Experimental and Theoretical Studies of a Coupled Chemical Oscillator: Phase Death, Multistability, and In-Phase and Out-of-Phase Entrainment

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The oscillatory Belousov-Zhabotinskii reaction with acetylacetone as substrate has been studied in a pair of stirred tank reactors coupled by mass flow. The inputs to the two cells, and hence the uncoupled oscillation frequencies, are slightly different. Depending upon the coupling strength, three types of behavior are observed: in-phase entrainment, out-of-phase entrainment, or phase death (cessation of oscillations and transition to a steady state). For some values of the coupling, more than one of these three states may be stable. The origins of this behavior are discussed in terms of the Field-Körös-Noves mechanism for the chemistry and the role of the intercell transport. Simulations using two coupled three-variable Oregonator models and a phase plane analysis of those results give good agreement with the experiments and support our mechanistic interpretation of the dynamical behavior.

Introduction

Coupled chemical oscillators are key components of many naturally occurring and man-made systems. They have thus been the object of much study, including not only experimental but also mathematical efforts. There have been several investigations of coupled Belousov-Zhabotinskii (BZ) reactions. Marek and Stuchl^{2,3} coupled two stirred tank reactors (CSTR's) by mass transfer through a perforated wall. For certain values of the coupling strength they found entrainment of oscillations when the natural frequencies of the uncoupled BZ oscillators had ratios in the neighborhood of 1:1, 2:1, and 3:1. Fujii and Sawada⁴ and Nakajima and Sawada⁵ also coupled BZ oscillating reactions by mass transfer and constructed a phase diagram of observed entrainment ratios. The experiments and calculations of Crowley and Field^{6,7} on electrically coupled BZ reactions show entrainment at 1:1, 2:1, 3:1, etc., as well as quasi-periodic and chaotic oscillations for other frequency ratios.

Bar-Eli⁸ has simulated several models of chemical oscillators coupled via mass transfer. The simulations and steady-state analysis show that coupling can cause a pair of oscillators that would oscillate independently if uncoupled to reach a stable steady state where all oscillations stop. Entrained oscillations resume at coupling strengths above and below those producing the steady state. In most models studied, a bifurcation occurs with hysteresis at the stronger coupling side of the region of stability of the steady state, giving rise to a region of coexistence between the steady state and the entrained oscillations. In particular, these phenomena occur in all models of coupled BZ reactions. Experiments to confirm the simulations were done9 in which the mass transfer was effected by pumping solution between cells. The oscillations stopped and started as predicted, but no hysteresis was observed. Although the pumping makes the coupling well-defined and controlled, there is a delay between the time the solution leaves one cell and enters the other cell. Such delays may play a significant role in the dynamics of a system.

There have been many theoretical investigations of other models of coupled oscillators. Tyson and Kauffman¹⁰ studied in-phase and out-of-phase oscillations in coupled Brusselator models. Two recent examples are a normal form analysis of the behavior of

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two coupled Brusselators¹¹ and a simulation of two diffusively coupled enzyme-induction systems.¹² Probably the most detailed recent study is that of Aronson et al.,¹³ in which a simple twovariable model chosen not for its chemical relevance but for its mathematical tractability is used as the basis for a thorough analysis of the modes of behavior available to a coupled oscillator system.

The aim of the present study is to examine the behavior of two nearly identical BZ oscillators physically coupled by mass transfer. In particular, we are interested in the phenomenon of phase death in coupled chemical oscillators. Phase death is the name given¹⁴ to the steady state produced by coupling two or more oscillators. Two kinds of phase death are predicted for linearly coupled oscillating systems. The first type involves the decay, as the coupling is increased, of the coupled limit cycle toward a central, homogeneous steady state lying within both of the uncoupled limit cycles. This effect of coupling was observed by Bar-Eli⁸ in his computations. The second form of phase death is characterized by the appearance of one or two steady states on the limit cycle traced out by stable out-of-phase entrained oscillations. The calculations and experiments of Crowley and Field^{6,7} show no noticeable deviation from the limit cycle trajectory with increase in coupling. Instead, the coupling changes the amount of time spent by the system in different parts of the trajectory. The results of the experiments so far suggest that the steady state produced by the coupling lies on the limit cycle. To confirm this observation, a more detailed and well-controlled experiment is necessary. In particular, it is desirable to measure more than one variable, such as [Ce(IV)] and [Br⁻], simultaneously. In order to eliminate experimental problems caused by unequal mass transfer and delay time, we have designed a new type of coupled reactor. This apparatus is described in the next section.

In our experiments we observed various coupled behaviors whose regions of stability overlapped, giving bistability and tristability. These behaviors were confirmed in numerical simulations. Since coupled oscillators are so important in biological and other systems, we discuss in some detail how oscillations are suppressed and multistability arises in terms of how coupling affects the individual oscillators' limit cycles.

Experimental Section

Materials. The BZ reaction consisting of organic substrate, cerium ion, bromate ion, and sulfuric acid was run in a pair of coupled flow reactors (CSTR's) with acetvlacetone substituted for the usual substrate, malonic acid. This substitution was made to avoid the bubbles produced in the malonic acid BZ reaction.8 The following materials were used without further purification:

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Figure 1. Schematic diagram of reactor for coupled BZ reactions: (a) side view; (b) top view.

2,4-pentanedione (acetylacetone, 99+%, Aldrich Gold Label), Ce(NO₃)₃·6H₂O (Fisher Purified Grade), NaBrO₃ (Fisher Certified 99.7+%), and H₂SO₄ (Fisher Reagent ACS). The reactant solutions were made with stock 1.1 M H₂SO₄. There were two feedstreams to each reactor: one containing cerium and acetylacetone the other containing bromate. The concentrations of all feedstream species except acetylacetone were identical in the two reactors where, after mixing in the reactor, $[BrO_3^-] = 0.053$ M and $[Ce(III)] = 2.3 \times 10^{-3}$ M. The concentrations of acetylacetone after mixing were 0.015 M in cell 1 and 0.016 M in cell 2. All solutions were purged with N₂ to remove oxygen. The purging of the acid-bromate solutions also served to remove the Br₂ resulting from the presence of bromide ion in the salt.

Reactor. The reactor is schematically pictured in Figure 1. There are two identical cells side by side with conical roofs and motor-driven stirrer impellers. Reactants are pumped in through small inlets in the floors of the reactors, and overflow takes place through a small hole in the top of each reactor. Coupling is effected via ports in the walls of the cells through which solution is forced by impellers. The coupling strength may be adjusted by needle valves in these ports. The rate of mass transfer in each direction is strongly affected by small changes in the configuration of the overflow ports. A small change in the dimensions of one port can even stop the mass transfer in one direction. Thus, if equal mass transfer is to take place, it is not sufficient to open the valves equally in each reactor or to open a porous wall between reactors. We ensure that the mass transfer is equal in both directions by requiring that the outflows of the reactors remain constant. The rate of outflow of one reactor is measured continuously by timing the interval between drops at the overflow. When the valves are opened or changed, adjustments are made to maintain the rate of outflow constant and equal to the rate when the reactors are uncoupled. This procedure ensures that the flows



Figure 2. Experimental traces of Pt electrode potential. Bottom trace is the voltage V1 from reactor 1. Middle is V2 from reactor 2 and has been moved up by 200 mV. Top trace is (V2 - V1)/2 and is shifted to 0 mV at 450 mV on the scale. 0-20 min: uncoupled oscillations; 23-43 min: out-of-phase entrainment at $\rho = 0.5$; 45-60 min: in-phase entrainment at $\rho = 0.75$.



Figure 3. Experimental coupled oscillations. Bottom trace is V1 and top is V2. Out-of-phase oscillations for $\rho = 0.5$ from 0 to 5 min. Steady state I for $\rho = 0.75$ from 5 to 11 min. Coupling off from 11 min to 11 min 40 s. Steady state II for $\rho = 0.75$ (11.7–19.5 min) and $\rho = 0.65$ (19.5–22.5 min). Out-of-phase oscillations for $\rho = 0.56$ (22.5–36 min).

into and out of each reactor due to coupling are equal. The reaction is monitored by measuring the potential between a mercurous sulfate reference electrode and a shiny platinum electrode inserted in the sides of each cell. Solutions enter the reactors by gravity feed from columns fed by a peristaltic pump. Pulsing from the pump is eliminated by this method of feed.

Methods. All experiments were begun by filling the reactors, waiting for oscillations to begin, and then starting the flow. The reactions were allowed to stabilize for several hours to determine the uncoupled frequencies and rate of outflow. When coupling was started or changed, the system was again allowed to stabilize in view of the fact that each reactor was taking on a new set of feedstream concentrations intermediate between those of the two uncoupled reactions. Data were recorded on a laboratory microcomputer and analyzed on a VAX 8600.

Results

Experiments. The possible outcomes of coupling two BZ reactions by mass transfer include the two extreme cases of infinite and zero coupling. Zero coupling yields the trivial result of independent oscillations determined totally by input concentrations and flow rate into each reactor. At very high coupling there is enough mass transfer to equalize the concentrations of all species in the two reactors, producing in effect a single, two-lobed reactor. As the coupling is increased, we approach a homogeneous reaction in which the concentrations of input reactants are the averages of the concentrations in the feedstreams to the two reactors. In our experiments, this affects only the concentration of acetylacetone, since the concentrations of Ce(III) and BrO_3^- are equal in the two feedstreams. If strong coupling between significantly different reaction mixtures is to be studied, one must begin with larger differences in input concentrations. In this paper we deal only with coupling of nearly identical oscillators.

The results shown in Figures 2-4 are from experiments with residence time 16.5 min. Coupling strength is reported as ρ , the



Figure 4. Stability diagram for experimental behaviors showing ranges of ρ for which different behaviors are stable. IP = in-phase entrained oscillations, SS = both complementary steady states, and OP = out-ofphase entrained oscillations.

dimensionless ratio of the rate of mass transfer between reactors to the flow rate into each reactor. (Flow rates into each reactor were equal.)

Each reaction was allowed to equilibrate to its natural frequency before coupling. The natural uncoupled periods were 112.1 and 99.6 s. Since the oscillators are not identical, they move in and out of phase approximately every eight oscillations of the faster oscillator.

Figure 2 shows the uncoupled oscillations from time 0 to 20 min. The oscillations move in and out of phase. In-phase oscillations appear as small fluctuations in the difference trace (top), and out-of-phase oscillations appear as large fluctuations. At 23 min the coupling is set to 0.5, and the oscillators are entrained at the same frequency out of phase by approximately 180° with a period of 138.9 s, much longer than that of either of the uncoupled oscillators. While oscillator 1 is in the high [Ce(IV)] state, oscillator 2 is in the low [Ce(IV)] state. Figure 2 also shows the result of increasing the coupling to 0.75 at 45 min when the oscillators are nearly in phase. The oscillator synchronize in phase with a period of 105.2 s, intermediate between the uncoupled frequencies, as expected for thorough mixing between the two reactors.

When the oscillators are in out-of-phase synchronization, the period lengthens as the coupling is increased. At $\rho = 0.56$ the period is 193 s. With further increase of the coupling to $\rho = 0.60$, the system reaches a steady state. The experiment is not precise enough to determine whether the period asymptotically approaches a very large value or becomes infinite. However, calculations in the next section indicate that there is an infinite period bifurcation.

The stationary state that is stable between $\rho = 0.60$ and $\rho =$ 1.0 has three important characteristics. In Figure 3 the oscillations stop at $\rho = 0.75$ with oscillator 1 in a high [Ce(IV)] state but below the maximum. Likewise, oscillator 2 stops in a low [Ce(IV)] state but above the minimum. The value of the potential changes with the coupling parameter throughout the range of stability. The oscillators are in opposite phases; the complementary steady state is also stable. To realize the complementary stationary state, the coupling was momentarily stopped at 11 min for 40 s to allow the oscillations to proceed in each oscillator about one-half cycle toward the opposite phase. Coupling was resumed with $\rho = 0.75$, and the complementary state was achieved with oscillator 1 in the low [Ce(IV)] state and oscillator 2 in the high [Ce(IV)] state. When the coupling was decreased to $\rho = 0.63$, the potential of oscillator 2 increased toward the maximum and that of oscillator 1 decreased toward the minimum. Then the coupling was further decreased to 0.56. The potential of oscillator 2 increased beyond the maximum and proceeded toward the minimum, the potential of oscillator 1 decreased to the minimum, and oscillations began again. Thus the out-of-phase oscillations returned.

When the coupling is increased to its maximum attainable value, $\rho = 2.5$, the oscillations synchronize in phase at a frequency intermediate between the uncoupled frequencies. As the coupling is reduced from this value, the synchronized behavior persists through the region where the oscillations had been stopped and into the region where stable out-of-phase entrainment was present.

TABLE I: Parameter Values^a

Concentrations	Scaling Parameters
A = 0.05 M	$X_0 = k_5 H A / 2k_4 = 2.5 \times 10^{-7} \text{ M}$
C = 0.01 M	$Y_0 = k_5 A / k_2 = 5.0 \times 10^{-9} \text{ M}$
H = 2.00 M	$T_0 = 2k_4C/(k_5HA)^2 = 2 \times 10^3 \text{ s}$
Rate Constants	Dimensionless Parameters
$k_2 = 2 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	g = 0.30
$k_3 = 2.0 \text{ M}^{-3} \text{ s}^{-1}$	b = 80
$k_4 = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	b' = 81.6
$k_5 = 2 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$	$q = 2k_3k_4/k_2k_5 = 4 \times 10^{-4}$
Flow Rate $k_0 = 0.015 \text{ s}^{-1}$	$\epsilon_x = X_0/C = 2.5 \times 10^{-5}$ $\epsilon^y = Y_0/C = 5.0 \times 10^{-7}$

^{*a*} All calculations were carried out with the GEAR numerical integrator in double precision on an IBM 3090 with error tolerance EPS = 10^{-7} .

Thus, there is a range of ρ for which both in-phase and out-ofphase entrainment are stable and a region where there are two stable complementary stationary states and stable oscillations that are entrained 1:1 in phase. The ranges of stability of the various behaviors are diagrammed in Figure 4.

Calculations. The purpose of the numerical simulations of the coupled BZ reactions is to elucidate how the chemistry of the system generates the various behaviors displayed in the experiments. The calculations of Bar-Eli⁸ show several of the phenomena found in these experiments in simulations using the FKN mechanism,¹⁵ the Noyes-Field-Thompson mechanism,¹⁶ and the three-variable Oregonator model.¹⁷ Bar-Eli performed a steady-state stability analysis of the models to confirm the existence, coexistence, and stability of the limit cycles and steady states. He did not, however, find the two complementary steady states, an infinite period (i.e., not a Hopf) bifurcation nor coexistence of stable in-phase and out-of-phase entrainment. Stortti¹⁸ did, however, find similar phenomena in a study of coupled van der Pol relaxation oscillators.

The main thrust of the present simulations is a phase plane analysis of the model to try to draw conclusions that relate directly to the chemistry and to the physical processes. The model used here is the three-variable Oregonator¹⁷ with two different parametrizations. The flow is not explicitly included, as it generates terms in the differential equations that do not significantly affect the results and that add unnecessary complexity to the analysis. The feedstreams are taken into account by treating the concentrations of all input species as constant parameters. The basic model is given by the following differential equations which have been scaled for simplicity according to Tyson:¹⁹

$$dx/d\tau = \epsilon_x^{-1}[x(1-x) - y(x-q)]$$
(1)

$$dy/d\tau = \epsilon_y^{-1}[bgz - y(x+q)]$$
(2)

$$dz/d\tau = 2x - bz \tag{3}$$

where

$$\tau = t/T_0 \tag{4a}$$

$$x = [HBrO_2]/X_0 \tag{4b}$$

$$y = [Br^{-}]/Y_0 \tag{4c}$$

$$z = [Ce(IV)] / [Ce(III)]$$
(4d)

The values of the rate constants are those given by Tyson.¹⁹ The parameters b, T_0 , X_0 , Y_0 , ϵ_x , and ϵ_y are determined by the

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Figure 5. Simulated coupled oscillators: lower trace, log (z); middle trace, log (z'); top trace, 3 log (z'/z) + 2.5. In-phase entrainment at $\rho = 0.33$ (0-33 min), uncoupled oscillations at $\rho = 0.0$ (33-67 min), and out-of-phase entrainment at $\rho = 0.33$ (67-100 min).

rate constants and the constant concentrations of $\operatorname{BrO}_3^-(A)$, total Ce (C), and H⁺ (H). The values used are summarized in Table I. The parameter g is the adjustable (stoichiometric) parameter f in the Oregonator¹⁷ and reflects the number of Br⁻ ions produced per Ce(IV) reduced in process C, while b includes the contributions of the organic material to the differential equations. For quantitative comparison of the simulations with the experimental results, this parameter was adjusted to account for the use of acetylacetone (AA) as the organic substrate in the BZ reaction, since the chemistry of process C depends upon the nature of the substrate.

Two sets of Oregonator equations are used with coupling terms included as follows. The parameter ρ determines the amount of coupling as the ratio of flow rate to the rate of transfer of material between reactors. A term such as $\rho k_0 T_0(x - x')$ is included in each differential equation to account for the mass transfer between the reactors. The effective feedstream concentrations are affected by the coupling only via the parameter b, since the concentrations of all feedstream species are identical for both oscillators with the exception of the organic material, and b is the only parameter containing information about the organic species. Thus, b depends on the value of ρ as follows (unprimed quantities refer to reactor 1, primed quantities to reactor 2):

$$b = [(1+\rho)b_0 + \rho b_0']/(1+2\rho)$$
(5a)

$$b' = \left[(1+\rho)b_0' + \rho b_0 \right] / (1+2\rho)$$
(5b)

where the subscript 0 denotes values of b and b' in the absence of coupling. All other parameters are equal for the two oscillators, including the time scaling and flow rates. The final equations are

$$dx/d\tau = \epsilon_x^{-1}[x(1-x) - y(x-q)] + \rho k_0 T_0(x'-x)$$
 (6a)

$$\frac{dy}{d\tau} = \epsilon_y^{-1} [bgz - y(x+q)] + \rho k_0 T_0(y'-y)$$
(7a)

$$dz/d\tau = 2x - bz + \rho k_0 T_0(z' - z)$$
 (8a)

$$dx'/d\tau = \epsilon_x^{-1} [x'(1-x') - y'(x'-q)] - \rho k_0 T_0(x'-x)$$
 (6b)

$$dy'/d\tau = \epsilon_y^{-1} [b'gz' - y'(x' + q)] - \rho k_0 T_0(y' - y)$$
(7b)

$$dz'/d\tau = 2x' - b'z' - \rho k_0 T_0(z' - z)$$
(8b)

Figure 5 displays the simulated oscillations, which are in excellent qualitative agreement with the behavior seen experimentally. In Figure 6 we show the behavior obtained by following the same sequence of coupling as in Figure 3. The limit cycles for the two uncoupled oscillators are shown in Figure 7. The trajectories of the coupled behavior from Figure 5 coincide with these uncoupled limit cycles without any significant deviation until very high coupling strengths are reached. The steady states found for strong coupling are marked on the phase planes in Figure 7 and lie on the limit cycles of the uncoupled oscillators. Figure



Figure 6. Simulated coupled oscillators: upper trace, log (z) + 3.00; lower trace, log (z'). Out-of-phase oscillations at $\rho = 0.33$ (0-1000 s); steady state A at $\rho = 1.00$ (1000-2000 s); $\rho = 0.6$ from 2000 to 2100 s; steady state B1 at $\rho = 1.33$ (2100-2600 s); steady state B2 at $\rho = 1.00$ (2600-3000 s); out-of-phase entrainment resumes at $\rho = 0.33$ (3000-4000 s).



Figure 7. Phase planes of both oscillators showing limit cycles traced out by all oscillations in Figures 5 and 6 and the positions of the steady states A, B1, and B2. The unprimed and primed oscillators are shown in (a) and (b), respectively. In (a), states B1 and B2 are nearly indistinguishable and are shown as a single point labeled B.



Figure 8. Stability diagram for simulated coupled oscillators. Labeling as in Figure 4.



Figure 9. Period of out-of-phase entrained oscillations as a function of ρ . The period tends to infinity at about $\rho = 0.6451$.

8 (cf. Figure 4) gives the regions of stability of the various modes of behavior as a function of ρ .

The coupled behavior is qualitatively the same in the calculations as in the experiments. The oscillation period becomes longer as the coupling is increased in the out-of-phase synchronized regime. The steady-state concentrations are close to those at the peak and trough of the uncoupled oscillators, and changing the coupling affects the steady-state values more in the troughs than in the peaks.

There are indications of a saddle-node (infinite period) bifurcation in the calculated system. As ρ is increased toward the bifurcation point, the period becomes very large, as shown in Figure 9. In the phase planes, the time spent in the portions of the limit cycles where the steady states ultimately appear increases dramatically with no significant change in the shape or size of the cycle. The steady states develop on the limit cycle as expected for the appearance of a saddle-node pair. If the system is perturbed away from one steady state, the trajectory of the uncoupled oscillators is followed to the other (complementary) steady state.

Discussion

The FKN mechanism¹⁵ has been extremely successful in modeling the enormous range of dynamical behavior exhibited by the BZ reaction.²⁰ In this mechanism the system spends the bulk of each cycle in two major processes, denoted process A and process B. After a transition from A to B, a feedback process, C, returns the reaction to process A. A chemical understanding of the observed effects of coupling can be derived from this schematic description of the reaction mechanism.

For a large range of conditions the BZ reaction behaves as a relaxation oscillator. This property of the reaction is key to the observed response of the system to the coupling. Transitions between processes A and B are rapid compared to the relatively slow processes themselves. These transitions occur when the concentrations of certain key species reach critical levels. Most authors have considered bromide ion to be such a critical species.^{15,21} Tyson,¹⁸ however, has shown that HBrO₂ is at least an equivalent choice, and Crowley and Field^{6,7} have successfully adopted that view in simulating electrically coupled BZ reactions. Reaction R2 of the FKN mechanism¹⁵ determines the dominant

$$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr$$
 (R2)

species to be either bromide ion or bromous acid. When [Br⁻] becomes small enough, [HBrO₂] can increase autocatalytically,

and the fast transition from process A to process B occurs. Then process C causes $[Br^-]$ to rise above another critical point; the autocatalysis is quenched, with the resulting fast return to process A.

There are several advantages to viewing Ce(IV) as the controlling species in the reaction. Reduction of Ce(IV) to Ce(III) produces the bromide that returns control to process A. When [Ce(IV)] becomes low enough, bromide is generated too slowly to maintain its concentration above the critical level. In process B, Ce(IV) is produced until its concentration is sufficiently high to give a bromide ion concentration that will return the reaction to process A. The cycle contains two slow segments: one in which [Ce(IV)] is increasing, identified with process B, and the other, in which [Ce(IV)] decreases, identified with process A. The fast transition from A to B occurs when [Ce(IV)] reaches its minimum (critical value) and that from B to A when [Ce(IV)] achieves its maximum.

The Pt electrode potential monitors the variation in [Ce-(III)]/[Ce(IV)]. The experimental data can thus be examined to determine which process the reaction in a particular cell is in. When the potential is increasing, the reaction is in process B. If the reaction comes to a steady state due to coupling before it reaches the maximum in its cycle, the reaction remains in process B. Similarly, for a cell initially in process A, process B does not begin until the potential reaches the minimum and the rapid increase in potential is observed.

It has been shown⁶ that removing or supplying Ce(IV) can increase the time spent in processes B or A, respectively, even to the point of keeping the reaction from proceeding to the next process. The same arguments should apply here, if the exchange of the other species between cells does not significantly affect the behavior of the system. Calculations in which intercell coupling is allowed for all species except Ce(IV) show negligible coupling effects until extremely high coupling strengths are achieved. No significant difference was found between calculations where mixing of all species is allowed and simulations in which only Ce(IV) is allowed to exchange between cells. Thus, we conclude that coupling takes place essentially through Ce(IV). We therefore expect an increase in the oscillation period with coupling strength and the existence of complementary steady states with opposite values of [Ce(IV)] in the two cells, just as was found in the case of electrically coupled BZ oscillators.^{6,7}

In-phase entrainment is stable when the coupling is strong enough to damp out differences in concentration due to differences in phase. Out-of-phase entrainment results from competition between the coupling and the chemistry. For example, when oscillator 1 is in process A with [Ce(IV)] decreasing, its low concentration of Ce(IV) mixes into reactor 2, and it in return receives a high [Ce(IV)] from that reactor. This mixing tends to keep oscillator 1 in process A above the minimum critical value until reactor 2 moves beyond the maximum in [Ce(IV)] and begins to descend in process A. As reactor 2 proceeds in process A, the concentration that mixes into reactor 1 decreases until the chemistry of reactor 1 can push the [Ce(IV)] in that cell beyond its minimum and into process B. Then the same set of interactions keeps reactor 2 in process A until reactor 1 moves back to process A. The steady states occur when the reactors are out of phase and the coupling becomes strong enough to balance the chemistry in process B and keep the oscillator in process B from reaching the maximum and proceeding to process A. Since the oscillators are nearly identical, there is a pair of complementary steady states with reactor 1 caught in process A and reactor 2 in process B, and vice versa. The experimental results confirm this picture. The steady states are almost symmetric; the reactors are in opposite processes near, but not at, the critical values.

Out-of-phase entrainment is characterized by an increase in period with ρ , especially in the process A part of the cycle, as the system approaches the balance described above. The effect of changing the coupling while in the steady state is particularly evident in the oscillator that is in process A. When the steady state is reached, the decrease in [Ce(IV)] due to reaction is exactly equal to the increase in [Ce(IV)] due to coupling. When the

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Figure 10. Nullclines for eq 1-3. The dx/dt nullcline is labeled XN; the dz/dt nullcline is ZN. Dotted line shows the limit cycle followed by the integrated solution in a counterclockwise direction.

coupling is lowered somewhat, the consumption of [Ce(IV)] due to reaction is now greater than the influx due to coupling, and [Ce(IV)] falls to a value where its chemically generated consumption again equals its influx due to coupling.

The simulated oscillations show large bumps or secondary maxima at the troughs of the out-of-phase oscillations, especially at stronger coupling rates (Figures 5 and 6). These bumps are also evident, though much smaller in magnitude, in the experimental traces at the lower right of Figure 3. When oscillator 1 approaches its minimum, oscillator 2 begins process B with a rapid increase in [Ce(IV)]. The Ce(IV) entering reactor 1 soon exceeds the decrease in Ce(IV) due to reaction, and [Ce(IV)]₁ increases while oscillator 1 is still in process A. When process A is initiated in oscillator 2, and [Ce(IV)]₂ decreases, [Ce(IV)]₁ again decreases toward its minimum and eventually reaches it.

The Oregonator model of the BZ reaction not only reproduces the behavior of this coupled system, but it allows us to analyze the effect of coupling. The differential equations (6-7) for x, y, x', and y' each have two parts. The reaction terms are all multiplied by a large ϵ^{-1} term, while the coupling term is not. Thus, the coupling term is much smaller than the reaction terms, and any contribution due to coupling is quickly quenched by a slight change in the concentration variables. In other words, the reaction time scale is much faster than the coupling time scale, and the coupling can be ignored for the x's and y's (HBrO₂ and Br⁻). Coupling affects significantly only z and z' ([Ce(IV)]), just as suggested in the above discussion of the experiments.

Using the singular perturbation argument of Tyson,¹⁹ we can reduce the three-dimensional Oregonator to two dimensions, xand z, and the phase space becomes a plane. Since the coupling does not take the oscillators significantly away from their uncoupled trajectories, we can observe the effects of coupling in the same two-dimensional phase planes. Nullclines for the uncoupled system are shown in Figure 10. The factor of ϵ^{-1} in eq 8 indicates that trajectories move very quickly when not on the dx/dt nullcline (XN). Thus, rapid movement propels the system toward the left and right branches, making them stable, and away from the middle branch (between the minimum and the maximum), making it the unstable branch. Trajectories move up on the right of the dz/dt= 0 nullcline (ZN) and down on the left side of ZN. The intersection of the nullclines represents the steady state. It is unstable, since it is on the unstable branch of XN. As argued above, the coupling will not affect XN. However, the effect of coupling on ZN changes as the other oscillator goes through its cycle. The nullcline moves up and down, according to the other oscillator's value of z, through the range indicated in Figure 11. This value of ρ is in the range where out-of-phase entrainment is stable. As oscillator 1 is coming down the left side of the cycle, oscillator 2 enters process B (the right side of the cycle), and z'



Figure 11. Nullclines for the coupled system, eq 6-8. XN is the same as in the uncoupled system and is the same for both oscillators. ZN1-ZN4 are the nullclines dz/dt for oscillator 1 for the following values of log (z'): -4.0, -3.3, -2.7, -2.0. $\rho = 0.33$.



Figure 12. Nullclines for the coupled system at $\rho = 1.00$ at steady state A. Nullcline ZN is for log (z') = -1.99, and ZN' is for log (z) = -2.55. Point a is the steady-state position on the cycle of oscillator 1, and point b is the steady-state position of oscillator 2.

increases rapidly. As z' grows, ZN moves up, crossing ZN on the right stable branch, thereby forming a moving stable point that the trajectory of (x,z) must follow. This stable point moves back down and ultimately disappears as z' returns to the left side of the cycle and decreases. This motion is the source of the large bumps in the cycle of the out-of-phase entrained oscillators (right side of Figure 6). At this coupling strength, the moving intersection near the maximum of XN does not reach the stable side of XN, and thus the trajectory can move past the peak regardless of the value of z' (within the range of its cycle). The effect of coupling on the nullclines is nearly identical with that seen in the electrical coupling simulations.^{6,7} This suggests that the phenomena observed are not specific to the kind of coupling and are possible in relaxation oscillators in general when the coupling is through the slow variable.

The steady states occur when ZN intersects the left stable portion of XN (point a in Figure 12) when z' is near its peak and ZN' (the nullcline of the partner oscillator) intersects XN' on the right stable branch (point b) for the value of z at point a. This event is shown in Figure 12. ZN and ZN' are both plotted on XN, since XN' is essentially identical with XN. From these figures it is also evident that the steady states appear on the limit cycle trajectories of the individual oscillators.

The analysis of Aronson et al.²² revealed a steady state on the out-of-phase limit cycle that splits into a stable and an unstable steady state: a saddle and a node. In the present case, the node is evident on the out-of-phase limit cycle. The presence of the saddle can be seen as follows. Consider the oscillators in the steady state of Figure 12 with z'stopped at point b and z stopped at point a. To continue along the out-of-phase limit cycle (analogous to the π invariant manifold of Aronson), we push z'away from point b toward the peak. ZN will move up slightly, and z will follow the intersection. If we let z' go, the system will return to the steady state of points a and b. If we keep pushing z' along the cycle, it will soon be off XN' and take off toward the left branch, continuing in its cycle toward the other steady state. There will be a point, therefore, at which z' is exactly between the tendency to move toward the left branch and the tendency to return to the steady state of points a and b. Keeping this balance point for z', we now move z down along the limit cycle toward the minimum until it reaches its balance point between going back up the left branch and shooting toward the right branch. Because of the increasing downward pull as z is moved down, the value of z' must be continually adjusted to keep it at its balance point. This is the unstable steady state (saddle) that appears with the node on the out-of-phase invariant manifold. There is thus strong evidence for a pair of infinite period bifurcations occurring approximately simultaneously, causing the steady states to break into saddle-node pairs.

Conclusion

After this work was well under way, more accurate values were reported²³ for several of the rate constants of the inorganic reactions in the Field-Körös-Noyes (FKN) mechanism for the BZ reaction and hence, by implication, for the Oregonator. We have carried out some preliminary calculations to test whether using these Field-Försterling (FF) parameters has a significant effect

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(24) A partial study of this type involving two coupled chlorite-iodide oscillators has recently been carried out by Boukalouch et al. (Boukalouch, M.; Elezgaray, J.; Arneodo, A.; Boissonade, J.; De Kepper, P. J. Phys. Chem. **1987**, *91*, 5843).

on the results reported here. For the most part, the two sets of parameter values give results for the coupled system that are qualitatively the same. The oscillations of the uncoupled FF Oregonator are not so strongly relaxational in nature as those of the FKN Oregonator. This difference in the uncoupled systems leads to some quantitative differences in the behaviors of the coupled models. Where the two models disagree, the FKN simulations are generally closer to the experimental results. The most significant difference between the models is that the coupled FF model does not show the infinite period saddle-node bifurcation that occurs in the FKN model and that appears to occur in the experiments. We believe that the apparently superior performance of the "old" parameters in modeling our data arises from the fact that the Oregonator model, and in particular that part of the model that treats the organic part of the BZ reaction, was developed with those parameters. If one wishes to obtain accurate results with the "new" Oregonator, then it will be necessary to reexamine the modeling of the organic reactions (i.e., the parameters b and g) to make it compatible with the revisions in the inorganic steps.

While the experiments presented here cover only a very small portion of the phase space of the coupled system, they reveal a good deal about the possible modes of behavior of coupled chemical oscillators. In particular, we have demonstrated the existence of and bistability between in- and out-of-phase oscillatory modes as well as phase death emerging from out-of-phase entrainment.

The model calculations and phase plane analysis show that, at least when the chemistry is well-understood, it is possible to discern the origins of such complex behavior in the interaction of the chemistry of the system with the transport due to coupling. It will be of interest to see whether this approach can profitably be extended to the coupling of oscillators whose natural frequencies are significantly different either because of differences in input flows or because the two oscillators have different components except for one or more common species.²³

Acknowledgment. This work was supported by National Science Foundation Grants CHE-8419949 and CHE-8800169. We thank Nancy Kopell and Robert Olsen for helpful discussions. I.R.E. is grateful to the John Simon Guggenheim Memorial Foundation for a fellowship.

Registry No. Ce, 7440-45-1; BrO₃⁻, 15541-45-4; acetylacetone, 123-54-6.

Diffusion Model of Solid-State Catalytic Hydrogenation of Organic Compounds. Kinetics in a System with Parallel Reactions of Isotope Exchange and Hydrogenation

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It has been previously shown that the reaction kinetics experimentally observed can be interpreted in terms of the diffusion model, suggesting the presence in the organic compound phase of a concentration gradient of spillover hydrogen resulting from diffusion and from reactions with the organic compound. In this work a model was developed for a system with parallel reactions of isotope exchange and hydrogenation. Such a system is shown to exhibit a specific kinetic behavior within the diffusion model. The result has been experimentally confirmed.

Introduction

If some powdered compound is mechanically mixed with a hydrogenation catalyst (supported catalyst or metal black) or if a mixture is prepared by drying the catalyst suspension in solution with the compound exposure to hydrogen atmosphere results in hydrogenation of the solid. Such a reaction is called solid-state catalytic hydrogenation (SSCH). The possibility of SSCH of organic compounds has been demonstrated.¹ A number of specific features are typical for SSCH that offer new possibilities for the production of tritium-labeled compounds¹ and for performing asymmetric synthesis.²

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