-}-I^{-}$ and BrO₃⁻-I⁻ subsystems. Alamgir and Epstein⁴⁸ showed, in a comparative study of the BrO3--ClO2-I and BrO3--Mn2+-I coupled oscillator systems, that the coupling in the former is significantly stronger than in the latter.

A second chemically coupled oscillator system derived from the chlorite-iodide reaction is the chlorite-thiosulfate-iodideiodine reaction.⁵¹ In this system, which combines the chloriteiodide and chlorite-thiosulfate52 oscillators, one finds birhythmicity, tristability among two stationary and one oscillatory states, and a variety of other complex dynamical phenomena. No mechanism has been proposed for this system, largely because of the difficulties in elucidating the mechanism of the chlorite-thiosulfate subsystem.

Physical Coupling. A pair of stirred tank reactors coupled by mass interchange through a perforated wall constitutes perhaps the simplest means of investigating the behavior of physically coupled chemical systems. There have been a number of experimental studies in coupled CSTR's dealing with the coupling

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of autonomously oscillatory BZ reactions. These experiments have revealed a variety of phase-locked entrainment and chaotic-like phenomena.⁵³ Some experiments⁵⁴ have also produced "phase death", in which for an appropriate coupling strength (rate of mass transfer between the two reactors) oscillations cease. The coupled system is then left with the two reactors in two different steady states. In effect, the steady states of the oscillating systems have been stabilized by diffusion.

A complementary situation can be obtained with the chlorite-iodide reaction; that is, two uncoupled reactors in different steady states can be caused to oscillate by appropriately coupling them.^{41,55} In these experiments the reaction is performed in two vigorously stirred CSTR's fed in the PM mode in order to approximate two homogeneous tank reactors. The conditions are chosen so that each reactor can exhibit either monostability or bistability of two steady states, but not oscillation. With the constraint values used in Figure 12, each independent reactor exhibits bistability for $C_T = 9.7 \times 10^{-4} \text{ M} < [\text{ClO}_2]_0 < C_F =$ 1.06×10^{-4} M. If the chlorite feed of reactor I is fixed at $[ClO_2^{-1}]_0^{-1}$ = 8.0×10^{-4} M, the remaining adjustable control parameters for the coupled system are $[ClO_2^{-}]_0^{II}$, the chlorite feed concentration of reactor II, and the exchange rate D between the two reactors. Figure 12 shows the different dynamical regions observed in the $(D, [ClO_2^-]_0^{II})$ phase plane. As one might expect, at large D values the coupled system behaves as a single reactor, and only monostability and bistability are found, with both reactors in either the LI or the HI state. At very low values of D the two reactors act like uncoupled systems, and any combination of steady states in the reactors is possible.

In an intermediate range of D we find not only combinations of steady states but also, and more surprisingly, oscillatory behavior when the difference in chlorite feed concentrations between the two reactors is large enough. Large amplitude oscillations are observed in reactor I, while very small amplitude oscillations are recorded in reactor II (Figure 12). This is a nontrivial result, for an uncoupled homogeneous reactor cannot oscillate for any intermediate value of $[ClO_2^-]_0$ between $[ClO_2^-]_0^1$ and $[ClO_2^-]_0^{II}$. Oscillations result solely from the diffusion-like coupling and not from mixing artifacts, since the behavior in the two reactors has been shown to be independent of the stirring rate as long as the exchange rate D is maintained constant. Moreover, we have been able to simulate these coupling-induced oscillations⁴¹ using the reaction scheme discussed in the previous section. In the calculation, the rate constants were adjusted to simulate the behavior observed in the PM feeding mode with vigorous stirring, i.e., a nearly homogeneous reactor in which no oscillatory behavior is found at pH = 2.15 for physically reasonable iodide and chlorite input concentrations. Figure 12 shows the remarkably good agreement between the experimental and calculated phase diagrams without any further modification of the parameters beyond those mentioned above.

The oscillations induced by coupling two reactors and the enhanced oscillatory behavior found under NPM conditions may be viewed as two aspects of the more fundamental phenomenon of instability induced by inhomogeneities in a spatially distributed system.^{55,56} These experiments demonstrate that, contrary to a widely held belief, diffusion can be a destabilizing factor even when all species have essentially the same diffusion constant. Sensitivity

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Figure 12. Sections of phase diagram in the exchange rate constant (D_e) -[NaClO₂]₀^{II} plane in a system consisting of the chlorite-iodide reaction in two coupled CSTR's: (a) experimental, with $[NaClO_2]_0^{I} =$ $8 \times 10^{-4} \text{ M}, [\text{KI}]_0^{I} = [\text{KI}]_0^{II} = 3.5 \times 10^{-3} \text{ M}, [\text{H}_2\text{SO}_4]_0^{I} = [\text{H}_2\text{SO}_4]_0^{II} = 4.5 \times 10^{-3} \text{ M}, k_0^{I} = k_0^{II} = 2 \times 10^{-3} \text{ s}^{-1}, \text{ and } S^{I} = S^{II} = 800 \text{ rpm; (b)}$ calculated with rates given by the model of ref 5 except for $k_5 = 2 \times 10^6$ $M^{-2} s^{-1}$ and $k_6 = 100 M^{-1} s^{-1}$. [H⁺] fixed at 5 × 10⁻³ M; all other parameters as in the experiments. Symbols correspond to different combinations of states in the two CSTR's: ▲, LI^I-LI^{II}; ▼, HI^I-HI^{II}; △, $HI^{I}-LI^{II}$; ∇ , $MI^{I}-LI^{II}$; O, oscillations in I and II.

of the dynamics of a reaction to composition gradients may serve as a practical indicator that such a system is capable of supporting a variety of spatial self-organization phenomena, as we have seen in the chlorite-iodide reaction.

V. Spatial Behavior

Transient Patterns in Batch Systems. One of the most remarkable features of BZ-type reactions is their ability to generate spontaneous transient target or spiral wave patterns in an initially homogeneous, unstirred solution under batch conditions. Though the origin of the target patterns and the stability of the spiral core are still under debate, the nature of the propagating waves is well-understood. These wave structures develop because in many BZ systems excitable or oscillatory properties of the medium can

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Figure 13. Trigger wave pattern observed at 5 °C in a thin (2 mm) layer of solution with initial compositions $[CH_2(COOH)_2] = 0.0033 \text{ M}$, [NaI] = 0.09 M, $[NaClO_2] = 0.1 \text{ M}$, $[H_2SO_4] = 0.0056 \text{ M}$ and starch as indicator.



Figure 14. The continuous Couette flow reactor (schematic).63

persist over relatively long periods of time in closed reactors. Chlorite-iodide systems have essentially been developed as open-reactor oscillatory and bistable systems, and in batch they usually exhibit only a single switch, as shown in Figure 1. In a thin layer of solution a single sharp propagating front of chemical activity can be observed, sometimes followed by a soft recovery wave.43 As noted above (see Table I), two variants of the chlorite-iodide reaction show transient oscillatory behavior in batch. The chlorite-iodide-malonic acid system is the most effective batch oscillator of the chlorite-iodide variants. Batch trigger wave structures have been observed in unstirred solutions of this system. If starch is added as an indicator, repeated concentric pale yellow rings spread through a dark-blue solution as illustrated in Figure 13. As in BZ systems, waves annihilate on colliding and can be sheared to produce double rotating spirals. However, the phenomenon persists only for a brief while and is best observed at temperatures below 10 °C. The structures are only found in a narrow range of the chlorite:iodide concentration ratio. The wave propagation speed, which varies with the composition, is in the range 4-8 mm/min. Although, in contrast to BZ systems, the composition can easily be chosen to avoid precipitate or bubble formation, few studies have been carried out on the batch spatial behavior of the chlorite-iodide-malonic acid reaction.

Sustained Spatiotemporal Chemical Patterns. In recent years there has been a considerable effort to develop reactors for studying spatiotemporal behavior under open, continuum conditions. These studies have led to the discovery of sustained spiral wave patterns⁶⁰ and of a number of new chemical spatial structures.^{61–63} The



Figure 15. Light intensity profiles along the axis of the CCFR with identical flows from the two CSTR's. $[KI]_0^{I,II} = 3.5 \times 10^{-3} \text{ M}$, $[H_2S-O_4]_0^{I,II} = 4.5 \times 10^{-3} \text{ M}$, $[NaCIO_2]_0^{I,II} = 0.91 \times 10^{-3} \text{ M}$, T = 26 °C, inand outflow rate of each CSTR = 30 cm³ min⁻¹, $\Omega = 1080$ rpm ($D_e \simeq 0.39 \text{ cm}^2 \text{ s}^{-1}$).



Figure 16. Spatial bistability in wave front width Δ as D_e is varied with all other conditions as in Figure 15: circles, experiment; lines, computed.

chlorite-iodide reaction and its variants have shared top billing with the BZ-type reactions in these investigations, particularly in experiments performed in continuous Couette flow reactors (CCFR's). A CCFR consists of a long, thin, cylindrical annular reactor (Figure 14) with an inner cylinder rotating at an adjustable rate Ω and an outer cylinder at rest (i.e., a circular Couette flow⁶⁴). The reactor is connected to two CSTR's. The CSTR's provide a means to control the boundary feed compositions at each end of the Couette flow. The rapid rotation of the inner cylinder generates turbulent Taylor vortices,64 which enhance the mass transport in the interstitial fluid. The length of the annular reactor is much greater than its width, so that the chemicals are rapidly mixed in the radial and azimuthal directions, and the axial transport becomes the only relevant transport parameter. The axial transport can then be characterized by an effective diffusion coefficient $D_{\rm e}(\Omega)$.⁶⁵ The CCFR is thus a practical implementation of a one-dimensional reaction-diffusion system, with adjustable diffusion rates orders of magnitude larger than the molecular diffusion.

In this spatial reactor the chlorite-iodide reactions have produced the first examples of a spatial bistability and of a stationary spatial structure⁶³ not directly linked to the geometrical and time invariants of the environment. Spatial bistability can be obtained with the minimal chlorite-iodide reaction when the two end CSTR's are fed with identical compositions corresponding to the

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Figure 17. Space-time representation of sustained spatial and spatiotemporal structures observed⁶³ in the chlorite-iodide-malonic acid reaction. All boundary constraints are equal at both ends and fixed throughout the experiments, except for the chlorite input into CSTR II, which is different for each pattern. Fixed constraints: $\Omega = 840 \text{ rpm }(D_e \simeq 0.31 \text{ cm}^2 \text{ s}^{-1})$, $T = 26 \, ^{\circ}\text{C}$, in- and outflow rate = 10 cm³ min⁻¹, $[\text{KI}]_0^{\text{-I,II}} = 3.5 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO4}]_0^{\text{-I,II}} = 4.5 \times 10^{-3} \text{ M}$, $[\text{CH}_2(\text{COO-H})_2]_0^{\text{-I,II}} = 2.0 \times 10^{-3} \text{ M}$, starch (Prolabo iodine indicator) 2 g L⁻¹, and $[\text{NaClO}_2]_0^{\text{-II}} = 0$. (a) Single stationary front, $[\text{NaClO}_2]_0^{\text{-II}} = 8 \times 10^{-3} \text{ M}$; (b) simple oscillating front, $[\text{NaClO}_2]_0^{\text{-II}} = 11 \times 10^{-3} \text{ M}$; (d) $[\text{NaClO}_2]_0^{\text{-II}} = 12 \times 10^{-3} \text{ M}$; (e) $[\text{NaClO}_2]_0^{\text{-II}} = 14 \times 10^{-3} \text{ M}$; (f) nontrivial stationary structure, $[\text{NaClO}_2]_0^{\text{-II}} = 15 \times 10^{-3} \text{ M}$.

HI steady-state branch. For the same set of parameter values two quite different stable stationary concentration profiles can be observed along the axis of the cylinder as exemplified by the two transmitted light intensity profiles shown in Figure 15. The first state (Figure 15a) is characterized by a nearly constant low value of the light intensity and corresponds to a quasi-uniform state with chemical compositions belonging to the HI branch. The second state (Figure 15b) exhibits a sudden jump in the light intensity in the middle of the reactor, where the reaction switches to concentrations corresponding to the LI branch. The narrow region separating the parts of the Couette flow on the two different branches is associated with very steep concentration gradients and is referred to as a chemical front.

The distance Δ between the pairs of stable chemical fronts thus formed depends on the constraint values, especially the rotation rate Ω of the inner cylinder, that is, on D_e . Figure 16 shows the dependence of Δ on D_e . Note that on increasing D_e beyond 0.47 cm²/s the double-front structure suddenly collapses and the system undergoes a transition to the quasi-uniform ($\Delta = 0$) state. On decreasing D_e , the reverse transition occurs with hysteresis at D_e = 0.29 cm² s⁻¹. The hysteresis loop defines the domain of spatial bistability. These observations are well accounted for by a onedimensional diffusive description of the matter transport along the axis of the Couette flow together with the same kinetic model used in the coupled CSTR simulations.⁶⁶

Interesting spatiotemporal structures are obtained when the two end CSTR's are fed with quite different compositions. The experiments were conducted on the chlorite-iodide-malonic acid variant with chlorite feed concentrations chosen so that CSTR I was on the LI branch while CSTR II was on the HI branch. Under these conditions a stable front separating the regions on the two branches naturally develops. More surprisingly, this front becomes unstable if the chlorite feed concentration difference is greater than a critical value. Spatiotemporal behavior of front structures is conveniently represented in time (ordinate) plots of the position(s) (abscissa) of the front(s) as in Figure 17. The following sequence of states was observed when the chlorite feed concentration in CSTR II was gradually increased: (i) a single stationary front (Figure 17a); (ii) a single oscillating front (Figure 17b), i.e., the front position moves back and forth periodically in the axial direction, between two well-defined limits; (iii) temporary multiple moving fronts (Figure 17c,d), where different structures with temporal alternations of one and three fronts can

be distinguished; (iv) three permanent oscillating fronts which eventually stabilize to produce (v) a stable, multipeaked, timeindependent spatial structure. This spatial structure is the most significant discovery resulting from the CCFR. The quest for such structures has been, for many years, a major objective in the field of nonlinear chemical dynamics.

It is important to point out that in the CCFR, because of the turbulent diffusion, all the chemical species have the same effective diffusion coefficient. Thus, the observed structure is not related to the Turing bifurcation⁶⁷ so popular in theoretical works on reaction-diffusion instabilities. The stationary structure described above seems to be induced by the strong chemical gradients imposed at the boundaries of the system and not by differences in the diffusion coefficients of chemical species, as required for Turing structures. Recent numerical and analytical studies by Elezgaray and Arneodo⁵⁶ on a simple mathematical model of a reaction-diffusion system under asymmetric boundary conditions support the interpretation that the observed structure is induced by the external boundary gradient.

BZ-type reactions have also been studied in CCFR's. In these experiments the emphasis was initially on diffusion-induced spatiotemporal chaos.^{62c} More recently, the reaction has been shown to produce quasi-stationary spatial structures bearing some similarity to those discovered earlier in the chlorite-iodide system.^{63b,c}

VI. Conclusion

As the above survey of dynamical phenomena in the chloriteiodide and related reactions indicates, the reaction of ClO_2^- and I^- provides an extremely rich source of interesting and often surprising behavior. Although most laboratories studying nonlinear chemical dynamics have thus far chosen to work with the more familiar BZ reaction, the chlorite-iodide system not only provides an alternative but also has, we feel, several advantages. Perhaps the most important is that, as a purely inorganic system, it offers a better opportunity for fully characterizing its mechanism. Despite recent progress on the inorganic aspects of the BZ mechanism, the chlorite-iodide system is considerably better understood from a mechanistic point of view. As more detailed modeling of complex phenomena becomes possible, this feature will become increasingly important.

The other area in which the chlorite-iodide system has had and continues to have a major impact is in the study of spatiotemporal phenomena. Chemists' understanding of stirring and mixing effects in CSTR's has arisen largely as a result of experiments and modeling on the $ClO_2^{-}-I^{-}$ reaction. Similarly, the phenomenon of rhythmogenesis by reaction-diffusion coupling was experimentally confirmed first for the chlorite-iodide system. The early preeminence of the BZ reaction in studies of chemical pattern formation derives from the capacity of BZ-type reactions to develop and sustain transient wave patterns in closed systems over long periods of time. This apparently unique property has become much less critical with the recent development of open spatial reactors. In these reactors, the absence of macroscopic quantities of product gas often gives chlorite-iodide systems a decisive advantage over BZ-type reactions.

The ongoing development of techniques for studying spatiotemporal patterning in open systems relies heavily on the chlorite-iodide-malonic acid reaction as a prototype system. This feature was recently highlighted by the unambiguous observation of the first Turing-type symmetry-breaking stationary structure in a single-phase isothermal chemical system.⁶⁸ The quest for such a self-organizing phenomenon has been a major goal of research in the field of chemical dissipative structures for more than three decades.

In less than a decade, the chlorite-iodide system has established itself as one of the most useful reactions in nonlinear chemical dynamics. We anticipate that its role will continue to grow as

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more workers in the field become aware of its versatility.

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ARTICLES

Nuclear Magnetic Resonance Studies of Carboxylic Acids. 2. Dilution Shift of the Hydroxylic Proton in the Acetic Acid–Pyridine System

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NMR dilution shifts have been measured for the binary acetic acid-pyridine system at 35, 60, 80, and 100 °C. The entire pattern of the dilution shift curve is explained in terms of the monomer-dimer-chain polymer equilibria among the acid and acid monomer-pyridine and acid polymer-pyridine complexes formation equilibria. The molar enthalpy of hydrogen-bonded complex formation was found to be 36 kJ/mol.

Introduction

The first paper¹ of this series is a report on NMR study on acetic acid in an inert solvent which is cyclohexane, showing that when the residual moisture in the solvent is carefully excluded, the observed dilution shift curves differ substantially from those reported earlier, and the entire pattern of the curves can be interpreted by the use of the modified Goldman-Emerson model² to obtain thermodynamic and spectroscopic parameters. The change of the total pattern of the dilution shift curves for the acetic acid-pyridine binary system by the exclusion of residual moisture in pyridine has been described previously.³ In this paper an attempt to interpret the previously published dilution shift curve of acetic acid in rigorously dried pyridine is reported. The interpretation is based on the modified Goldman-Emerson model.

Experimental Section

The procedures for purification of acetic acid, cyclohexane, and pyridine and sample preparation were the same as previously described.^{1,3} NMR spectra were measured with Varian V4300B (opening at 60 and 40 MHz) and Hitachi R42 (operating at 90 MHz) high-resolution NMR spectrometers.

The temperature control unit of a Varian V4300B operating at 60 MHz was modified⁴ to improve the accuracy of the temperature setting and to suppress the drift and the fluctuation of sample temperatures within ± 0.1 °C. An ambiguity with regard to the concentration of the solution at the position of the NMR probe detector coil caused by refluxing of the solution at elevated temperatures was also avoided by the modification of the probe structure.

When the observed chemical shift values on different spectrometers do not agree with each other within ± 0.001 ppm, the value obtained by a Varian V4300B at 60 MHz was taken as the final data since the spectrometer has been modified to keep the accuracies of sample temperature and concentration at elevated temperatures.⁴ For the determination of chemical shift value on the order of 0.001 ppm, the sideband technique was employed instead of reading the chemical shifts on the calibrated chart.

Results and Discussion

The concentration dependences of the chemical shift of the hydroxylic proton in the acetic acid-pyridine binary system at various temperatures are shown in Figure 1. The entire patterns of the shift curves have slightly changed with the change of the temperature. The feature of change of the pattern of shift curves indicates the decrease of the fraction of acid polymer at elevated temperature.

The observed line width was sharp enough to determine the center of peak without difficulty, and it was not increased upon dilution indicating the absence of significant amounts of exchangeable impurities.

There have been numerous studies on interactions in acid-base systems or acid-base-solvent ternary systems. Spectrophotometric titrations⁵ suggested that the degree of ionization was negligibly small, and Raman,⁶ infrared,⁷⁻⁹ or dielectric^{9,10} studies suggested that proton transfer did not occur in the acetic acid-pyridine system. Therefore, the obtained dilution shift curves have been interpreted in terms of hydrogen-bonding interactions. The model which has been used for the interpretation of the acetic acidcyclohexane system is employed for the interpretation of the current system with some modifications.

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