knowledge there is no better procedure available for these calculations. For the ring positions, the same deuterium quadrupole couplings were found as for comparable molecules in singlet or triplet spin states within experimental error, indicating that there is no significant dependence of quadrupole couplings on the electron spin state in these systems. The observed quadrupole splittings of ^2H ENDOR lines depend strongly on the orientation of the C-D bond and thus might give information about the geometry of the radical.

The use of smectic A phases of liquid crystals has proved to be superior to the conventionally applied nematic phases in ^1H ENDOR studies, since the isotropic coupling constants and the shifts can be measured under the same experimental conditions. This is especially advantageous if the difference of coupling constants is small or in the case of strongly temperature or solvent dependent isotropic hyperfine couplings.

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Detailed Studies of Trigger Wave Initiation and Detection[1d]

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Abstract: A Belousov-Zhabotinsky solution in a marginally stable but excitable steady state can propagate trigger waves of oxidation that move undamped through the solution. Such a wave can be initiated by a positive square wave pulse of 0.8 V or more applied to a silver electrode previously biased negatively with respect to a platinum electrode in the same solution. The critical pulse duration necessary to initiate a wave can be measured within a few tenths of a millisecond and has been determined as a function of composition of the solution and of other relevant parameters. Passage of a trigger wave can be followed by recording potentials between platinum electrodes in its path. Because velocity of propagation at any point is a positive function of time since the last previous wave passed that point, three or more successive waves separated by no more than a few minutes will tend to approach more uniform separations as they propagate. If a pulse is applied to an electrode less than 50 s after the solution underwent an induced oxidative excursion (IOE), the incipient wave may be "localized" for up to 2 min before it leaves the electrode to propagate as a trigger wave; pulses applied 50 s or more after an IOE generate waves without delay. Repetitive pulses at a frequency of about 0.8 min^{-1} or less each generate a wave, but it is not possible to generate waves at a frequency greater than this no matter how frequently pulses are applied. Dissolved oxygen increases the concentration of bromide ion in the solution apparently by affecting the stoichiometry of oxidation by ferriin of a malonic-bromomalonic acid mixture; this increased bromide makes the system less sensitive to trigger wave initiation. An agar gel impregnated with silver nitrate solution can also initiate trigger waves. If a pair of silver electrodes is connected by a wire, a trigger wave impinging on the first can be discontinuously advanced so that future propagation is as though the wave had continued in the same direction but had been at the second electrode at the time it actually reached the first. All of these observations can be interpreted by a chemical mechanism previously developed to explain other features of this remarkable system. The behavior reported here exhibits several features similar to those observed during transmission of signals by a nervous system, and it may suggest useful analogies to neurophysiologists.

Introduction

Several unusual features can be exhibited by a Belousov[2]-Zhabotinsky[3] solution containing malonic and sulfuric acids, bromate, and ferroin catalyst. Temporal oscillations in a uniform solution are now well understood[4,5] and have been modeled.[6]

Because of a prior perturbation of an initially uniform os-

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cillating system, or because of a gradient in some property such as temperature or acidity, the phase of oscillation may become dependent upon position in the system. An apparent wave of reaction will traverse such a system even if there is no flow of matter. Such a coupling of oscillations in space and time has been treated by Kopell and Howard.[7] Because severe local concentration gradients develop, diffusion is also important in such a system; its influence has been modeled by Reusser and Field.[8]

Still another very interesting effect is exhibited in a solution that is initially uniform and stable to oscillation but is excitable. A local excitation can then couple with diffusion to generate a "trigger wave" that propagates through the medium undamped at almost constant velocity. Winfree[9] has reported the detailed behavior of such waves initiated at adventitious nucleation centers. Although the medium is homogeneous, trigger wave propagation exhibits obvious analogies to passage of a signal down a nerve axon.

We have previously reported[10] that trigger waves can also be generated deliberately by applying a positive pulse to a silver electrode immersed in an excitable but nonoscillatory medium. We now describe these observations in detail and discuss their implications for chemical mechanism and for coupling chemical reactions with diffusion to transmit signals.

Basic Chemical Mechanism

Overall chemical change involves bromate oxidation of malonic acid catalyzed by ferroin. Let MA designate malonic acid and BrMA its brominated derivative. Then three net processes are essential to the behavior of this remarkable system:

$$\mathrm{Br(V)} + 2\mathrm{Br}^- + 3\mathrm{MA} \rightarrow 3\mathrm{BrMA} \tag{A}$$

$$\mathrm{Br(V)} + 4\mathrm{Fe(II)} + \mathrm{MA} \rightarrow 4\mathrm{Fe(III)} + \mathrm{BrMA} \tag{B}$$

$$\mathrm{Fe(III)} + g\mathrm{BrMA} \rightarrow \mathrm{Fe(II)} + g\mathrm{Br}^- + \text{oxidized organic products} \tag{C}$$

Process A is bromate oxidation of bromide by successive oxygen atom transfers and bromination of malonic acid by the resulting HOBr or elementary bromine.

Process B is bromate oxidation of ferroin and bromination of malonic acid by the resulting HOBr. This process is strongly inhibited by bromide ion and goes at a very slow, almost constant rate as long as $[\mathrm{Br}^-]$ exceeds a specific critical value of about 10^{-6} M. Whenever $[\mathrm{Br}^-]$ falls to this value, the rate of process B rises almost discontinuously to about 100 000 times the rate when $[\mathrm{Br}^-]$ was only twice the critical value! Whenever this major rate change occurs, the residual bromide is simultaneously depleted by a factor of the order of 1000. The mechanistic reasons for this peculiar behavior have been described elsewhere.[4,11,12]

Process C is first order in the ferriin product of process B and produces the bromide that is such a remarkable inhibitor of that process. The net behavior of the system depends upon the rate and particularly upon the stoichiometry of process C. If the factor g is close to the 0.5 that corresponds to equal time average rates for processes A and B, the steady state becomes unstable to perturbation and the system is a chemical oscillator. Systems with $g < 0.5$ have not been explored much except in stirred tank reactors,[13,14] but Smoes[15] has recently reported that it is possible to generate excitable steady states in which iron is in the blue oxidized ferriin state; such steady states can only form if $g < 0.5$.

If ferriin reacts rapidly enough and produces enough bromide ion to keep process B inhibited, the system settles to a steady state in which bromate is only slowly reduced. In such a system, the iron is mostly in the orange reduced ferroin state, and $g > 0.5$. Winfree[9] discovered conditions for producing such states that were very sensitive to perturbation, and we have followed his recommendations. The concentration of bromide in such a steady-state system can be decreased to the critical value either by direct chemical reaction or by temporarily making g smaller. In such an event, process B will be "turned on", and the blue ferriin formed will dominate the color of the solution until process C produces bromide rapidly enough to turn process B off again. Whenever a perturbation of bromide concentration converts the indicator to the oxidized form, we call the event an induced oxidative excursion (IOE).

Table I. Compositions of Reactant Solutions

	α	β	range
$[\mathrm{BrO_3^-}]$/M	0.0746	0.0785	0.0562–0.1170
$[\mathrm{H_2SO_4}]$/M	0.371	0.375	0.259–0.538
[MA]/M	0.0257	0.0298	0.0056–0.0458
[BrMA]/M	0.0748	0.0767	0.0523–0.1196
[Fe(II–III)]/M	0.001 30	0.001 33	0.000 65–0.002 16

Initiation of a trigger wave is accomplished by generating an IOE in a small region of solution. This region then acts as a sink for bromide ions, and as they diffuse into it the surrounding solution attains the condition for initiation of process B. This propagation mechanism has been described qualitatively[16] and theoretically[17] and has been modeled numerically.[8] As reported previously,[10] effective initiation can be accomplished by a positive pulse applied to a silver electrode in the solution.

Experimental Section

Materials. Reagent grade chemicals were used throughout. Solutions were prepared with triply distilled water and were filtered through 0.8-μm Millipore filters before use. Concentrations of $\mathrm{NaBrO_3}$, NaBr, and $\mathrm{Fe(phen)_3SO_4}$ solutions were calculated from weights of dissolved chemicals; concentrations of malonic and sulfuric acids were determined by titration with standard base. Stock solutions were mixed to prepare for a specific run. This mixing was facilitated by making a combined stock solution of sodium bromide with malonic and sulfuric acids at the start of each day.

Equipment. The reaction vessel was a Petri dish about 12 cm in diameter with an optically flat bottom and surrounded with a jacket through which water at 25.0 ± 0.2 °C was pumped. The dish was illuminated from below and could be leveled by adjusting screws until the intensity of color became uniform.

Electrodes consisted of silver (B and S Gauge no. 28) and platinum (B and S Gauge no. 26) wires mounted in a holder so they could be lowered to just touch the bottom of the Petri dish. Distance of electrode separation was not important for experiments on generation of trigger waves. For studies of detection of waves, the holder was modified so spacing of the electrodes could be set reproducibly at values between 2.0 and 15.0 mm. Some experiments at 0.64 mm or less separation were done with a central silver electrode and a platinum electrode bent to approach it like a point in an automotive spark plug. The separation was set with a spark plug spacer.

The silver electrode could be biased up to 1.2 V negative with respect to the platinum. A square wave generator could deliver to the silver electrode a positive pulse of from 0 to 6 V for a period from 30 μs to 30 ms.

Procedure for Studying Trigger Wave Initiation. In order to start a run, a solution of sodium bromate was added to a solution containing sodium bromide and malonic and sulfuric acids, and process A was allowed to go to completion. The ferroin was then added. The experiments for generating trigger waves used concentrations designated α in Table I with a total solution volume of 19.5 mL.

The solution was placed in the Petri dish, making a layer less than 2 mm deep, and was swirled until the whole solution underwent an induced oxidative excursion. The electrodes were introduced later, and at a specified time after the IOE the pulse was delivered. Pulse duration and voltage were monitored with an oscilloscope. The system was then observed visually for several minutes to determine whether or not a trigger wave had been initiated. The electrodes were subsequently removed, the solution was again swirled until it underwent an IOE, and the process of pulsing was repeated.

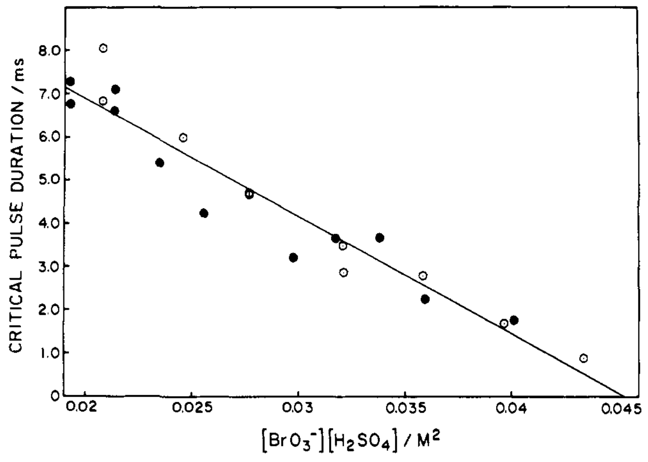

Figure 1. Critical pulse duration as a function of $[BrO_3^-][H_2SO_4]$ for pulses of 2.0 V applied 6.0 min after the last IOE to a silver electrode previously biased −0.6 V against platinum. Open circles correspond to $[H_2SO_4] = 0.371$ M and closed circles to $[BrO_3^-] = 0.0746$ M. Concentrations of other species correspond to composition α in Table I. The least-squares line corresponds to $\tau/\text{ms} = 12.37 - 273.3\ [BrO_3^-]\cdot[H_2SO_4]/M^2$.

About ten pulses were usually delivered during the study of a single solution. The quantity reported is the critical pulse duration, τ, defined as the average of the minimum pulse in the series that started a trigger wave and the maximum pulse that did not. In the 85 solutions that were studied in this way, the average difference in these maximum and minimum pulse durations was 0.43 ms and the maximum difference was 2.4 ms; in over half of these experiments the difference was 0.3 ms or less.

Critical pulse duration was measured as a function of solution composition, pulse voltage, electrode bias, and time since the last IOE.

Procedure for Measuring Wave Detection Times. During the measurements of pulse duration necessary to initiate a trigger wave, it became apparent that it would sometimes be desirable to measure the time before a wave reached a known distance from the initiating electrode. These experiments employed two platinum electrodes at known distances from the silver one, and a strip recorder monitored the potential between them.

These experiments used the concentrations of column β in Table I prepared in a volume of 19.0 mL. Solutions were spread out like those described above with a −1.1-V bias on the silver electrode. At a known time after the last IOE, that electrode was pulsed 2.0 V for 30 ms; this pulse ensured generation of a trigger wave. The time at which the wave reached a platinum electrode was automatically measured by the recorder. When the same solution was used for successive measurements, we found that the time for detection under the same conditions drifted about 20% during 1 h since the solution had been mixed. We therefore used a freshly mixed solution for each reported measurement of time of passage between paired electrodes.

In another set of wave detection experiments, the silver electrode was pulsed regularly at a specified frequency, and the frequency at which the resulting waves reached a detection electrode was recorded.

Measurements of Critical Pulse Duration

Effects of Solution Composition. Values of τ were determined for five series of experiments. In each series, the concentrations of four reactant species corresponded to column α in Table I while the other concentration was varied over the range indicated. All of these measurements were made with pulses of 2.0 V applied to a silver electrode previously biased −0.6 V against platinum. Pulses were each applied 6.0 min after the last IOE.

Each of the five series generated an approximately linear plot of τ against [X], the concentration that was varied. Table II reports slopes of those plots as $d\tau/d \ln [X]$ calculated by multiplying $d\tau/d[X]$ by the [X] corresponding to composition α from Table I.

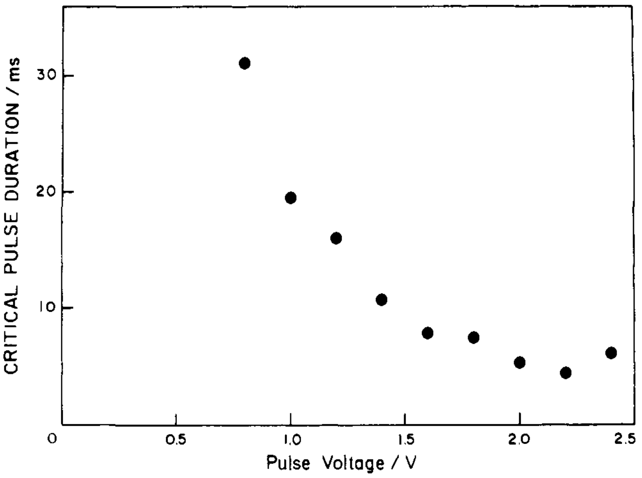

Figure 2. Critical pulse duration as a function of pulse voltage 6.0 min after the last IOE at a silver electrode previously biased −0.6 V against platinum. Composition is that of column α in Table I.

Table II. Effect of Composition on Critical Pulse Duration

component varied	$(d\tau/\text{ms})/(d \ln [X]/M)$	component varied	$(d\tau/\text{ms})/(d \ln [X]/M)$
BrO_3^-	−8.1 ± 0.1	BrMA	1.9 ± 0.1
H_2SO_4	−7.3 ± 0.4	Fe(II-III)	1.2 ± 0.7
MA	0.3 ± 0.4		

Fractional changes in $[BrO_3^-]$ and in $[H_2SO_4]$ have almost the same effect as shown in Figure 1. This result is entirely consistent with the observation of Field and Noyes[18] that the product of these two concentrations is the only composition parameter significantly affecting the rate of trigger wave propagation. The plot in Figure 1 predicts that for $[H_2SO_4]\cdot[BrO_3^-] > 0.0453$ M^2 the bias of −0.6 V would not be sufficient to prevent spontaneous initiation of trigger waves at the silver electrode.

Table II indicates that changes in concentration of malonic acid and ferroin have no significant effect on the ease of trigger wave initiation but that bromomalonic acid does have some influence. As [BrMA] increases, the *g* factor in process C should also increase, and this would make it more difficult to initiate waves just as is observed.

Effect of Pulse Voltage. Figure 2 shows τ as a function of pulse voltage for solutions of composition α from Table I. Pulses were applied 6.0 min after the last IOE to a silver electrode previously biased −0.6 V against platinum. Figure 2 shows the anticipated result that a more positive voltage is more effective at initiating a trigger wave.

Effect of Electrode Bias. Figure 3 shows τ as a function of electrode bias for solutions of composition α from Table I. Pulses were at 2.0 V, and Figure 3 shows measurements both 1.0 and 6.0 min after the last IOE.

If the bias is significantly less than 0.6 V, trigger waves start spontaneously because the bias does not suppress the process

$$Ag(s) + Br^-(aq) \rightarrow AgBr(s) + e^- \qquad (a)$$

If the bias is more negative, this process is suppressed until the pulse is applied. Between about 0.8 and 1.05 V the critical pulse duration seems virtually independent of bias, but a much longer pulse is needed at 1.0 than at 6.0 min after the IOE. The difference arises because the solution has a considerably greater concentration of bromide ion immediately after it has undergone an oxidative excursion.

If the bias becomes more negative than about 1.1 V, the critical pulse duration falls precipitously. At the same time,

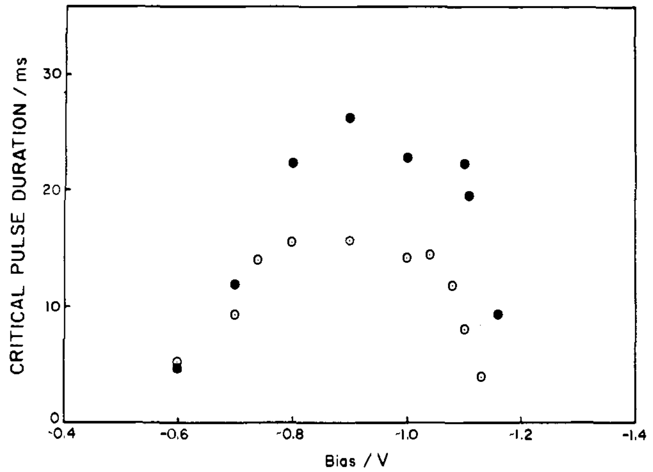

Figure 3. Critical pulse duration as a function of bias of silver against platinum. Pulses were 2.0 V to solutions of composition α from Table I. Open circles are for pulses 6.0 min after the last IOE, and filled circles are for 1.0 min after.

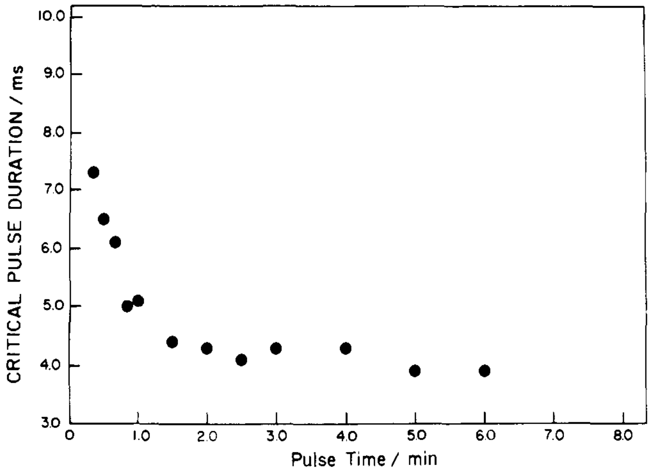

Figure 4. Critical pulse duration as a function of time since last induced oxidative excursion. Pulses were 2.0 V to a silver electrode previously biased -1.1 V against platinum. Solution composition was that of column α in Table I.

the blue color of ferriin appears around the platinum electrode. When the difference in electrode potentials becomes great enough, the Fe(II) is oxidized at the platinum and the silver electrode becomes less negative relative to the solution and more able to initiate process B.

It is interesting to note that a trigger wave is detected visually by the blue color of Fe(III) which is formed and advances through the solution once process B is turned on. The presence of Fe(III) is thus necessary for a trigger wave, but it is not sufficient. Formation of a blue zone of oxidation around the platinum electrode is not the result of process B and does not propagate. The difference in conditions when blue oxidation zones do and do not propagate provides further support for the mechanism we have proposed.

Effect of Time Since IOE. Figure 4 shows τ as a function of time since the last induced oxidative excursion in the solution. The mechanism predicts that immediately after process B has been turned off there will be an enhanced concentration of bromide ion produced during consumption of Fe(III) by process C. This enhanced bromide will produce a refractory period during which a stronger perturbation will be needed to initiate a trigger wave. Figure 4 is fully consistent with this model. Most of the enhanced bromide concentration seems to have decayed by somewhat over 1 min after the IOE, and by 6 min

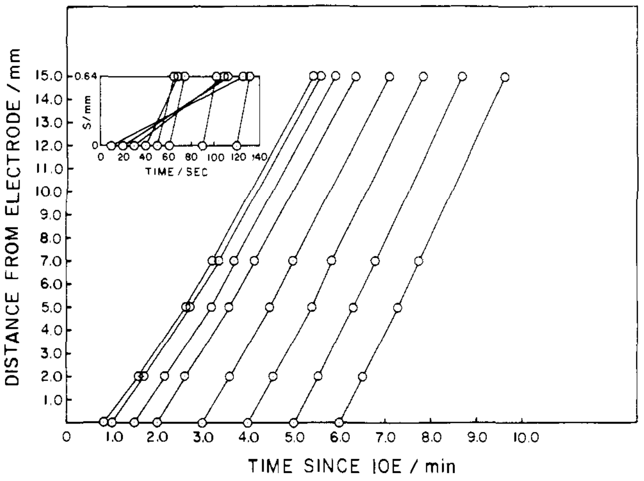

Figure 5. Times after the last IOE at which trigger waves reached electrodes 0.64, 2.0, 5.0, 7.0, and 15.0 mm from a silver electrode that had been pulsed at the times corresponding to curve intersections with the abscissa. Pulses were for 30 ms at 2.0 V to a silver electrode previously biased -1.1 V against platinum. Composition of solutions corresponded to column β in Table I. The main figure only shows results for pulses delivered at least 50 s after the last IOE. Inset shows results for pulses delivered 2.0 min or less after the last IOE and gives time for reaching the electrode at 0.64 mm only.

the system has attained an excitable steady state where any further delay would have a negligible effect on excitability.

Solutions less than 1 min after an IOE required longer pulses in order to initiate trigger waves. They also exhibited anomalous "localization" phenomena in which incipient trigger waves did not start propagating until considerably after the pulse had been delivered. It was these observations that led us to study the detection of trigger waves.

Studies of Detection of Trigger Waves

Rates of Trigger Wave Propagation. The main portion of Figure 5 shows times at which trigger waves reached electrodes situated at known distances from the point of initiation. Times shown are those since the entire solution underwent an IOE. The full curves in Figure 5 all describe propagation of waves initiated at least 50 s after the last IOE.

The curves in Figure 5 are concave up, but at any particular time since an IOE all curves have about the same slope. Rate of propagation of a trigger wave is a property of the medium and depends upon the time since the last IOE but does not depend specifically upon time since initiation nor upon distance from the initiating electrode. A comparison of times for passage between electrodes at known positions indicates that the waves propagate at 2.9 mm/min 2 min after an IOE, and the rate has increased to an apparently steady value of 4.2 mm/min by 8 min after an IOE.

Passage of a trigger wave creates a local IOE, and the rate of a following wave will depend upon time since the previous wave passed. If three or more waves are moving in sequence with each separation less than 8 min, their spacings will tend to become more uniform as they propagate. However, the dependence of velocity upon time since an IOE is not strong enough to create a rapid approach to uniform spacing unless the spacing is less than about 3 min.

"Localization" of Incipient Waves. In the detection experiments, trigger waves were initiated by a 2.0-V pulse of 30 ms. Figure 4 shows that such a pulse should certainly initiate a wave at least as little as 20 s after an IOE, and it invariably did. However, waves initiated shortly after an IOE took much longer to reach the detection electrodes than would be predicted from the full curves in Figure 5. After the pulse had been delivered, a small blue zone could be seen around the silver electrode. This zone might even decrease at first and it might be more than 1 min before it began to grow. Once growth really started, the zone propagated like any other trigger wave at a rate determined solely by the age of the solution since the last IOE.

The inset in Figure 5 shows times at which pulses delivered soon after an IOE were detected as trigger waves 0.64 mm from the initiating electrode. For pulses delivered 10–40 s after an IOE, there is an *inverse* relation between time of pulsing and absolute time of detection! For pulses delivered 50 s or more after an IOE, the resulting trigger waves are detected at 0.64 mm at times comparable to or even a little shorter than those calculated from anticipated rates of propagation at long distances from the initiating electrode.

We also made some experiments with an electrode spacing only 0.07–0.10 mm. Absolute times were less reproducible than for larger electrode spacings, but the qualitative behavior was unequivocal. If a pulse of 30 ms was delivered to the silver electrode 10 s after an IOE, a small transient perturbation was detected at the platinum electrode about 3 s later. It was over 2 min after this that the signal due to the true trigger wave was recorded.

Explanation of Localization of Waves. These unanticipated results can be described almost quantitatively by the mechanism already developed. A trigger wave consists of a region of oxidation in which process B is dominant propagating into a region of reduction in which the rate of A is comparable to or greater than that of (B). It is convenient to define three specific bromide ion concentrations:

$[Br^-]_{ip}$ is the concentration of bromide in a region of reduction that can just inhibit propagation of oxidation into that region. If $[Br^-] < [Br^-]_{ip}$, the region of oxidation will propagate. If $[Br^-] > [Br^-]_{ip}$, the region of reduction will actually propagate into the oxidation. This latter inequality will always apply in the trailing edge of a trigger wave because of production of bromide by process C. If a propagating trigger wave encounters a region of reduction in which the concentration of bromide is persistently greater than $[Br^-]_{ip}$, the wave will be squeezed until it is annihilated.

$[Br^-]_{ss}$ is the steady-state concentration of bromide when there is no net change in the concentrations of the Br^- and Fe(III) intermediates. In such a situation, the rates of the component processes satisfy $2gv_A = v_B = 4v_C$.

$[Br^-]_{cr}$ is the critical concentration of bromide that can no longer prevent process B from accelerating so that it overwhelms (A).

For the compositions considered here, $[Br^-]_{ip} > [Br^-]_{ss} > [Br^-]_{cr}$. Whenever the solution undergoes an IOE, the temporary dominance of process B generates Fe(III) which then produces enough bromide by process C so that $[Br^-] > [Br^-]_{ip}$ temporarily. If a zone of oxidation is created while that inequality applies, the zone will not propagate but will actually contract.

If a positive pulse is applied to a silver electrode, the first effect is

$$Ag(s) \rightarrow Ag^+(aq) + e^- \qquad (1)$$

This process is rapidly followed by

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s) \qquad (2)$$

Of course the net effect of (1) + (2) is process a above. If a pulse is sufficiently strong to create a zone near the electrode in which $[Ag^+] > 10^{-8}$ M, then within that zone $[Br^-] < [Br^-]_{cr}$ and process B is dominant. The rate of process B in such a zone is virtually independent of how much the concentration of silver exceeds the critical amount necessary to create the zone.

If we assume that small ions have diffusion coefficients about 2×10^{-5} cm^2 s^{-1}, a pulse of 30-ms duration will create a zone about 0.01 mm thick in which bromide ion is severely depleted. This thickness is several times that of the leading edge of a propagating trigger wave,[18] and the pulse will immediately start a trigger wave provided that $[Br^-] < [Br^-]_{ip}$ in the surrounding solution. The inset in Figure 5 indicates that such a situation will apply if it is at least 50 s since the solution underwent an IOE.

If the pulse is applied less than 50 s after an IOE, $[Br^-] > [Br^-]_{ip}$ in the surrounding medium, and the oxidation zone will not immediately initiate a trigger wave. However, the zone of excess silver ion will diffuse outward from the electrode consuming bromide ion and extending the zone of oxidation as it moves. It should take about 3 s for this zone of excess silver ion to travel 0.1 mm just as is observed.

Our previous studies of this system[10] indicated that the current during a pulse was about 6×10^{-4} A. If all of that current was used in process 1, a pulse of 30 ms would generate about 2×10^{-10} mol of silver ion, which would probably be equivalent to the bromide ion in about 5×10^{-3} mL of a solution soon after an IOE. The solution had a depth of about 2 mm, so the silver ion produced in the pulse could react with the bromide for a distance of about 1 mm from the electrode. This analysis predicts that a pulse in a medium with $[Br^-] > [Br^-]_{ip}$ would create a zone of oxidation that would grow in 1 min or so to a radius of a few tenths of a millimeter and would then slowly contract. These distances and times are certainly of the orders of magnitude observed experimentally.

As has been indicated above, bromide in the solution as a whole falls to $[Br^-]_{ip}$ in about 50 s after an IOE, while the zone of oxidation created by a pulse may remain localized for longer than this. In the oxidation zone close to the electrode, Fe(III) is being produced by process B. This ion diffuses into the surrounding reduction zone and produces more bromide by process C. Therefore, bromide ion around the oxidation zone still exceeds $[Br^-]_{ip}$ after the bromide elsewhere in the solution has fallen below that value. The longer process B has been producing Fe(III), the more of this excess bromide will be formed, and the longer it will be before a trigger wave can begin to propagate just as is shown in the inset of Figure 5.

The above semiquantitative analysis appears fully consistent with our unusual observations. Numerical modeling can further test its consistency with experiment.

Detection of Repetitive Trigger Waves. We could generate a trigger wave with certainty with a pulse delivered 10 s after the bulk solution had undergone an IOE. It would therefore appear that the system should be able to respond individually to pulses delivered at a frequency of at least 6/min. However, the localization of incipient waves greatly complicates the ability to respond to repetitive pulses.

Figure 6 shows the frequency at which repetitive pulses at the silver electrode were detected at a platinum electrode 2 or 5 mm removed. The pulsing began 2.0 min after an IOE and involved 30-ms pulses of 1.5 V to an electrode biased −1.1 V. This pulse voltage was used because repetitive pulsing at 2.0 V produced so much silver ion that spurious additional trigger waves were sometimes initiated even though no pulse had been delivered. The 1.5-V pulse was the minimum that could initiate a single trigger wave with certainty.

When the frequency of pulsing was sufficiently small, the detection electrode responded to each pulse. At a pulsing frequency of about 0.75 min^{-1} (80-s interval), the detection frequency reached a maximum corresponding to about 0.64 min^{-1} (94-s interval) and was actually *less* at all greater pulsing frequencies. Our experiments thus indicate that 94 s is the minimum interval at which successive trigger waves can be made to pass a point while 50 s is the minimum time after an IOE at which a wave can propagate at all. The two numbers are not inconsistent.

The individual points in Figure 6 exhibit a structure that is

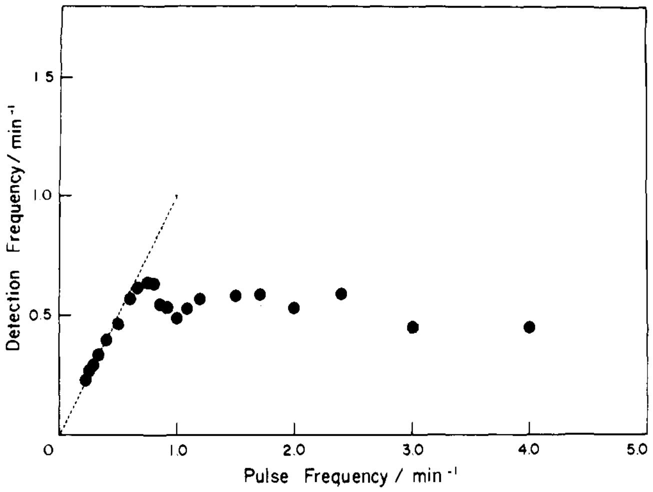

Figure 6. Frequency at which trigger waves were detected as a function of frequency at which 30-ms pulses of 1.5 V were delivered to a silver electrode otherwise biased −1.1 V against platinum. Composition of solution corresponded to column β in Table I. Dashed line represents equal frequencies of pulsing and of detection.

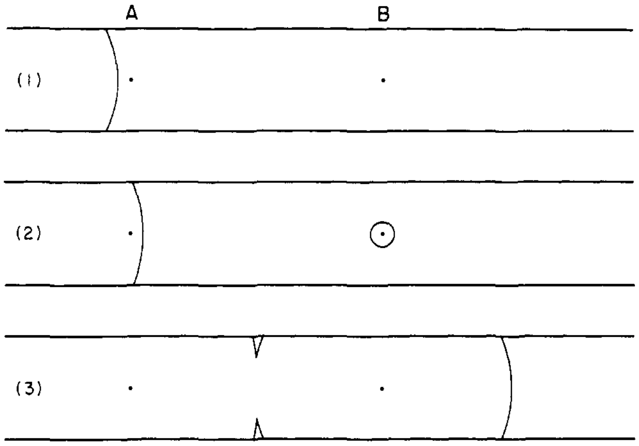

Figure 7. Discontinuous advancement of a trigger wave moving from left to right. Points A and B represent two silver electrodes connected by a wire. In (1) the trigger wave has not yet reached electrode A. In (2) the original wave has passed beyond A and the new trigger wave is expanding from B. In (3) the original wave and the left branch of the new one are in the process of annihilating each other while the new wave is advanced by the distance between A and B beyond the position it would have been if the electrodes had not been connected.

not pronounced but that seemed to be real and reproducible. Relative maxima in detection frequency appeared at pulsing frequencies of about 0.8 and 1.6 min^{-1} while relative minima appeared at 1.0 and 2.0 min^{-1}. The appearance of successive maxima and minima at integral multiples of specific frequencies suggests that wave initiation at high pulse frequencies is more complex than a simple saturation effect. If about 80 s is the minimum interval to which the system can still respond repetitively, an integral number of pulses during this interval will still generate a response of once each such interval.

Additional Observations

Effects of Oxygen. The above studies were greatly facilitated because gentle swirling or tilting of the Petri dish reaction cell could usually initiate an oxidative excursion during which the entire solution turned blue for a couple of seconds. It then reverted to the reduced state and when spread in a thin layer less than 2 mm deep remained orange unless a trigger wave was initiated either by an electrode pulse or adventitiously at a dust particle or other heterogeneous center.

Apparently maintenance of a sufficient concentration of dissolved oxygen is necessary to keep the solution in a reduced state. Barkin et al.[19] and Roux and Rossi[20] independently reported effects associated with peroxidation of organic free radicals formed as intermediates in process C. Bar-Eli and Haddad[21] have studied the different effects of oxygen and nitrogen on a system in which the steady state is unstable and oscillatory.

We used a bromide ion specific electrode to study a well-stirred solution of composition β in Table I. It approached a steady state in which $[\text{Br}^-]$ was about 1×10^{-5} M. When oxygen gas was then bubbled through the solution for 1 min, the concentration of bromide rose to 9×10^{-5} M. After bubbling was stopped, the concentration decayed to the previous value with a rate constant of $(2.37 \pm 0.08) \times 10^{-2}\ \text{s}^{-1}$. For this composition, we calculate[4,22] that the reaction $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HOBr}$ (which is rate determining for process A) would cause bromide concentration to decay with an apparent first-order rate constant of $4.92 \times 10^{-2}\ \text{s}^{-1}$. The comparison neglects bromate depletion and bromide production, so the agreement to a factor of 2 appears satisfactory. This half-life of about 28 s for decay of $[\text{Br}^-]$ to $[\text{Br}^-]_{\text{ss}}$ is consistent with the observation in Figure 4 that most of the decay in τ takes place in a little more than 1 min after an IOE.

We also modeled the system roughly with the original irreversible Oregonator[11] mechanism applied to this composition with $k_5 = 1.0\ \text{s}^{-1}$, $f = 2g = 1.5$. The system went to a stable steady state, but reduction of f to 1.3 made it unstable. An IOE could be simulated by temporarily reducing f to 1.3 and restoring it to 1.5 when the Z parameter (proportional to $[\text{Fe(III)}]$ in our system) had reached its maximum value.

All of these results are consistent with a mechanism in which saturation with atmospheric oxygen increases the g factor in process C enough to generate a stable steady state maintaining the catalyst in the reduced Fe(II) form. In a 2-mm layer of solution, diffusion can maintain saturation with atmospheric oxygen provided that an oxygen molecule has a lifetime of a few minutes before it is consumed by reacting with an organic radical. However, when the dish is tilted, oxygen becomes sufficiently depleted in the deeper portions that an oxidative excursion can start. The agitation can then transmit it to the entire solution. Although this explanation is somewhat hypothetical, the excitable medium is extremely sensitive to any perturbation that even locally decreases the rate of bromide formation, and an IOE is a common consequence of rather mild tilting and swirling.

Effect of Silver Nitrate. An agar gel containing silver nitrate was prepared. If a small piece of this gel was placed in a Petri dish containing solution of composition β from Table I, a trigger wave was initiated immediately provided that the time was more than 2 min after an IOE. If a piece of gel was added to the solution 10 s after an IOE, the trigger wave did not start to propagate until 2 min after the IOE. These observations are consistent with our interpretation of localization of incipient waves as discussed above.

Although the silver impregnated gel was able to immediately initiate a trigger wave, a single large crystal of silver nitrate once generated a blue zone of oxidation that did not propagate. We are still unsure of the apparent difference in behavior depending on amount of added silver ion.

Connected Silver Electrodes. If a silver and a platinum electrode are electrically connected, the silver electrode will initiate trigger waves unless it is negatively biased as described above. Trigger waves are not initiated by an isolated silver electrode nor by two electrically connected silver electrodes. However, if a trigger wave impinges upon one such electrode, another wave is instantaneously initiated at the other one. This phenomenon is somewhat unusual because no amplification circuitry or power consumption is involved and because the output generated at the second electrode is identical with the input at the first one with no diminution associated with transmission of the signal. Of course this peculiar behavior arises because the system uses chemical energy stored in the solution surrounding the electrodes.

Trigger waves can also be directed down "waveguide" channels cut in a block of Teflon, and specific arrays of channels and connected silver electrodes could generate a number of interesting effects. Figure 7 illustrates how two connected electrodes in a single channel could discontinuously advance the position of a trigger wave and hence also advance the time at which it will subsequently be detected at another electrode.

Discussion

Mechanistic Implications. The Belousov[2]-Zhabotinsky[3] system is presently unique in the complexity of behavior exhibited by a nonliving collection of chemicals. Phenomena reported include temporal oscillations in uniform homogeneous medium,[4] stable but excitable steady states,[18,23] phase waves,[8] kinematic waves,[7] trigger waves,[9] multistability in flow reactors,[24-26] complex and perhaps "chaotic" behavior in flow reactors,[13,14] frequency synchronization in connected reactors,[27,28] etc. The present studies of trigger wave initiation and detection have generated other unprecedented phenomena such as an inverse relation between time of receipt and transmission of a signal (inset Figure 5) and ability to discontinuously advance the time at which a signal will be received (Figure 7).

We become ever more impressed that the entire body of observation can be explained at least semiquantitatively and often precisely with a comparatively simple chemical mechanism employing an internally consistent set of rate constants. New observations sometimes require minor modifications (such as the proposal that the g factor in process C is a function of dissolved oxygen concentration), but these are incorporated as refinements rather than as major changes. If only a few of these phenomena were known, there would be reason to question whether any molecular mechanism could be accepted as a unique explanation of such a complicated system. However, the mass of unusual observations is now so great it is becoming inconceivable that any radically different mechanism could be generated to duplicate such a variety of unusual phenomena.

Potential Applications. The effects reported here are so unusual that we are convinced useful applications should be possible. The present solutions are so sensitive to perturbation that trigger waves are also initiated adventitiously by dust particles and other uncontrolled events. A composition of reduced sensitivity might be found such that trigger waves could be restricted to those deliberately initiated at electrodes. Potential applications in such a system might include smoothing the interval between repetitive pulses, arrangement of a circuit so that delay in application of a signal could hasten the time at which it was actually transmitted, discontinuous advance of the time at which a signal in transit will be received, etc. Time scales in this chemical system are so long we have not been able to think of any useful applications that could not be accomplished more effectively with conventional electronic circuitry, but we anticipate that potential useful applications do in fact exist.

Implications for Modeling Neural Behavior. During this work we have become impressed with the number of ways in which our system mimics physiological observations of transmission of nerve signals.[29] Both systems require a critical impulse to initiate a signal whose intensity is then independent of that of the initiating impulse. Rapidly repeated subcritical impulses can generate a signal in both systems. After a signal has been transmitted, there is a dead time before another signal will propagate, and there is therefore an upper limit to the frequency in which impinging signals can be transmitted.

Some of these phenomena may be independent of mechanism and inherent in any system capable of transmitting signal pulses. Certainly the two systems are entirely different in the detailed chemistry and in the relevant time constants. However, we hope the work described here may suggest model chemical mechanisms and relevant questions which physiologists may ask. For instance, when a nerve axon is in a "dead" period during which it cannot transmit a second signal, is another signal impinging on the synapse totally ignored or is it "localized" until the axon is able to receive it?

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