considerations[4] indicate it is not necessary in all bromate-driven oscillators. Iodomalonic acid is indubitably subject to attack by species like Mn^{3+} and HO·; I^- should be one of the products. Cooke[21] specifically invokes this very process in his mechanistic proposals for the Briggs–Rauscher[3] oscillator. Briggs and Rauscher themselves noted that $[I^-]$ oscillated somewhat in a system containing no manganous compounds; that observation might suggest that radical species were attacking RI to form I^-. However, the next paper shows we can model oscillations by a skeleton mechanism that regards iodination of malonic acid as irreversible. We choose for now to ignore the potential complexities of other assumptions.

Conclusions

Malonic acid or a similar organic compound is an essential component of the oscillating reaction, and we have identified five reaction types that might occur. Three of these are considered unnecessary for oscillations. The essential characteristic of malonic acid is that its enol scavenges low oxidation states of iodine by net processes f and g. That scavenging reduces the total concentration $[HOI] + 2[I_2] + [I^-]$, but it simultaneously increases the ratio $[I^-]/[HOI]$ and may actually increase $[I^-]$ itself enough to shut off the 1-equiv processes that dominate the iodate–peroxide–manganous system.

Experimental Section

Reagent grade chemicals were used whenever obtainable. H_2O_2 was Fisher stabilizer free. KIO_3 and crotonic acid were recrystallized from water. Triple-distilled water was used to prepare all solutions. Ionic strength was adjusted to 0.3 with $NaClO_4$.

Spectrophotometric measurements were done on either a Beckman DU or Beckman DBGT spectrophotometer, both with thermostated cell compartments. All solutions were brought to constant temperature before mixing; all measurements were made at 25.0 °C.

Gas evolution was conducted with a thermostated gas buret with the solution rapidly stirred by a submersible magnetic stirrer. Iodide ion was monitored by an Orion iodide sensitive electrode vs. a Ag/AgCl double junction reference electrode with $NaClO_4$ in the outer compartment.

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(19) Belousov, B. P. *Ref. Radiats. Med.* **1959**, *1958*, 145–147.
(20) Zhabotinsky, A. M. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 392–395.
(21) Cooke, D. O. *Inorg. Chim. Acta* **1979**, *37*, 259–265.

The Oscillatory Briggs–Rauscher Reaction. 3. A Skeleton Mechanism for Oscillations[1]

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Abstract: The essential mechanistic features of the full iodate–peroxide–manganous–malonic acid system can be modeled with a skeleton mechanism involving only 11 pseudoelementary processes. The rate constants of seven of those processes are known from experiment. Judicious assignment of the other four values creates a system that mimics the essential feature of oscillations. This mechanism differs from those of other known oscillators in that both radical and nonradical paths generate the same net chemical change.

The first paper of this series[3] reported and attempted to explain the remarkably effective catalysis by manganous ion of the oxidation of hydrogen peroxide by iodate. The second paper[1] discussed the reactions by which malonic acid and other organic species act as sinks to remove iodine present as I_2 and HOI. In this paper, we attempt to show how these mechanisms can be combined to generate the oscillations observed in the full Briggs–Rauscher[4] system.

We have not attempted a detailed experimental study of the malonic acid, MA, oscillator. Such studies have been carried out by others including Cooke,[5] De Kepper,[6] Roux and Vidal,[7] and Dutt and Bannerjee.[27] Because MA can add two iodines, it was considered desirable to make some observations of oscillations with the substrate methylmalonic acid, MMA, which can only undergo monoiodination. Those observations are reported elsewhere.[8] Oscillations with MMA exhibit longer periods than with MA, apparently because enolization of MMA[9] is several fold slower than that of MA.[10] However, we did not find any reason to believe the two substrates reacted by significantly different mechanisms.

This oscillatory system is so complex it is not considered profitable to attempt to model the full experimental system quantitatively. We choose rather to assign plausible rate constants to a skeleton mechanism which then reproduces the essential experimental fact of oscillation.

A Set of Elementary Processes

The objective of mechanistic understanding is to identify the elementary processes occurring in a complex system. Such a process takes place in a single step and involves no more than two or at most three reactant species. We have simplified the description by assuming that proton transfers to and from oxygen and iodine are so rapid they can be considered equilibrated at all times. The effects of such equilibration are superimposed on the truly elementary steps.

The listing in Scheme I organizes reaction types according to a useful system originally developed by Liebhafsky[11] for consideration of the simpler Bray[12] oscillatory system. An IODINE step involves two species containing this element; one is oxidized and one is reduced, but the average oxidation number must remain constant. An OXYGEN step involves mutual oxidation and

(1) Part 42 in the series Chemical Oscillations and Instabilities. Part 41: Furrow, S. D.; Noyes, R. M. *J. Am. Chem. Soc.*, part 2 in this issue.
(2) (a) University of Oregon. (b) Pennsylvania State University.
(3) Furrow, S. D.; Noyes, R. M. *J. Am. Chem. Soc.*, part 1 in this issue.
(4) Briggs, T. S.; Rauscher, W. C. *J. Chem. Educ.* **1973**, *50*, 496.
(5) Cooke, D. O. *Inorg. Chim. Acta* **1979**, *37*, 259–265.
(6) De Kepper, P. Dr. es Sci. Thesis, Université de Bordeaux, 1978.
(7) Roux, J. C.; Vidal, C. *Nouv. J. Chim.* **1979**, *3*, 247–253.
(8) Furrow, S. D., manuscript in preparation.
(9) Furrow, S. D. *Int. J. Chem. Kinet.* **1979**, *11*, 131–145.
(10) Leopold, K. R.; Haim, A. *Int. J. Chem. Kinet.* **1977**, *9*, 83–95.
(11) Liebhafsky, H. A.; McGavock, W. C.; Reyes, R. J.; Roe, G. M.; Wu, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 87–91.
(12) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262–1267.

0002-7863/82/1504-0045$01.25/0

reduction of this element with no change in average oxidation number. A DOWN step involves reduction of an iodine species and oxidation of an oxygen species. An UP step involves oxidation of an iodine species by an oxygen species. MANGANESE and CARBON steps are in addition to the original Liebhafsky[11] classification.

Scheme I. Elementary Processes Postulated in the Briggs–Rauscher[4] System

IODINE Steps

$$HOI + I^- + H^+ \rightleftarrows I_2 + H_2O \quad (I1)^*$$

$$HIO_2 + I^- + H^+ \rightarrow 2HOI \quad (I2)^*$$

$$IO_3^- + I^- + 2H^+ \rightleftarrows HIO_2 + HOI \quad (I3)^*$$

$$2HIO_2 \rightarrow IO_3^- + HOI + H^+ \quad (I4)^*$$

$$IO_3^- + HIO_2 + H^+ \rightleftarrows 2\cdot IO_2 + H_2O \quad (I5)^*$$

$$\cdot IO_2 + HOI \rightleftarrows HIO_2 + \cdot IO \quad (I6)$$

OXYGEN Steps

$$HO\cdot + H_2O_2 \rightarrow H_2O + HOO\cdot \quad (O1)$$

$$2HOO\cdot \rightarrow H_2O_2 + O_2 \quad (O2)^*$$

DOWN Steps

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \quad (D1)^*$$

$$HIO_2 + H_2O_2 \rightarrow HOI + O_2 + H_2O \quad (D2)$$

$$IO_3^- + H_2O_2 + H^+ \rightarrow HIO_2 + O_2 + H_2O \quad (D3)$$

$$HOO\cdot + IO_3^- + H^+ \rightarrow O_2 + H_2O + \cdot IO_2 \quad (D4)$$

$$HOO\cdot + I_2 \rightarrow O_2 + I^- + H^+ + \cdot I \quad (D5)$$

UP Steps

$$\cdot I + H_2O_2 \rightarrow HOI + HO\cdot \quad (U1)$$

$$HO\cdot + I_2 \rightarrow HOI + \cdot I \quad (U2)$$

$$\cdot IO + H_2O_2 \rightarrow HIO_2 + HO\cdot \quad (U3)$$

$$HOO\cdot + HOI \rightarrow H_2O_2 + \cdot IO \quad (U4)$$

$$HOO\cdot + HOI \rightarrow HIO_2 + HO\cdot \quad (U5)$$

$$HO\cdot + HOI \rightarrow H_2O + \cdot IO \quad (U6)$$

$$HOO\cdot + I^- + H^+ \rightarrow H_2O_2 + \cdot I \quad (U7)$$

MANGANESE Steps

$$\cdot IO_2 + Mn^{2+} + H_2O \rightleftarrows HIO_2 + Mn(OH)^{2+} \quad (M1)^*$$

$$Mn(OH)^{2+} + H_2O_2 \rightarrow Mn^{2+} + H_2O + HOO\cdot \quad (M2)^*$$

$$Mn(OH)^{2+} + HOI \rightarrow Mn_2^+ + H_2O + \cdot IO \quad (M3)$$

$$HO\cdot + Mn^{2+} \rightarrow Mn(OH)^{2+} \quad (M4)$$

$$Mn(OH)^{2+} + I^- + H^+ \rightarrow Mn^{2+} + \cdot I + H_2O \quad (M5)$$

CARBON Steps

$$HO\cdot + RH \rightarrow H_2O + R\cdot \quad (C1)$$

$$R\cdot + H_2O_2 \rightarrow ROH + HO\cdot \quad (C2)$$

$$RH \rightleftarrows \text{enol} \quad (C3)^*$$

$$I_2 + \text{enol} \rightarrow RI + I^- + H^+ \quad (C4)^*$$

$$HOI + \text{enol} \rightarrow RI + H_2O \quad (C5)$$

A Skeleton Mechanism for Oscillations

Scheme I contains 30 pseudoelementary processes that might reasonably be significant in this system. It is very far from a complete enumeration of possibilities. Eleven of those steps have been indicated with an asterisk (*). We believe these eleven steps are sufficient to generate the behavior observed in the Briggs–Rauscher[4] (but not necessarily in the Bray–Liebhafsky[11]) system. The objective of this paper is to demonstrate that a plausible set of equilibrium and rate constants can generate oscillations.

Table I. Initial Composition Assumed for Computations

$[H_2O_2] = 1.1$ M	$[Mn^{2+}] = 0.004$ M
$[IO_3^-] = 0.019$ M	[MA] = 0.013 M
$[H^+] = 0.057$ M	

Conditions for Computations

Table I lists the concentrations of major reactant species which were maintained constant during our model computations. Roux and Vidal[7] made a particularly careful experimental study in which they continuously added these five species to a stirred reactor and maintained their concentrations almost invariant at the values in Table I. Of course their experiments also involved outflow of all reactants, products, and intermediates. Our computations did not include any flow terms, and the distinction is discussed below.

Table II lists those rate constants for which reasonably satisfactory experimental values are available. The other rate constants can be treated as disposable parameters in the effort to reproduce experimental observations.[19]

Table III lists the remaining rate constant assignments as selected for our modeling calculations. The value selected for k_{I2} is comparable to that estimated[23] for the analogous process in the oxybromine system. The value selected for k_{M1} is in the range observed for similar processes. The equilibrium constant for step M1 is less than unity, and k_{M1} was selected small enough that the reverse of step M1 could not compete with step M2 for the consumption of $Mn(OH)^{2+}$. This restriction was imposed to simplify the selection of rate constants; the kinetic observations reported in the first paper[3] suggest reversibility of step M1 may need to be included in more exact modeling.

The three remaining rate constants k_{I5}, k_{-I5}, and k_{I4} were assigned on the basis of the following rationale.

The net chemical change (H) is generated by two component stoichiometric processes F and G. Process G is generated by the

$$IO_3^- + 2H_2O_2 + H^+ \rightarrow HOI + 2O_2 + 2H_2O \quad (F)$$

$$HOI + RH \rightarrow RI + H_2O \quad (G)$$

$$IO_3^- + 2H_2O_2 + RH + H^+ \rightarrow RI + 2O_2 + 3H_2O \quad (H)$$

path (I1) + (C3) + (C4). The stoichiometry of process F can be generated by two different paths. The nonradical path involves no step in which oxidation number changes by only one equivalent; it is given by (I3) + (I2) + 2(D1). The radical path includes single-equivalent changes; it is given by 2(I5) + 4(M1) + 4(M2) + 2(O2) + (I4). Let the two paths be indicated by subscripts n and r, respectively.

The small concentration of the radical species $\cdot IO_2$ can be calculated from steady-state expression 1. Let q be the fraction

$$2k_{I5}[H^+][IO_3^-][HIO_2] = k_{M1}[Mn^{2+}][\cdot IO_2] + 2k_{-I5}[\cdot IO_2]^2 \quad (1)$$

of $\cdot IO_2$ (formed by step I5) that reacts by step M1 rather than by step −I5. Let v_{I5} be the *net* rate of step I5. Then

$$q = \frac{k_{M1}[Mn^{2+}]}{k_{M1}[Mn^{2+}] + 2k_{-I5}[\cdot IO_2]} \quad (2)$$

(13) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355–1361.
(14) Furuichi, R.; Liebhafsky, H. A. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 745–750.
(15) Behar, D.; Czapski, G.; Dorfman, L. M.; Schwarz, H. A. *J. Phys. Chem.* **1970**, *74*, 3209–3213.
(16) Liebhafsky, H. A. *J. Am. Chem. Soc.* **1932**, *54*, 3499–3508.
(17) Davies, G.; Kirschenbaum, L. J.; Kustin, K. *Inorg. Chem.* **1968**, *7*, 146–154.
(18) Edelson, D.; Noyes, R. M.; Field, R. J. *Int. J. Chem. Kinet.* **1979**, *11*, 155–164.
(19) Of course no rate constant in either direction for an elementary process should exceed that for a diffusion-controlled reaction.

$$v_{I5} = \tfrac{1}{2}v_{M1} = qk_{I5}[H^+][IO_3^-][HIO_2] \quad (3)$$

These relations lead to the steady-state expression

$$d[HIO_2]/dt \simeq 0 \simeq k_{I3}[H^+]^2[IO_3^-][I^-] + \{qk_{I5}[H^+][IO_3^-] - k_{I2}[H^+][I^-]\}[HIO_2] - 2k_{I4}[HIO_2]^2 \quad (4)$$

When either the radical or nonradical path for process F is dominant, $[HIO_2]$ is approximated by the appropriate choice of (5) or (6). The system will switch rapidly between these two

$$[HIO_2]_n \simeq (k_{I3}/k_{I2})[H^+][IO_3^-] \quad (5)$$

$$[HIO_2]_r \simeq (qk_{I5}/2k_{I4})[H^+][IO_3^-] \quad (6)$$

approximations whenever the concentration of iodide passes through the critical value $[I^-]_c$.

$$[I^-]_c = (qk_{I5}/k_{I2})[IO_3^-] \quad (7)$$

We made the arbitrary assumptions that when the system switches from the nonradical to the radical path, $[HIO_2] = 10\text{-}[HIO_2]_n$, and that when it switches from the radical to the nonradical, $q = 0.01$. These two conditions led to the values of k_{I5} and k_{-I5} in Table III; they are reported to four significant figures not because they are known to such precision but because the dynamic behavior of the model is very dependent upon the values selected.

The value of k_{I4} is now the only quantity unassigned and must be small enough that $v_F > v_G$ when the system switches from the radical to the nonradical path for process F; otherwise a radical steady state would be attained. We found that behavior was very sensitive to the value selected for k_{I4} and that small changes generated a hard transition between a steady state and $[I_2]$ oscillations of several orders of magnitude. The value in Table III was selected empirically in order to generate oscillations.

Results of Model Calculations

The rate constants and concentrations from the tables were used to calculate behavior of various concentrations as functions of time. Figure 1 illustrates the results for $[I_2]$, $[I^-]$, and $[HIO_2]$; the first two of these quantities can be compared to the experimental observations of Roux and Vidal.[7]

Discussion

Comparison with Experiment. The behavior in Figure 1 resembles the experimental observations of Roux and Vidal[7] in several ways. Thus $[I_2]$ reaches its maximum when $[I^-]$ is small but rising, and $[I^-]$ rises dramatically soon afterward. Similarly, $[I_2]$ reaches its minimum when $[I^-]$ is large but decreasing, and $[I^-]$ decreases rapidly soon afterward. However, there are also quantitative discrepancies between our model computations and the experimental observations.

One of the most serious discrepancies is that $[I_2]$ varies by a factor of almost 200 in Figure 1, while Roux and Vidal[7] observe a factor of only about 5. Because of the hard transition we encountered when varying k_{I4}, we could not greatly reduce this range.

Another quantitative discrepancy is that the maximum value of $[HIO_2]$ in Figure 1 is much too large to be plausible and is comparable to values of $[I_2]$. Part of the reason is associated with the small value of k_{I4} necessary to get oscillations at all. We are not sure that all rate constants and concentrations could be brought simultaneously into ranges we consider plausible.

Furthermore, the calculations in Figure 1 generate a period of about 2 min with the nonradical path of process F dominant for about a third of the time, while Roux and Vidal[7] observe a period of about 30 s with the nonradical path dominant for at least three quarters of the time.

After a first draft of this manuscript had been prepared, Professor Irving Epstein pointed out that Roux and Vidal[7] were using a flow reactor and that a proper model computation would include inflow terms for reactants and outflow terms for all reactant, product, and intermediate species. Inclusion of flow terms did alter the behavior of the system, but we could adjust parameters to obtain plots very similar to Figure 1. The computations with flow terms required about twice as much time, and we did not believe the difference was justified for a model that was never expected to generate quantitative agreement with experiment.

Table II. Rate Constants Available from Experiment

rate constant	ref	rate constant	ref
$k_{I_1} = 3.1 \times 10^{12}\ M^{-2}\ s^{-1}$	13	$k_{M_2} = 3.2 \times 10^{4}\ M^{-1}\ s^{-1}$	17
$k_{-I_1}{}^a = 2.2\ s^{-1}$	13	$k_{C_3} = 3.9 \times 10^{-3}\ s^{-1}$	10
$k_{I_3} = 1.4 \times 10^{3}\ M^{-3}\ s^{-1}$	14	$k_{-C_3} = 91\ s^{-1}$	10
$k_{O_2} = 7.5 \times 10^{5}\ M^{-1}\ s^{-1}$	15	$k_{C_4} = 9.1 \times 10^{5}\ M^{-1}\ s^{-1}$	10
$k_{D_1} = 37\ M^{-1}\ s^{-1}$	16		

[a] The rate constant is defined to consider solvent water at unit activity.

Table III. Rate Constants Assigned for Computations

$k_{I_2} = 2.0 \times 10^{9}\ M^{-2}\ s^{-1}$	$k_{-I_5}{}^a = 1.607 \times 10^{9}\ M^{-1}\ s^{-1}$
$k_{I_4} = 45.30\ M^{-1}\ s^{-1}$	$k_{M_1}{}^a = 1.0 \times 10^{4}\ M^{-1}\ s^{-1}$
$k_{I_5} = 1.516 \times 10^{4}\ M^{-2}\ s^{-1}$	

[a] The rate constant is defined to consider solvent water at unit activity.

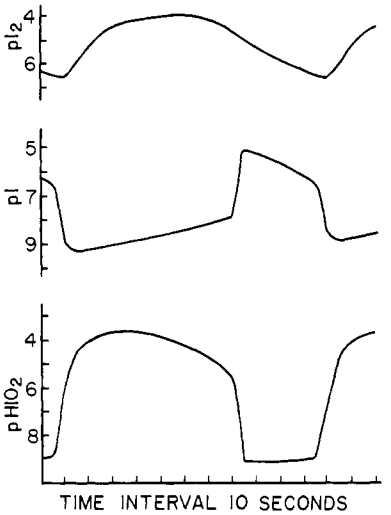

Figure 1. Computed time dependence of three intermediate species computed with rate constants from Tables II and III while concentrations of major species were held constant at the values from Table I. These results can be compared with Figure 4 in ref 7.

Comparison with Model of Subsystems. Careful examination will reveal inconsistencies between the model used here and that in the first paper of this series.[3] The principal difference is that the model of the iodate–peroxide–manganous subsystem included step D4 and omitted step O2. The model of the full oscillating system includes (O2) and omits (D4).

Step D4 was used in the subsystem model because it was thought step I5 would not be fast enough to explain the manganous catalysis unless it initiated a chain, and step D4 was included in order to create such a chain. The modeling of oscillations was sufficiently difficult that it seemed easiest to avoid a radical chain.

We now believe that the subsystem could be modeled without the necessity for step D4, but we do not believe it would be useful to do so until other rate constants are better known.

Possible Amplification of Mechanism. The skeleton mechanism used here is certainly incomplete in other ways than the omission of (D4). Thus, model calculations on the Bray–Liebhafsky reaction showed[20] that the rate of (D3) is comparable to that of (I3) when nonradical paths are dominant. We also completely neglect the radical processes that cause oxidation of iodine to iodate in the Bray–Liebhafsky[12] reaction. We prefer to model oscillations with the minimum number of component reactions and to leave amplification to a time when the system is better characterized.

(20) Edelson, D.; Noyes, R. M. *J. Phys. Chem.* **1979**, *83*, 212–220.

Effects of Various Organic Substrates. Our second paper[1] reported remarkably different effects of additions of malonic acid, methylmalonic acid, crotonic acid, and phenol. The mechanism as developed here should at least suggest how these effects might occur.

The net chemical change (H) is the sum of the effects of reduction of iodate to oxidation state +1 by stoichiometric process F and iodination of organic substrate by stoichiometric process G. The rates of these component stoichiometric processes need not be equal at all times. Thus, $v_F > v_G$ when $[I_2]$ is increasing and the system is in the radical regime, while $v_F < v_G$ when $[I_2]$ is decreasing and the system is in the nonradical regime.

The rates of the component stoichiometric processes can be related to those of selected steps of the detailed mechanism if certain steady-state approximations are invoked. Thus, if HIO_2 can be treated as a transient intermediate at low concentration, and if step I1 is a rapid equilibrium, then

$$v_F = v_{I2} + v_{I4} = v_{I3} + v_{I5} \quad (8)$$

$$v_G = v_{C4} + v_{C5} \quad (9)$$

Let $[I]_L$ be the total concentration of iodine in oxidation states +1 or less but not organically bound. It is given by eq 10. The

$$[I]_L = [HOI] + 2[I_2] + [I^-] \simeq 2[I_2] \quad (10)$$

approximation that neglects both [HOI] and $[I^-]$ may not be valid in the presence of extremely efficient scavengers like crotonic acid or phenol but probably is acceptable for malonic acid. To the validity of that approximation, the time dependence of $[I]_L$ is given by eq 11.

$$d[I]_L/dt = v_F - v_G = 2d[I_2]/dt = 2v_{I1} - 2v_{C4} \quad (11)$$

Because step I1 reaches equilibrium in a very few seconds, we can always apply eq 12.

$$[I_2] = K_{I1}[H^+][HOI][I^-] \quad (12)$$

The final relationship for describing process G derives from assuming a steady-state approximation for iodide ion.

$$d[I^-]/dt = 0 = v_{D1} - v_{I1} - v_{I2} - v_{I3} + v_{C4}$$
$$= v_{D1} - v_{I2} - v_{I3} - \tfrac{1}{2}v_F + \tfrac{1}{2}v_{C4} + \tfrac{1}{2}v_{C5} \quad (13)$$

The above equations rationalize the observed behavior. If the system contains no organic substrate, $v_G = 0$. Equation 11 then predicts a monotonic increase in $[I_2]$. The maximum in concentration discussed in the first paper[3] arises because of steps omitted from the skeleton mechanism for oscillations. In the absence of organic substrate, the system remains in the radical regime.

If the system contains a modestly efficient iodine scavenger such as malonic or methylmalonic acid, oscillations are possible. As v_{C4} and v_{C5} increase with increasing $[I_2]$, eq 13 indicates v_{D1} must decrease. That decrease requires that [HOI] also decreases and $[I^-]$ increases to satisfy eq 12. If $[I^-]$ increases above the critical value of eq 7, the system switches to the slower nonradical path for process F. When v_F becomes less than v_G, eq 11 then predicts that $[I_2]$ will decrease until $[I^-]$ falls below the critical value of eq 7 and the system again switches to the more rapid radical path for process F. The longer period of oscillations for MMA than for MA arises because v_{C4} and v_{C5} are smaller for MMA and lead to a longer time for decay of $[I]_L$ after a sudden increase.

If the system contains a still more efficient iodine scavenger like crotonic acid, v_G can become as large as v_F for the radical path and eq 11 predicts a steady state in which $[I]_L$ is so small that $[I^-]$ never attains the critical value of eq 7 even though eq 13 predicts a small value of $[HOI]/[I^-]$.

The above analysis concludes that oscillations are possible only with an organic substrate whose efficiency for scavenging iodine falls in a specific range. Scavengers with either greater or lesser efficiencies are unable to switch to the slow nonradical path for process F.

As indicated previously,[1] the extremely efficient inhibition by phenol indicates that this species is reacting with iodine species in high oxidation states and by steps not included in Scheme I.

Concluding Remarks. All halate-driven oscillators are now exhibiting a common mechanistic pattern. Halate is reduced by two separate stoichiometric processes, one of which is radical and the other nonradical. The two processes generate very different steady-state concentrations of halous acid, and dominance between them is switched by a critical condition that usually consists of attainment of a specific concentration of halide ion. A third stoichiometric process, which must not be too fast, couples with the two other processes to generate the net chemical change that drives the oscillations. This third process becomes particularly rapid when the radical reduction process has become dominant, and it drives the system toward the critical switching condition in a way that causes that condition to be overshot before the third process can be turned off.

In bromate-driven oscillators,[21] the nonradical reduction process is by bromide ion, and the radical reduction is by a metal ion catalyst or by the organic substrate. The third process generates bromide ion from the products of the radical reduction and continues long enough to drive the bromide concentration well past the critical switching condition.

In the Briggs–Rauscher[4] iodate-driven oscillator, the radical and nonradical reduction processes have identical stoichiometries. We do not yet see all the implications of this presently unique identity. One implication will certainly be that there are both minimum and maximum rate parameters for process G beyond which oscillations are impossible. This pair of limits contrasts with the bromate situation where the Oregonator[22] model sets only a maximum rate constant beyond which the steady state must be stable and nonoscillatory.

The mechanism developed here does not describe the full system quantitatively. However, it is probably more complete than was the first FKN[23] mechanism for the Belousov[24]–Zhabotinsky[25] reaction. It illustrates the paradox that more complex systems are sometimes those that permit more detailed mechanistic understanding. Thus, the work reported here will require a considerable revision of the oscillatory mechanism assigned[26] to the ostensibly simpler iodate–peroxide[12] system.

Additional Comment. After a final draft of this paper had been prepared, we discovered that Drs. Irving R. Epstein and Patrick De Kepper at Brandeis University had independently selected the identical 11 steps in order to explain their observations of the oscillating system! They appear to have progressed further than we have in selecting rate constants to reproduce experiments. This identity of conclusion adds confidence that chemical oscillators can indeed be understood in terms of established mechanistic criteria.

(21) Noyes, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 4644–4649.
(22) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877–1884.
(23) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649–8664.
(24) Belousov, B. P. *Ref. Radiats. Med.* **1959**, *1958*, 145–147.
(25) Zhabotinsky, A. M. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 392–395.
(26) Sharma, K. R.; Noyes, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 4345–4361.
(27) Dutt, A. K.; Banerjee, R. S. *J. Indian Chem. Soc.* **1980**, *57*, 751–753.