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–Zhabotinskii (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 systems covered, 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" 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 mechanism$^2$ 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 concentrations$^5$ 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.$^7$ 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,$^8$ has been characterized by Nagypáll and Epstein.$^9$ The distribution of reaction times, which is reproducible, is sensitive

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attributed to amplification of internal fluctuations by the high-steady-state branches is noteworthy. The continuation of the thermodynamic equilibrium state observed in the also to the ability of the system to produce chemical waves (vide infra).

Figure 1. Batch behavior of the chlorite-iodide reaction at 25 °C and pH 3.3 with initial concentrations [ClO$_2^-$] = 2.5 × 10$^{-4}$ M and [I$^-$] = 4 × 10$^{-4}$ M: (a) experimental; (b) calculated.

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 high-order auto-catalysis or "supercatalysis." 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 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 pl$^+$ and [I$^-$] 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. 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 experimental and theoretical investigations 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. 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. If, in contrast to the original NPM feeding mode, the major reactants are mixed just before they enter the reactor through a single port, a mode of the state could take place between the input species.

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

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

(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.

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 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.\(^1\)\(^2\)\(^3\)

(of the order of the smallest hydrodynamic turbulent scale) involve
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 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 suppressed12
if the reaction is dominated by nonlinear kinetic terms (second
order of the order of the smallest hydrodynamic turbulent scale) involve
reactor geometry (position of input ports, shape of stirrer, etc.)
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micromixing effects are manifest even when the reacting medium
strongly dependent on the feeding mode of the reactor.

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)
dissolved (O3) 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 Zhabotinski’s malonic
acid either released or dissolved by the medium. Studies20 of stirring rate effects
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system premixing can lead to significant initial reaction in the
premixer.

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 oscilla-
tor,2 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 os-
cillatory 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 I3 or I2, or as a reductant of iodine
or iodate to generate I1, 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

\[ I(V) + 5I^- \rightarrow 6I(0) \]  
\[ 4I(0) + CI(III) \rightarrow 4I(0) + CI^- \]  
\[ 4I(0) + 5Cl(III) \rightarrow 4I(0) + 5Cl^- \]  
where I(0), I(V), and CI(III) represent 1/2I2, IO3, and IO3 respectively.

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

\[ \text{Ox} + I^- \rightarrow \text{Red} + I(0) \]  
\[ 5\text{Ox} + I(0) \rightarrow 5\text{Red} + I(V) \]  
\[ \text{Ox} + CI(III) \rightarrow \text{Red} + CI(IV) \]  
\[ 2\text{Ox} + CI(III) \rightarrow 2\text{Red} + CI(V) \]  
where CI(IV) and CI(V) represent CI2 and CI3 respectively.

If processes 4 and 5 are fast enough, then oscillation becomes
possible in regions of the phase diagram where [CI2]/[I-] 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

\[ I(V) + 6\text{Red} \rightarrow I^- + 6\text{Ox} \]  
\[ I(0) + \text{Red} \rightarrow I^- + \text{Ox} \]

De Kepper et al.

Figure 9. Tristability in the chlorite-iodide-arsenite-iodate system. B<sub>t</sub> indicates region of bistability between SS and SS<sub>t</sub>. T indicates region of tristability. Fixed constraints: [ClO<sub>3</sub>]<sub>o</sub> = 2.5 x 10<sup>-3</sup> M, [IO<sub>3</sub>]<sub>o</sub> = 5 x 10<sup>-3</sup> M, pH 3.35, k = 5.35 x 10<sup>4</sup> s<sup>-1</sup>, T = 25 °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<sup>-</sup> is generated of tristability. Fixed constraints [ClO<sub>3</sub>]<sub>o</sub>

Examples of ClO<sub>3</sub>−I<sup>-</sup>Ox, ClO<sub>3</sub>−IO<sub>3</sub>−Red, and ClO<sub>2</sub>−I<sup>-</sup>Red oscillators are given in Table I. Three systems in particular merit special mention. The chlorite−iodide−malonic acid reaction<sup>29</sup> features have made it a useful system for the study of nonlinear 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−arsenite system<sup>30</sup> 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<sub>3</sub>−I<sup>-</sup> 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 oscillator<sup>1</sup> and the proposal of a satisfactory mechanism<sup>30</sup> for it, development of a mechanism for the chlorite−iodide system<sup>27</sup> 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 kinetic 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 Kustin<sup>27</sup> constructed a 13-step mechanism for the chlorite−iodide reaction. The mechanism accounted for 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, IO<sub>3</sub><sup>-</sup>. 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<sup>-</sup> was established in the early part of the century by Bray<sup>23</sup> as

\[ \text{ClO}_3^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2H_2O \] (10)

More recent kinetics studies<sup>31</sup> showed that the reaction has a multitem period autocatalytic rate law:

\[ \frac{1}{2} \frac{d[\Sigma I_2]}{dt} = (k_a[ClO_3^-][I^-] + k_b[ClO_3^-][I^-] + k_c[I_2]) \] (11)

The k<sub>b</sub> term in eq 11, which is autocatalytic in the product I₂ and inhibited by the reactant I<sup>-</sup>, plays a key role in promoting the oscillations.

The I<sub>2</sub> produced in reaction 10 can be further oxidized to iodate in another reaction whose stoichiometry was determined by Bray<sup>23</sup> as

\[ 5\text{ClO}_3^- + 2I_2 + 2H_2O \rightarrow 5\text{Cl}^- + 4\text{IO}_4^- + 4H^+ \] (12)

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

\[ \frac{1}{2} \frac{d[IO_3^-]}{dt} = (k_a[ClO_3^-][I^-] + k_b[ClO_3^-][I^-] + k_c[I_2]) \] (13)

Finally, the Dushman reaction<sup>34</sup>

\[ \text{IO}_3^- + 3\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \] (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 law<sup>35</sup>

\[ -d[IO_3^-]/dt = k_a[H^+][IO_3^-][I^-] + k_b[I_2] \] (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 mechanism<sup>30</sup> for the BZ reaction has undergone a number of revisions and improvements since it was first proposed, the initial chlorite−iodide mechanism<sup>27</sup> has also been modified so as to improve the agreement with experiment and to reduce the number of steps. Citri and Epstein<sup>28</sup> 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. This simplified mechanism, shown in Table II, does not invoke either radicals, the intermediate IClO<sub>4</sub> or ICl, whose formation was proposed by Beck and Rábáti<sup>26</sup> as a route to regenerating I<sub>2</sub>. The quality of the agreement between simulations based on the mechanism and the experimental results is shown in Figures 1 and 3–5.

### Table II: An Elementary Step Mechanism for the Chlorite−Iodide Reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Law</th>
</tr>
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<tbody>
<tr>
<td>C1</td>
<td>Cl(III) + I&lt;sup&gt;-&lt;/sup&gt; + H&lt;sup&gt;+&lt;/sup&gt; → HOCl + HOI</td>
</tr>
<tr>
<td>C2</td>
<td>HOI + I&lt;sup&gt;-&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O → I&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>C3</td>
<td>HClO&lt;sub&gt;2&lt;/sub&gt; + HOI → HOCl + HIO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>C4</td>
<td>HOCl + I&lt;sup&gt;-&lt;/sup&gt; + Cl&lt;sup&gt;-&lt;/sup&gt; → ClO&lt;sub&gt;3&lt;/sub&gt;^- + I&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>C5</td>
<td>HIO&lt;sub&gt;2&lt;/sub&gt; + I&lt;sup&gt;-&lt;/sup&gt; + H&lt;sup&gt;+&lt;/sup&gt; → 2HOI</td>
</tr>
<tr>
<td>C6</td>
<td>2HIO&lt;sub&gt;2&lt;/sub&gt; → HOI + IO&lt;sub&gt;3&lt;/sub&gt;^- + H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>C7</td>
<td>HIO&lt;sub&gt;2&lt;/sub&gt; + HOI → IO&lt;sub&gt;3&lt;/sub&gt;^- + I&lt;sup&gt;-&lt;/sup&gt; + 2H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>C8</td>
<td>HIO&lt;sub&gt;2&lt;/sub&gt; + HOCl → IO&lt;sub&gt;3&lt;/sub&gt;^- + Cl&lt;sup&gt;-&lt;/sup&gt; + 2H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

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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. Again, a parallel situation exists in the chlorite–iodide system, where Song et al. 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

$$\frac{1}{2} d[\text{S}_{1}] / dr = (k_1[H^+] + k_2[H^+]_0)[\text{Cl(III)}]/[H^+] + K_3$$

(16)

where $K_4$ 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 Epstein have shown that the chlorite–iodide mechanism may be combined with an earlier model of the bromate–iodide oscillator to yield a good description of the behavior of the chemically coupled bromate–chlorite–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. for account of the oscillatory instability induced by mass interchange between two physically coupled steady-state CSTR’s, while Saguès et al. have combined the CITRI–Epstein mechanism with a Langevin equation approach to simulate and analyze the stochastic behavior of the batch reaction.

In a similar vein, Weitz and Epstein 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$_2^--$I$^-$ reaction.

**Mixing Effects.** Mixing imperfections were initially attributed to macroscopic inhomogeneities arising from stagnation zones or from localized composition gradients around the feed ports, 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 homogenous 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 and provide significant insight into the micromixing phenomenon. Several of the 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 themselves or with their averaged environment on a time scale characteristic of the mixing time $t_m$. In a well, but not ideally, mixed reactor, the residence time distribution of the fluid elements can be characterized by $\tau$, 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 $t_m/\tau$. 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. But with the bulk composition of the reaction lies in a more fundamental problem: the main origin of stirring and feeding mode sensitivity, irrespective of the reactor geometry, in the chlorite–iodide reaction.

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, HIO$_2$, and I$_2$ are in relatively high concentrations. On mixing with the bulk, most of the iodide from the iodide-rich droplets is oxidized to iodate 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 chlorine 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 $[I^-]_m/\tau = 10^{-7}$ 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. 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. 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.
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 Curf [56] or with the interaction by exchange with the mean (JEM) model of micromixing. [44] Studies employ either overall rate equations [36] 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 systems [48] 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 chlorite-iodide system, both ClO₂⁻ 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 chlorite-iodide reaction plays the role of one subsystem while the other subsystem is an oscillator involving either ClO₂⁻ 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.

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 [26] 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 be understood from consideration of the uncoupled ClO₂⁻-I⁻ and BrO₃⁻-I⁻ subsystems. Alamgir and Epstein [49] showed, in a comparative study of the BrO₃⁻-ClO₂⁻-I⁻ and BrO₃⁻-Mn⁺⁺⁻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-iodide-iodine reaction. [5] In this system, which combines the chlorite-iodide and chlorite-thiosulfate [29] oscillators, one finds birhythmicity, bistability 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...
of autonomously oscillatory BZ reactions. These experiments have revealed a variety of phase-locked entrainment and chaotic-like phenomena. Some experiments 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. 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 \( C_5 = 9.7 \times 10^{-4} \text{ M} < [\text{ClO}_2^-]_1 < C_6 = 1.06 \times 10^{-3} \text{ M} \). If the chloride feed of reactor I is fixed at \([\text{ClO}_2^-]_1 = 8.0 \times 10^{-4} \text{ M}\), the remaining adjustable control parameters for the coupled system are \([\text{ClO}_2^-]_2\); the chloride feed concentration of reactor II, and the exchange rate \( D \) between the two reactors. Figure 12 shows the different dynamical regions observed in the \((D, [\text{ClO}_2^-])\) 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 chloride 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 \([\text{ClO}_2^-]_2\) between \([\text{ClO}_2^-]_1\) and \([\text{ClO}_2^-]_2\). 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 oscillations 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 \( \text{pH} = 2.15 \) 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. 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 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 Bath 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
The chlorite-iodide reaction and its variants have shared top billing in recent years with the minimal chlorite-iodide reaction when the system is maintained at a low temperature and concentration ratio. The reaction has been used to study spatial bistability and the generation of stationary and propagating patterns.

**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 patterns and of a number of new chemical spatial structures.

**Open Reactor Oscillatory and Bistable Systems**

Open-reactor oscillatory and bistable systems, and in batch they exhibit only a single switch, as shown in Figure 1. In a thin layer of solution a single sharp propagating front of chemical precipitate or bubble formation, few studies have been carried out on the batch spatial behavior of the chlorite-iodide-malonic acid reaction. The continuous Couette flow reactor (schematic) shows transient oscillatory behavior in the 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 with an inner cylinder rotating at an adjustable rate and an outer cylinder at rest (i.e., a circular Couette flow). 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, 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. 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 structure 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 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 with an inner cylinder rotating at an adjustable rate and an outer cylinder at rest (i.e., a circular Couette flow). 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, 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. 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.

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Figure 17. Space-time representation of sustained spatial and spatiotemporal structures observed 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: $D = 840 \text{ rpm}$ ($D_o = 0.31 \text{ cm}^2 \text{s}^{-1}$), $T = 26^\circ\text{C}$, in- and outflow rate $= 10 \text{ cm}^2 \text{min}^{-1}$, $[\text{Kl}]_{\text{in}} = 3.5 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4]_{\text{in}} = 4.5 \times 10^{-3} \text{ M}$, $[\text{CH}_2\text{COOH}]_{\text{in}} = 2.0 \times 10^{-3} \text{ M}$, starch (Prolabo iodine indicator) 2 g L$^{-1}$, and $[\text{NaClO}_2]_{\text{in}} = 0$. (a) Single stationary front, $[\text{NaClO}_2]_{\text{liq}} = 8 \times 10^{-3} \text{ M}$; (b) simple oscillating front, $[\text{NaClO}_2]_{\text{liq}} = 9 \times 10^{-3} \text{ M}$. Multiple oscillating fronts: (c) $[\text{NaClO}_2]_{\text{liq}} = 11 \times 10^{-3} \text{ M}$; (d) $[\text{NaClO}_2]_{\text{liq}} = 12 \times 10^{-3} \text{ M}$; (e) $[\text{NaClO}_2]_{\text{liq}} = 14 \times 10^{-3} \text{ M}$; (f) nontrivial stationary structure, $[\text{NaClO}_2]_{\text{liq}} = 15 \times 10^{-3} \text{ M}$.

VI. Conclusion

As the above survey of dynamical phenomena in the chlorite–iodide and related reactions indicates, the reaction of $\text{ClO}_2^-$ and $\text{I}^-$ 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 been largely a result of experiments and modeling on the $\text{ClO}_2^- – \text{I}^-$ reaction. Similarly, the phenomenon of rhythmosgenesis 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 asymmetry-breaking stationary structure in a single-phase isothermal chemical system. 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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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 paper\(^1\) 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 model\(^2\) 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.\(^3\) 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 modified\(^4\) 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.\(^5\) 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 titrations\(^6\) suggested that the degree of ionization was negligibly small, and Raman,\(^7\) infrared,\(^8\) 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 acid–cyclohexane system is employed for the interpretation of the current system with some modifications.

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