

EPR experiments in the same solvent for the planar and pyramidal nitroxides.

The dependence of the orientation of the principal component $A_{\parallel}(\text{N})$ upon bending at the radical site is given in Figure 9. The deviation of the $A_{\parallel}(\text{N})$ direction from the normal to the NO bond is clearly visible. This is expected since rehybridization at nitrogen certainly occurs when bending increases. It can be remarked that a bending of 20° of the H_2NO model which corresponds to the actual geometry of nitroxide 1 gives a displacement of 6° for $A_{\parallel}(\text{N})$ equal to that observed in the single-crystal experiment. This numerical agreement is, of course, fortuitous but the overall trend is perfectly reliable. Therefore, it can be expected that the more pyramidal a nitroxide is, the larger the displacement of $A_{\parallel}(\text{N})$

from the normal direction to the NO bond will be. On another hand, the NH component of the a_{H} tensor (Figure 7) is not oriented along the NH internuclear axis. The deviation is about 9° . One must emphasize that such a result is not a particularity of the nitroxide series (see also ref 15) but a general property of the anisotropic tensors when the directions are not determined by symmetry.

Therefore, conclusions as to the geometry of free radicals drawn only from the analysis of the anisotropic coupling tensors with the assumption that chemical bonds have the same direction as one of the tensor components may be largely in error.

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The Oscillatory Briggs-Rauscher Reaction. 1. Examination of Subsystems¹

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Abstract: In acidic aqueous solution at 25°C , only slow or nonexistent reaction is observed for any two of the three species iodate ion, hydrogen peroxide, and manganous ion. However, if all three species are present, 0.002 M Mn^{2+} catalyzes the iodate oxidation of peroxide at a rate almost 1000 times that in the absence of a catalyst! This remarkable observation, which has already been reported by Cooke, can be explained by postulating that the radical oxidant $\cdot\text{IO}_2$ is very sluggish at abstracting hydrogen atoms from species like H_2O_2 but can oxidize Mn^{2+} by electron transfer. A detailed mechanism has been proposed that models semiquantitatively not only the manganous catalyzed iodate oxidation of peroxide but also the simultaneous induced disproportionation of the peroxide and the fact that the concentration of elementary iodine does not increase to a limiting value but rises to a maximum and then decreases toward a small value. Despite this single extremum, the subsystem does not exhibit oscillatory behavior.

The most dramatic oscillating reaction in solution is probably that discovered by Briggs and Rauscher.³ If appropriate amounts of acidic iodate, hydrogen peroxide, manganous salt, malonic acid, and starch indicator are mixed in aqueous solution, the system repeats several times the sequence colorless \rightarrow yellow \rightarrow black \rightarrow colorless. The frequency is a few times per minute, and the transition from yellow to black is particularly sharp. Shakhshiri⁴ has described conditions for an effective demonstration.

If reactants are added at a constant rate to a continuously stirred tank reactor (CSTR), a specific mode of behavior can be maintained indefinitely. De Kepper and others at the University of Bordeaux^{5,6} have made especially careful studies of conditions generating different types of behavior such as oscillations and multiple stationary states. They have even identified a single set of flow rates that can generate two different stationary states and one oscillatory state depending upon the previous history of the system.⁷

The investigations in Bordeaux have been primarily phenomenological with little effort to identify the elementary processes responsible for such bizarre behavior. Cooke⁸ has recently published an effort to isolate component processes and to develop a

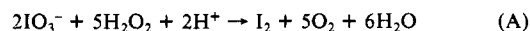
detailed mechanism. Our own studies were carried out independently before we knew of his work. They are reported here in spite of some overlap as noted.

Our efforts to develop an understanding of the mechanism have involved two alternative types of approach. This first paper is concerned with examining various subsystems containing only some of the reactants present in the full system. We have found it particularly informative to examine subsystems containing none of the organic matter present in the full oscillator. The important reactants other than acid are then iodate, hydrogen peroxide, and manganous ion.

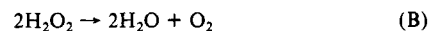
The second paper will examine the effects of additions or substitutions of various species. The third paper will attempt to fit all of the information together in order to determine the essential features responsible for the behavior of the full oscillatory system.

Experimental Observations⁹

The Iodate-Peroxide Subsystem. The definitive study of this reaction was by Liebafsky.¹⁰ If product I_2 is removed rapidly such as by shaking with carbon tetrachloride, the major part of chemical change can be described by stoichiometry A.



Even with his best efforts to remove iodine, Liebafsky¹⁰ observed a stoichiometry that required (A) to be accompanied by some induced disproportionation of hydrogen peroxide according to (B).



(9) Details of procedures are described at the end of the second paper of this series.

(10) Liebafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 896-911.

(1) Part 40 in the series Chemical Oscillations and Instabilities. Part 39: Noyes, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 4644-4649.

(2) (a) University of Oregon. (b) Pennsylvania State University.

(3) Briggs, T. S.; Rauscher, W. C. *J. Chem. Educ.* **1973**, *50*, 496.

(4) Sakashiri, B. Z. "Handbook of Chemical Demonstrations"; University of Wisconsin Press, in press.

(5) De Kepper, P.; Pacault, A. *C. R. Hebd. Acad. Sci., Ser. C* **1978**, *286C*, 437-441.

(6) Roux, J. C.; Vidal, C. *Nowv. J. Chim.* **1979**, *3*, 247-253.

(7) De Kepper, P. Dr. es Sci. Thesis, Université de Bordeaux, 1978.

(8) (a) Cooke, D. O. *Inorg. Chim. Acta* **1979**, *37*, 259-265. (b) *Int. J. Chem. Kinet.* **1980**, *12*, 683-698.

The initial rate of (A) is first order in $[\text{IO}_3^-]$ and in $[\text{H}_2\text{O}_2]$ and less than first order in $[\text{H}^+]$. There is an induction period of a few minutes before the maximum rate is attained; this period is shorter at larger concentrations of H_2O_2 . If iodine is not removed, the species HOI , I_2 , and I^- all accumulate and the rate increases. At sufficiently large concentrations of I_2 , the system may become oscillatory.¹¹ When this happens, periods of reduction of iodate alternate with those of oxidation of iodine.

Although this subsystem is obviously complex, the only importance for the present work is that process A is slow. Most of Liebhafsky's work was at temperatures of 50 °C and above. If his data are extrapolated to 25 °C and applied to a system with $[\text{H}^+] = 0.1 \text{ M}$, $[\text{IO}_3^-] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}_2] = 1 \text{ M}$, the rate of iodate reduction is only about 0.4%/h. If such a solution also contained manganous ion and malonic acid, it would oscillate several times per minute!

The Peroxide-Manganous Subsystem. Disproportionation reaction B is catalyzed by manganous salts, but Nabe and Gyani¹² find they are several fold less efficient than iron salts. At concentrations comparable to those in a Briggs-Rauscher³ oscillator, we found destruction of hydrogen peroxide to be less than 0.1%/h.

The Iodate-Manganous Subsystem. The reduction potential of the $\text{IO}_3^-/\text{I}_2(\text{aq})$ couple is 1.178 V while that of the Mn(III)/Mn(II) couple is about 1.5 V.¹³ In a solution containing only iodate and manganous ions, no significant oxidation-reduction can occur. We could not find any evidence for significant complexation either.

Initial Behavior of the Complete Subsystem. In spite of the sluggishness of any pair of reactants, both iodine and oxygen are produced rapidly when acidified solutions of the three species iodate, peroxide, and manganous ions are mixed! The stoichiometry can be described by a linear combination of reactions A and B. Manganous ion behaves as a catalyst. Concentrations of a few thousandths molar increase the rate of (A) by 3 orders of magnitude, but we could not detect any net change in oxidation state of manganese.

Cooke^{8b} reports the rate of reaction A is first order in both $[\text{Mn}^{2+}]$ and in $[\text{H}_2\text{O}_2]$ and is zero order in $[\text{IO}_3^-]$ when $[\text{IO}_3^-] > 0.02 \text{ M}$. He reports a maximum rate when $[\text{H}_2\text{SO}_4]$ is about 0.1 M.

We used HClO_4 instead of H_2SO_4 to acidify our solutions, but our other conditions were similar to those of Cooke.^{8b} Our spectrophotometric measurements of I_2 production were complicated by oxygen bubbles, by occasional induction periods, and by mild autocatalysis. However, the maximum rate of reaction A could be determined to about 20% accuracy, and trends could be identified. Production of O_2 was followed with a gas burette.

Our rate of I_2 production was first order in $[\text{H}_2\text{O}_2]$ just as reported by Cooke.^{8b} At $0.05 \text{ M} < [\text{H}^+] < 0.15 \text{ M}$ and $[\text{IO}_3^-] > 0.02 \text{ M}$, we found the rate was nearly independent of $[\text{IO}_3^-]$ as claimed by Cooke. However, at $[\text{H}^+] < 0.05 \text{ M}$ our rate was first order in $[\text{IO}_3^-]$. Cooke^{8b} found little rate dependence on $[\text{Mn}^{2+}]$ at low $[\text{IO}_3^-]$ and first order in $[\text{Mn}^{2+}]$ at $[\text{IO}_3^-] = 0.022 \text{ M}$. We found dependence on $[\text{Mn}^{2+}]$ to be slightly greater than first order at $[\text{IO}_3^-] = 0.015 \text{ M}$ and nearly second order at $[\text{IO}_3^-] = 0.05 \text{ M}$. Plots of $\log(\text{rate})$ vs. $\log(\text{concentration})$ were not linear, and the results clearly cannot be represented by a simple rate law.

At 25 °C with $[\text{H}_2\text{SO}_4] = 0.076 \text{ M}$ and $[\text{IO}_3^-] = 0.0215 \text{ M}$, the Cooke^{8b} rates in M s^{-1} can be summarized over a modest interval by eq 1.

$$d[\text{I}_2]/dt = ((8 \pm 2) \times 10^{-3})[\text{Mn}^{2+}][\text{H}_2\text{O}_2] \quad (1)$$

For the conditions $5 \times 10^{-4} \text{ M} < [\text{Mn}^{2+}] < 5 \times 10^{-3} \text{ M}$, $0.0125 \text{ M} < [\text{IO}_3^-] < 0.125 \text{ M}$, and $0.2 \text{ M} < [\text{H}_2\text{O}_2] < 0.5 \text{ M}$, our observations can be summarized by eq 2.

$$d[\text{I}_2]/dt = 0.24 \pm 0.05[\text{Mn}^{2+}]^2[\text{H}_2\text{O}_2]/[\text{H}^+] \quad (2)$$

At $[\text{Mn}^{2+}] = 0.0022 \text{ M}$ and $[\text{H}^+] = 0.15 \text{ M}$, eq 1 predicts a rate about 2.3 times as great as does (2). Although the two studies with different sources of acid are not entirely self-consistent, they agree that the manganous catalysis is first order in hydrogen peroxide and that the rate may be little affected over a considerable range in the concentration of iodate.

If amounts of product I_2 and O_2 are measured as functions of time, contributions of (A) and (B) to total reaction can be calculated. Let α = moles of H_2O_2 reacting by (B)/moles of H_2O_2 reacting by (A). Then

$$\alpha = \frac{\Delta[\text{O}_2] - 5\Delta[\text{I}_2]}{2.5\Delta[\text{I}_2]} \quad (3)$$

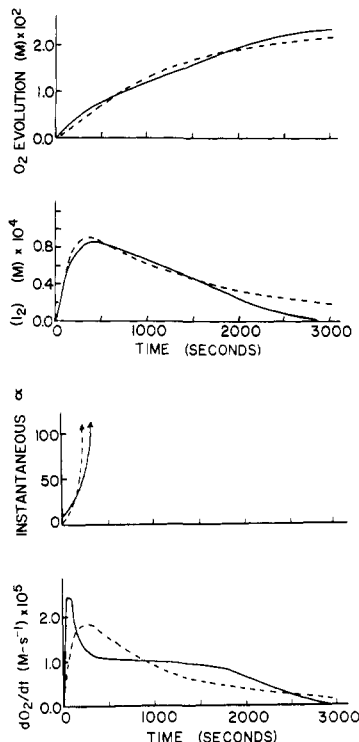
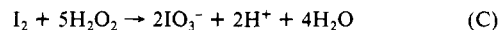


Figure 1. Experimental observations (full curves) and computations based on Table I (dashed curves) for stoichiometric parameters in a subsystem with initial composition $[\text{IO}_3^-]_0 = 0.015 \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 0.050 \text{ M}$, $[\text{Mn}^{2+}]_0 = 0.0020 \text{ M}$, and $[\text{H}^+]_0 = 0.10 \text{ M}$. Meanings of instantaneous concentration of iodine, of total oxygen evolved, and of instantaneous rate of oxygen evolution are obvious. Instantaneous α is defined as moles of H_2O_2 reacting by (B)/moles reacting by (A) and is calculated as the differential form of eq 3. This quantity becomes infinite when $[\text{I}_2]$ reaches a maximum.

Initial values of α were always at least 4. They increased with increasing $[\text{IO}_3^-]$, with decreasing $[\text{H}_2\text{O}_2]$, and with decreasing $[\text{Mn}^{2+}]$. The value of α also increased with extent of reaction until virtually all of the stoichiometry could be described by process B.

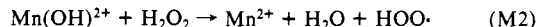
Long-Time Behavior of the Complete Subsystem. The full curves in Figure 1 illustrate the behavior of various stoichiometric parameters during a representative run. Although free energy values indicate that reaction A should be virtually irreversible, $[\text{I}_2]$ does not approach a limiting value but rather rises to a maximum and then decreases. This behavior can be explained by also invoking the stoichiometry of irreversible process C.



Although reaction C does not produce elemental oxygen, Figure 1 demonstrates that reaction B continues even when (C) has become dominant. Of course the stoichiometries A, B, and C are not independent, and $(\text{A}) + (\text{C}) = 5(\text{B})$. Reaction C is essential to understanding the oscillatory Bray-Liebhafsky¹¹ reaction. We shall see below that it need not be invoked in order to explain most features of the Briggs-Rauscher³ reaction.

The Manganese(III)-Peroxide Subsystem. Solutions of uncomplexed manganese(III) rapidly disproportionate with precipitation of MnO_2 . However, pyrophosphate, $\text{P}_2\text{O}_7^{4-}$, forms relatively stable complexes. We have found that such a solution rapidly oxidizes hydrogen peroxide.

This oxidation is presumably initiated by the pseudoelementary process M2 in which Mn(OH)^{2+} is written as the dominant Mn(III) species



at $\text{pH} \approx 1$.¹⁴ Of course our observations do not determine whether or not step M2 involves an intermediate manganese(III) peroxide complex that undergoes an intramolecular electron transfer in the rate-determining step.

Subsystems Containing Malonic Acid. Thermodynamic considerations indicate that malonic acid could be oxidized either by acidic iodate or by hydrogen peroxide. However, the reactions are slow when only one

(11) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262-1267.

(12) Nabe, D. R.; Gyani, B. P. *J. Indian Chem. Soc.* **1958**, *35*, 579-588.

(13) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall, New York, 1952.

(14) Davies, G.; Kirschenbaum, L. J.; Kustin, K. *Inorg. Chem.* **1968**, *7*, 146-154.

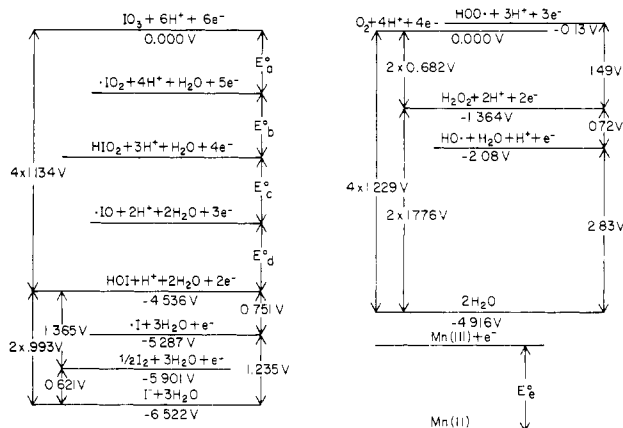


Figure 2. Free energy changes in volt equivalents for various half-reactions in the iodine, oxygen, and manganese subsystems.

of these oxidants is present. Of course malonic acid undergoes no oxidation-reduction reaction with manganous ion, and we could not obtain any evidence for unusual complex formation. Reactions of malonic acid with potential intermediates are considered in the second paper of this series.

A Proposed Mechanism of Manganous Catalysis

Constraints on Mechanism. In the absence of catalyst, the steps that generate stoichiometry A apparently involve either oxygen atom transfer between iodines or electron rearrangements in peroxyiodo compounds.¹⁵ All reactant, product, and transition-state species contain an even number of electrons. We are convinced that the remarkable catalytic behavior of manganous ion is not associated with any unusual complexing abilities of this species but arises rather because the Mn(II)–Mn(III) transition provides an entree to species having odd numbers of electrons.

Figure 2 illustrates the thermodynamic constraints imposed at 25 °C on redox processes in the oxyiodine¹⁶ and peroxide systems. The numerical values are taken from Latimer¹³ with the standard state for I₂ based on ideal 1 m solution. Sharma and Noyes¹⁵ attempted previously to assign the values marked E_a^0 to E_d^0 based on analogies with the other halogens. The work reported here indicates those assignments were almost certainly in serious error.

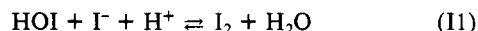
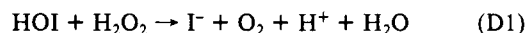
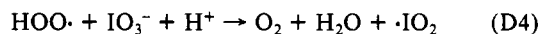
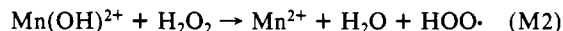
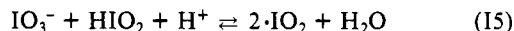
The potentials in the hydrogen–oxygen system are well established. Figure 2 illustrates that HO· can oxidize any possible reductant in the system, while HOO· can reduce any potential oxidant and is also a strong oxidant itself. The reduction potential of Mn(III), E_e^0 , is still poorly known and may be pH dependent; it is certainly large enough to make Mn(OH)²⁺ a strong 1-equiv oxidant in this system.

Although the potentials E_a^0 to E_d^0 are not known, the absence of any reported observation of HIO₂ in acid solution strongly implies that $E_c^0 + E_d^0 > E_a^0 + E_b^0$ consistent with the chemistry of the other halogens. The usual instability of radical species also implies that $E_b^0 > E_a^0$, and it appears inescapable that $E_a^0 < 1.134$ V. Direct reaction of IO₃[−] with Mn²⁺ can hardly contribute to the remarkable catalysis that is observed.

Mechanism of Catalyzed Reaction A. The various thermodynamic and kinetic constraints have left us few options as we tried to devise a mechanism consistent with the behavior of the major subsystem of this paper. Scheme I lists a skeleton mechanism of pseudoelementary processes¹⁶ that can generate the manganous

catalysis of reaction A. The designation of these processes is based on a classification to be developed later. Many of these steps have been proposed independently by Cooke.^{8b}

Scheme I. Steps Generating Manganous Catalysis of Reaction A



Step I5 initiates radical processes; it is well preceded by analogy with the oxybromine system.¹⁷

The sequence (M1) + (M2) + (D4) constitutes a chain generating the net stoichiometry of reaction D. The strong evidence



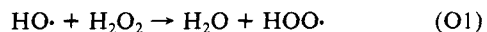
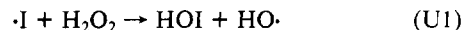
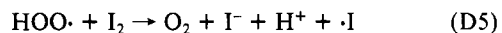
that the rate is first order in [H₂O₂] seems to require that (M1) is reversible (as would be anticipated by the thermodynamic constraints) while (M2) is almost irreversible under the conditions prevailing.

Reaction D generates the species HIO₂ that contributes to the initiation reaction, but indefinite autocatalysis is avoided because (I4) provides for second-order destruction of this species.

Steps D1 and I1 complete the skeleton mechanism. The stoichiometry of reaction A is generated by 4(M1) + 4(M2) + 4(D4) + 2(I4) + (D1) + (I1).

Mechanism of Reaction B. The skeleton mechanism in Scheme I can generate the stoichiometry of reaction A corresponding to oxidation of hydrogen peroxide. However, the large values of α require that disproportionation reaction B is proceeding simultaneously with reduction of peroxide. Nonradical rates of reduction of peroxide are sluggish, and we are convinced that the large rate of reaction B requires intervention of HO· radicals as intermediates. Appropriate steps can not be assigned as unequivocally as for modeling reaction A, but a plausible set of pseudoelementary processes¹⁶ is presented in Scheme II. The sum of these three steps with (I1) from Scheme I generates the stoichiometry of reaction B.

Scheme II. Steps Generating Reaction B (with Step I1)



Steps D4 and D5 mean that I₂ and IO₃[−] are in competition for the strongly reducing species HOO·. The mechanism as developed in Scheme II is thus consistent with the observation of Liebafsky¹⁰ that in the iodate-peroxide subsystem the extent of reaction B could be greatly reduced if I₂ was continuously removed from the solution by shaking with carbon tetrachloride.

Mechanism of Reaction C. At long times, the concentration of iodine decreases again. This decrease cannot be explained by volatilization of I₂, and it is necessary to invoke reaction C. This behavior seems to require that the strongly oxidizing species HO· and perhaps also Mn(III) can attack HOI and perhaps also I₂. The mechanistic possibilities are even less uniquely defined than for the other reactions, but Scheme III lists some pseudo elementary processes¹⁶ that might account for the observed behavior. Others are conceivable. Some of the reasons for selecting specific

(15) Sharma, K. R.; Noyes, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 4345–4361.

(16) Except for consideration of both I₂ and ·I, we have included only one species representing each oxidation state of iodine. Selections of IO₃[−], ·IO₂, HIO₂, ·IO, HOI, and I[−] assumed them to be dominant species under the experimental conditions. Other species like H₂IO₃⁺, IO⁺, IO[−], I⁺, etc. have been proposed by others as mechanistic intermediates but should be in rapid equilibrium with the species we have selected to represent those oxidation numbers; it would serve no useful purpose to invoke them here. The radicals ·IO₂ and ·IO should be scavenged too rapidly to form the dimers I₂O₄ and I₂O₂. We have ignored polynuclear oxyacids like H₂I₂O₃ because we are unaware of any firm evidence for their existence.

(17) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649–8664.

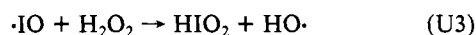
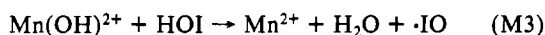
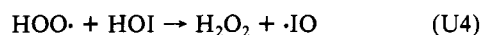
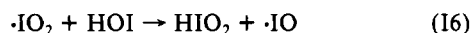
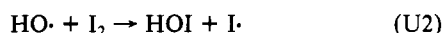
Table I. Rate Constants Used in Computations for Dashed Curves in Figure 1

step	forward rate	backward rate (if included)
I1	$3.1 \times 10^{12} \text{ M}^{-2} \text{ s}^{-1}$	$2.2 \text{ s}^{-1} \text{ }^a$
I2	$2.0 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	$90 \text{ M}^{-1} \text{ s}^{-1}$
I3	$1.4 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$	$2.8 \text{ M}^{-1} \text{ s}^{-1}$
I4	$1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	$0.86 \text{ M}^{-2} \text{ s}^{-1}$
I5	$1.9 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$	$1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ }^a$
U1	coupled to U2 and D5	
U2	$2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
U3	coupled to U4	
U4	$3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
D1	$37 \text{ M}^{-1} \text{ s}^{-1}$	
D4	$3.5 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$	
D5	$2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	
O1	$4.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	
M1	$1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \text{ }^a$	$2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
M2	$3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	$6.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \text{ }^a$

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

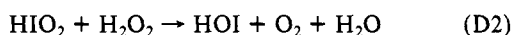
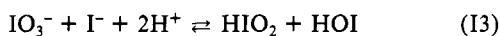
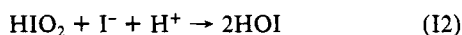
steps will be discussed below and in the subsequent paper on the full oscillating system.

Scheme III. Additional Steps Generating Reaction C



Mechanism of Uncatalyzed Reaction A. Reaction A occurs slowly even in the absence of the manganous ion catalyst.^{10,15} Scheme IV contains some additional steps that are then important but that need not all be included in a model of the subsystem including catalyst. These steps involve only species with even numbers of electrons.

Scheme IV. Additional Nonradical Steps Contributing to Reaction A



Modeling the Subsystem

One test of the level of understanding of a mechanism is the ability to reproduce observations by computer simulation. Such a test is by no means unequivocal, but it can often reveal gross deficiencies in assumptions about a mechanism.

Table I lists numerical values assigned to rate constants for several of the steps from Schemes I–IV. Some of those values are based on experimental measurements, and some have been assigned arbitrarily but within limits we consider plausible. Reverse rates were ignored when they were clearly unimportant compared to forward rates, and several of the steps in the schemes were ignored completely as unnecessary to the computations. Those computations were further simplified by assigning no values to k_{U1} and k_{U3} but instead regarding $\cdot\text{I}$ and $\cdot\text{IO}$ as flow-through¹⁸ intermediates whose irreversible formation and destruction were stiffly coupled.

The dashed curves in Figure 1 show how well the rate constants from Table I reproduce the experimental data for a specific run. The fit is almost always to within a factor of 2, but we fail to reproduce the sharp peak in rate of oxygen evolution or the very low iodine concentrations at long times. Further adjustment of

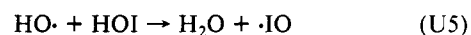
rate constants might improve the fit. Such an effort would be pointless because even this mechanism is considerably simplified. Thus, it involves the six high energy species $\cdot\text{IO}_2$, $\cdot\text{IO}$, $\cdot\text{I}$, $\text{HOO}\cdot$, $\text{HO}\cdot$, and $\text{Mn}(\text{OH})^{2+}$. In Schemes I–III, the reverse of step I5 is the only example in which one of these six species does not react either with Mn^{2+} or with a molecule having an even number of electrons. Other radical-radical reactions are certainly permissible and probable. They would provide additional chain-termination processes, but we do not believe the possible benefits of including such steps would balance the greatly increased complexity of the model.

Discussion

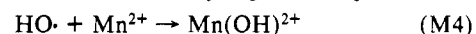
Possibilities for Iodide Control of Switching. The chemistry of bromate-driven oscillators¹ suggests that the Briggs-Rauscher³ oscillator should involve switching between two pseudo-stationary states. One of those states would involve large $[\text{I}^-]$ and small $[\text{HIO}_2]$, and oxidation state would never change except by 2 equivs in a single step. The other state would involve small $[\text{I}^-]$ and large $[\text{HIO}_2]$ and would include steps involving 1-equiv changes in oxidation state. Initiation by step I5 and the sequence generating stoichiometry D would lead to autocatalytic growth of $[\text{HIO}_2]$ provided $[\text{I}^-]$ were not great enough to inhibit that autocatalysis by step I2.

The subsystem considered in this paper is entirely concerned with dominance by the low $[\text{I}^-]$ state. The manganese reactions in Scheme I generate HIO_2 autocatalytically faster than step D1 can produce the I^- necessary to destroy HIO_2 by step I2. In spite of the peculiar maximum in $[\text{I}_2]$, the subsystem is not an oscillator. It can become an oscillator only if $[\text{I}^-]$ can be increased enough for step I2 to control the autocatalytic production of HIO_2 .

Permissible Hydroxyl Radical Reactions. As Figure 2 demonstrates, the $\text{HO}\cdot$ radical could conceivably oxidize any 1-equiv reductant in this system. However, the only steps proposed are (O1) and (U2). The reasons for this selectivity are kinetic rather than thermodynamic. The rate constant for step O1 is¹⁹ $4.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. No bimolecular reaction in solution can have a rate constant greater than about²⁰ $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Therefore, species at concentrations less than about 10^{-4} M cannot compete with step O1. We have rejected step U5 even though we would have found it very convenient to include in our mechanism.



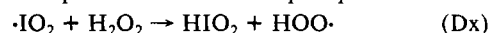
We have also somewhat arbitrarily neglected step M4. The



sequence (M4) + (M2) generates (O1), which is already so rapid that manganous catalysis could hardly be important. It is true that (M4) + (M3) could conceivably generate the stoichiometry of (U5) at a rate competitive with (O1), but we have ignored this possibility because iodine can be oxidized to iodate even in the absence of manganous salts.²¹ In that system, we²² find it necessary to invoke (U4) rather than (U5).

Distinction of Steps Transferring Hydrogen Atoms and Electrons. As we try to understand these complex systems, certain mechanistic constraints become of ever more obvious importance. One constraint is the need to distinguish between 1-equiv and 2-equiv changes in oxidation state as mentioned above. If no new phase is generated, oscillatory systems seem to switch between pseudo-stationary states that do and do not involve 1-equiv processes.

The subsystem described here indicates the importance of a further classification of 1-equiv reactants. The remarkable manganous catalysis of reaction A takes place through steps M1 and M2. The consequence of those two steps is process Dx. If



steps M1 and M2 are thermodynamically allowed, so is (Dx). If

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(22) Noyes, R. M.; Furrow, S. D., manuscript in preparation.

(18) Clarke, B. L. *J. Chem. Phys.* **1976**, *64*, 4168.

step Dx took place directly, there would be no manganous catalysis.

We believe the paradox can be resolved by distinguishing between electron transfer and hydrogen atom transfer mechanisms. A 1-equiv reductant like H_2O_2 or an organic compound can be oxidized either by abstraction of a hydrogen atom in a single step or by abstraction of an electron and a proton in successive steps. Other 1-equiv reductants like Fe^{2+} or I^- can be oxidized only by electron abstraction. If a 1-equiv oxidant like $\text{HO}\cdot$ or $\text{Cl}\cdot$ has an odd electron localized on a single atom, it can abstract either a hydrogen atom or an electron depending on the chemistry of the reductant with which it reacts. However, if the odd electron is delocalized as in $\cdot\text{IO}_2$, the oxidant is sluggish at abstracting a hydrogen atom regardless of the thermodynamic driving force.

When these principles are applied to the present system, $\cdot\text{IO}_2$ reacts only slowly or not at all by step Dx and preferentially abstracts an electron from Mn^{2+} while simultaneously or subse-

quently accepting a proton from the solvent as summarized by step M1. The resulting Mn(III) complexes with H_2O_2 and removes an electron by an intramolecular rearrangement while a proton is lost to solvent either at the same time or at some other stage of the process as summarized by step M2.

The above argument is developed as a rationalization to explain some interesting and unusual chemistry. It remains to be seen whether it has utility beyond the system for which it was developed.

Acknowledgment. This research was supported in part by a Grant from the National Science Foundation to the University of Oregon. Susan Tuckey^{2b} and Robert Gay^{2b} made some of the spectrophotometric studies on the iodate-peroxide-manganous subsystem. Dr. D. O. Cooke of the Hastings College of Further Education kindly made a manuscript available to us in advance of publication.

The Oscillatory Briggs-Rauscher Reaction. 2. Effects of Substitutions and Additions¹

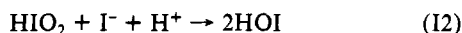
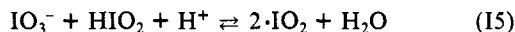
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Abstract: Addition of malonic acid can cause oscillatory behavior in the subsystem of the previous paper. Effects of various other organic and inorganic adducts have been examined to seek evidence on the mechanism of those oscillations. Methylmalonic acid, which has only one enolizable hydrogen, iodates by procedures similar to, but slower than, those observed for malonic acid. Crotonic acid is an efficient scavenger of HOI ; its presence slows and alters the stoichiometry of reaction in the iodate-peroxide-manganous subsystem. Phenol is an even more efficient radical scavenger and acts as an inhibitor of reaction in the subsystem. Acrylamide does not seem to be a particularly effective radical scavenger in this subsystem. Silver ion, which is a scavenger of I^- , has rather little effect on the behavior of the subsystem. Oxalic acid, pyrophosphate, and dichromate exhibit complex effects that have not been studied in detail. The importance of malonic acid to the oscillating reaction is ascribed to the fact that its enol scavenges iodine species with oxidation numbers +1 and 0. That scavenging reduces the total quantity $[\text{HOI}] + 2[\text{I}_2] + [\text{I}^-]$, but it may increase the $[\text{I}^-]/[\text{HOI}]$ ratio enough that $[\text{I}^-]$ actually increases.

The previous paper¹ shows that manganese salts catalyze an initial reaction in which hydrogen peroxide reduces iodate and the concentration of iodine rises to a maximum; that concentration subsequently declines as hydrogen peroxide oxidizes much of the iodine back to iodate. We believe that steps involving 1-equiv change are important at all times in this subsystem. The initial reduction of IO_3^- by H_2O_2 is initiated by step I5 and results in



an autocatalytic increase of $[\text{HIO}_2]$. We believe that in the subsystem of the previous paper this autocatalysis is always faster than the rate of HIO_2 destruction by step I2.

The iodate-peroxide-manganous subsystem is not an oscillator in spite of the single maximum in iodine concentration. However, Briggs and Rauscher³ have shown that addition of malonic acid to such a subsystem can create an extremely effective oscillator. Our experience with bromate-driven oscillators⁴ suggests that

during a portion of each cycle $[\text{I}^-]$ becomes large enough that step I2 is faster than the HIO_2 -promoted reduction of IO_3^- .

We can imagine the following number of ways in which an organic compound, RH , might interact with the reacting subsystem. (a) The organic compound might be attacked by the oxyhydrogen radicals $\text{HOO}\cdot$ and particularly $\text{HO}\cdot$. (b) The organic compound might be oxidized by iodine species with oxidation number greater than +1. (c) RH might be converted to RI , thereby acting as a sink for I_2 and for the species HOI and I^- in equilibrium with it. (d) Iodination of RH might shift the ratio $[\text{I}^-]/[\text{HOI}]$. (e) Subsequent reaction of RI might liberate the I^- necessary to affect the rate of step I2.

In order to assess the relative importance of these effects, we have compared the behaviors in this system of several selected organic compounds. Malonic acid is the substrate of choice for studies of oscillations and provides the reference for comparison with other adducts. Methylmalonic acid has only one enolizable hydrogen and does not form any of the especially reactive diiodo compounds. Crotonic acid, phenol, and 2-naphthol were selected as scavengers of iodine and hypiodous acid. Studies with all of these compounds were particularly relevant to understanding the mechanism of the oscillations and are reported in the second part of this paper.

We also examined the effects of acrylamide, oxalic acid, and various inorganic species. These adducts were selected in an-

(1) Part 41 in the series Chemical Oscillations and Instabilities. Part 40: Furrow, S. D.; Noyes, R. M. *J. Am. Chem. Soc.*, part 1 in this issue.

(2) (a) University of Oregon. (b) Pennsylvania State University.

(3) Briggs, T. S.; Rauscher, W. C. *J. Chem. Educ.* 1973, 50, 496.

(4) Noyes, R. M. *J. Am. Chem. Soc.* 1980, 102, 4644-4649.

icipation of effects that would be mechanistically significant. Often these systems were more complex than anticipated or the interpretations were ambiguous; no further studies were attempted. We report these qualitative observations in the third section even though we do not use them much for drawing mechanistic conclusions. We hope those reports may stimulate the thinking of others.

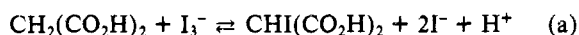
The discussion in the fourth section uses the observations from the second section to reach more specific conclusions about the ways in which organic substrates can act to promote oscillations.

Details of experimental procedures are described at the end of the paper.

Organic Substrates of Particular Mechanistic Significance

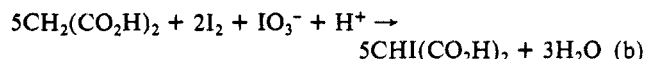
Reactions of Malonic Acid (MA). Malonic acid, $\text{CH}_2(\text{CO}_2\text{H})_2$, is the organic substrate that has been used most often in oscillating systems. It can be oxidized at higher temperatures either by IO_3^- or by H_2O_2 , but both reactions are negligibly slow at room temperature. Spectrophotometric observations indicate malonic acid forms a complex with Mn^{2+} , but at pH 1 most of these species are uncomplexed.

Leopold and Haim⁵ studied the kinetics of reaction a. The



mechanism involved prior enolization of the malonic acid, and the process went to a measurable equilibrium at the iodide concentrations they used. At the iodide concentrations in an oscillator,⁶ reaction a must be almost irreversible.

If I_2 and IO_3^- are both present, the iodide produced in (a) reacts further with iodate and the stoichiometry becomes that of (b).



Because enolization of malonic acid is rate determining, stoichiometries a and b require that rate of consumption of I_2 is 40% as much when iodate is present as when it is absent.

Jwo and Noyes⁷ showed that 6 equiv of cerium(IV) oxidized malonic acid according to stoichiometry c. Manganese(III) can

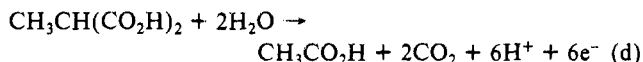


also oxidize organic compounds, but it is not easy to do quantitative experiments with this oxidant. However cerium(III) behaves very much like manganese(II) in catalyzing the reduction of IO_3^- by H_2O_2 . We hope as a trial assumption that Mn(III) will behave similarly to Ce(IV) in its reactions with organic species like malonic acid.

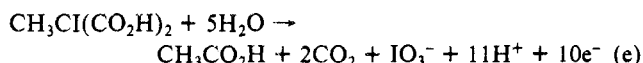
We also wished to study the stoichiometry of oxidation of monoiodomalonic acid, $\text{ICH}(\text{CO}_2\text{H})_2$. We were unable to isolate this material in pure form. We did try to oxidize a solution prepared by iodination of malonic acid; that solution consumed more than 10 equiv of cerium(IV) for each mole of malonic acid before iodination. This stoichiometry suggests that some of the material had been diiodinated and that the iodine was oxidized to iodate in addition to the stoichiometry of (c). However, conclusions were not firm.

Reactions of Methylmalonic Acid (MMA). As mentioned above, malonic acid is subjected to diiodination, and $\text{Cl}_2(\text{CO}_2\text{H})_2$ might exhibit complex behavior. Such complexities can be reduced by using methylmalonic acid, $\text{CH}_3\text{CH}(\text{CO}_2\text{H})_2$. This compound is also iodinated by an enolization mechanism, and the kinetics have been studied by Furrow.⁸ The iodination of MMA is several times slower than that of malonic acid, but no major mechanistic differences were indicated. Thus, the effect of added iodate is the same as with MA.

Just like malonic acid, MMA is oxidized by 6 equiv of cerium(IV). The indicated stoichiometry is (d).



Iodomethylmalonic acid consumes 10 equiv of Ce(IV) consistent with stoichiometry e.

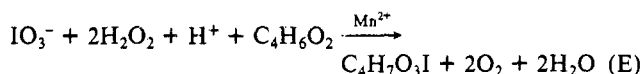
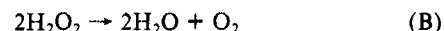
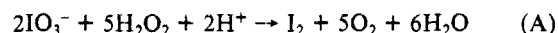


Reactions of Crotonic Acid. Crotonic acid, *trans*- $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$, was anticipated to scavenge iodine in 0 and +1 oxidation states. A detailed study of its reactions will be presented elsewhere⁹ and only summarized here.

Crotonic acid irreversibly adds HOI to form an iodohydrin with empirical formula $\text{C}_4\text{H}_7\text{O}_3\text{I}$. The kinetics at 25 °C correspond to eq 1.

$$-\text{d}[\text{HOI}]/\text{d}t = 4500[\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}][\text{HOI}][\text{H}^+] \text{ M s}^{-1} \quad (1)$$

Crotonic acid reacts negligibly slowly or not at all with any of the individual species IO_3^- , H_2O_2 , Mn^{2+} , and I_2 . However, when crotonic acid is added to the iodate-peroxide-manganous subsystem of the first paper, the stoichiometry is changed from (A) to (E). At the same time, induced disproportionation of hydrogen peroxide by reaction B is very much reduced.



The rate of reaction E can be followed conveniently by oxygen evolution. It exhibits a rather poorly defined induction period that depends upon various things including the order of addition of reagents. Other complexities of the kinetics will be described elsewhere.⁹

The change in stoichiometry from (A) to (E) demonstrates that crotonic acid is scavenging HOI and preventing the further reduction to I_2 that would otherwise occur. The scavenging should greatly reduce the concentrations of I_2 , $\cdot\text{I}$, and I^- . The simultaneous great reduction in rate of induced reaction B supports our previous¹ proposal that this reaction occurs by a radical chain involving iodine atom intermediates.

Reactions of Phenol. Phenol, $\text{C}_6\text{H}_5\text{OH}$, is a still more effective scavenger of iodine in low oxidation states. The rate of reaction with HOI is approximated by eq 2.

$$-\text{d}[\text{HOI}]/\text{d}t = (8 \times 10^4)[\text{C}_6\text{H}_5\text{OH}][\text{HOI}] \text{ M s}^{-1} \quad (2)$$

A little phenol was added to a subsystem like that of the previous paper to create a solution having composition $[\text{IO}_3^-] = 0.025 \text{ M}$, $[\text{H}^+] = 0.1 \text{ M}$, $[\text{H}_2\text{O}_2] = 0.1 \text{ M}$, $[\text{Mn}^{2+}] = 0.002 \text{ M}$, and $[\text{C}_6\text{H}_5\text{OH}] = 1 \times 10^{-4} \text{ M}$. This system exhibited an extreme induction period such that during 4 h only about 1 mL of oxygen was evolved. Then during a few minutes the rate of O_2 evolution increased by 2 orders of magnitude!

A comparison of eq 1 and 2 indicates that 10^{-4} M phenol should scavenge HOI less efficiently than 0.1 M crotonic acid. However, the phenol system inhibits the manganous-catalyzed oxidation of peroxide by iodate while the crotonic acid system does not. We conclude that the phenol is also scavenging some essential oxyiodine species intermediate between IO_3^- and HOI. A plausible interpretation is that phenol competes with Mn^{2+} for the $\cdot\text{IO}_2$ radical. We have no direct evidence for this suggestion. However, phenol and other aromatic substrates react in precisely this way with $\cdot\text{BrO}_2$ radicals during uncatalyzed bromate-driven oscillations.^{10,11}

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(6) Roux, J. C.; Vidal, C. *Nouv. J. Chim.* **1979**, *3*, 247–253.

(7) Jwo, J.-J.; Noyes, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 5422–5431.

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(10) Orbán, M.; Körös, E.; Noyes, R. M. *J. Phys. Chem.* **1979**, *83*, 2056–2057.

(11) Field, R. J., manuscript in preparation.

2-Naphthol, like phenol, is a powerful inhibitor, and a concentration of only 1×10^{-6} M causes a 10-min induction period.

Adducts Providing More Equivocal Evidence

Reactions of Acrylamide. Acrylamide, $\text{CH}_2=\text{CHCONH}_2$, is often an effective radical trap and has been used in this way with the oscillatory Bray-Liebafsky mixture.¹² However, it has a rather minor effect on the iodate-peroxide-manganous subsystem. Thus 10^{-3} M acrylamide reduced the rate of I_2 formation by only 15% and 10^{-2} M reduced by only about 70%. We find that acrylamide reacts with a mixture of I_2 and IO_3^- much the way crotonic acid does. Apparently acrylamide exerts at least much of its influence by reacting with HOI rather than by trapping radicals.

Reactions of Oxalic Acid. Oxalic acid, $(\text{CO}_2\text{H})_2$, forms weak complexes with Mn(II) ¹³ and is both a complexing agent and 1-equiv reductant of Mn(III) .¹⁴ When 0.026 M oxalic acid was added to a system having composition $[\text{IO}_3^-] = 0.025$ M, $[\text{H}^+] = 0.1$ M, $[\text{H}_2\text{O}_2] = 0.1$ M, and $[\text{Mn}^{2+}] = 0.002$ M, an induction period of 5 min was followed by a slower rate of I_2 production than in the absence of oxalic acid. If the concentration was increased to 0.10 M (where approximately 25% of the Mn^{2+} is complexed), the induction period was lengthened and the maximum rate of I_2 production was reduced by 2 orders of magnitude. However, this system was more complex than anticipated; after about 3 h when $[\text{I}_2]$ had gone through its maximum and decreased, it rapidly increased again. Oxalic acid is not only a complexing agent and reductant for manganese but can also react with HOI.¹⁵ These studies provide less information than had been hoped.

Effects of Pyrophosphate. Pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$, complexes Mn(II) and particularly Mn(III) and lowers the reduction potential from about 1.5 to 1.15 V.¹⁶ If a subsystem of iodate, peroxide, and manganous ions was made 0.05 M in $\text{Na}_4\text{P}_2\text{O}_7$ and adjusted to pH 1.0 with perchloric acid, reaction A was about 30% faster than at the same pH in the absence of pyrophosphate. If such a system also contained crotonic acid and was made 0.02 M in pyrophosphate, the rate of oxygen evolution increased by a factor of 3 and the fraction α (see first paper¹) of induced peroxide disproportionation increased from 0 to 0.25.

If 3×10^{-4} M Mn(III) in excess pyrophosphate was added to an acidic mixture of H_2O_2 and IO_3^- , some I_2 was rapidly produced. However, the ratio of $[\text{I}_2]$ formed to $[\text{Mn}^{3+}]$ consumed was no more than 0.17 and production of I_2 soon stopped. Apparently Mn(III) oxidation of H_2O_2 induces the simultaneous reduction of IO_3^- by H_2O_2 as would be expected from the mechanism of the previous paper.¹ However, that induction was not a true catalysis. If crotonic acid was also present, the ratio of O_2 formed to Mn^{3+} consumed was about unity, indicating that Mn(III) and iodate contributed about equally to the initial oxidation of peroxide.

Effects of Silver Ion. Silver ion is an obvious reagent to inhibit reactions of iodide ion. A precipitate of silver iodate, AgIO_3 , also forms in the subsystem, but with iodate in excess the equilibrium $[\text{Ag}^+]$ of about 10^{-6} M is sufficient to keep $[\text{I}^-]$ about 10^{-10} M or less. Addition of silver ion has little effect on $-d[\text{IO}_3^-]/dt$ in the subsystem of the first paper, but oxygen evolution is faster. When most of the silver ion has been converted to AgI , $[\text{I}_2]$ and $[\text{I}^-]$ both increase and the rate of oxygen evolution decreases.

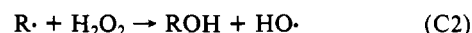
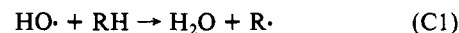
Effects of Other Additives. A few other additives were studied with the iodate-peroxide-manganous subsystem. Dichromate, $\text{Cr}_2\text{O}_7^{2-}$, at 5×10^{-6} M prevents iodine from forming; therefore cleaning solution was not used on our glassware and the reagents were never allowed to contact stainless steel. Chloride ion at 2×10^{-4} M noticeably slows the reaction; but fluoride ion at the same concentration has little effect. Ferric ion at the same concentration also has little effect even though this species is a

catalyst for hydrogen peroxide disproportionation.

Discussion

These observations demonstrate that crotonic acid and phenol, which are scavengers for HOI, have major effects on behavior of the iodate-peroxide-manganous subsystem. On the other hand, silver ion, which scavenges I^- and I_2 , has relatively little effect. We must conclude that *HOI is a very important intermediate in the manganous catalysis of reaction A* while I^- appears rather unimportant. According to superficial consideration, the mechanism of the previous paper¹ is not entirely consistent with that conclusion. We should now consider the possible reactions of organic matter as outlined in the Introduction.

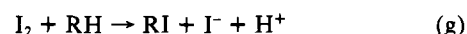
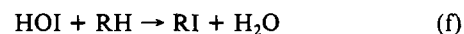
(a) Organic matter may be attacked by oxyhydrogen radicals. Such attack is eminently plausible and must occur. The gas evolved from a Briggs-Rauscher³ oscillator is mostly oxygen, but it also contains significant amounts of carbon dioxide. Some induced hydrogen peroxide oxidation of malonic acid evidently occurs. A schematic mechanism is illustrated by steps C1 and C2.



These steps provide a chain by which hydrogen peroxide can oxidize organic matter without net depletion of the $\text{HO}\cdot$ radicals. We choose to regard such steps as side reactions that consume some hydrogen peroxide and organic matter but that are not essential to the mechanism of the oscillating reaction itself.

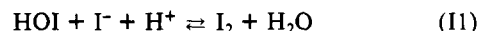
(b) The organic matter may be oxidized by iodine species with oxidation number greater than +1. The discussion above found it necessary to invoke just such processes in order to explain the extremely efficient inhibition by phenol. However, by invoking them for phenol, we concluded they were much less important for crotonic acid. They should be less important still for malonic acid. Unless and until further evidence requires a change, we shall assume that the only iodine species reacting directly with malonic acid and its derivatives are included in the set HOI, I_2 , $\cdot\text{I}$, and I^- .

(c) Iodination of RH may serve as a sink for I_2 and for the species HOI and I^- in rapid equilibrium with it. Malonic acid certainly serves as just such a sink. The reaction passes through an enol intermediate and generates the net stoichiometries f and g.



The discussion of the next paper will show that this sink function is essential to the mechanism of the oscillating reaction. However, a sink depletes the concentrations of all three species, I_2 , HOI, and I^- . The Introduction pointed out that oscillatory behavior required $[\text{I}^-]$ to increase enough to enhance the importance of step I2. It is not sufficient that malonic acid serve as a sink for iodine species with low oxidation number.

(d) Iodination of RH may shift the ratio $[\text{I}^-]/[\text{HOI}]$. Eigen and Kustin¹⁷ have shown that equilibrium I1 is established within



a time of the order of 1 s. Reactions f and g both have the effect of increasing the ratio $[\text{I}^-]/[\text{HOI}]$. By serving as a sink, those reactions indubitably decrease the sum $[\text{HOI}] + 2[\text{I}_2] + [\text{I}^-]$. However, they may actually serve to increase the value of $[\text{I}^-]$. We believe such an increase is necessary if malonic acid is to convert the iodate-peroxide-manganous subsystem to an oscillator.

(e) Subsequent reactions of RI may liberate I^- . Just such an organic bromide reaction is essential to the original FKN¹⁸ mechanism of the Belousov¹⁹-Zhabotinsky²⁰ oscillator. Subsequent

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considerations⁴ indicate it is not necessary in all bromate-driven oscillators. Iodomalonic acid is indubitably subject to attack by species like Mn^{3+} and $\text{HO}\cdot$; I^- should be one of the products. Cooke²¹ specifically invokes this very process in his mechanistic proposals for the Briggs-Rauscher³ oscillator. Briggs and Rauscher themselves noted that $[\text{I}^-]$ 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 $[\text{HOI}] + 2[\text{I}_2] + [\text{I}^-]$, but it simultaneously increases the ratio $[\text{I}^-]/[\text{HOI}]$ and may actually increase $[\text{I}^-]$ 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 DBG-T 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.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation to the University of Oregon. Mrs. Constance Ivey^{2b} conducted cerium oxidations of iodomalonic acid and iodomethylmalonic acid solutions.

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The Oscillatory Briggs-Rauscher Reaction. 3. A Skeleton Mechanism for Oscillations¹

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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 series³ reported and attempted to explain the remarkably effective catalysis by manganous ion of the oxidation of hydrogen peroxide by iodate. The second paper¹ 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-Rauscher⁴ 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 MMA⁹ 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 Liebhafsky¹¹ for consideration of the simpler Bray¹² 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

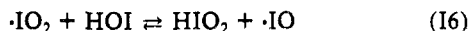
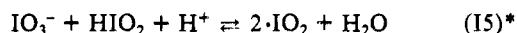
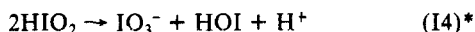
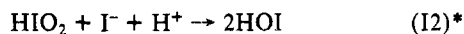
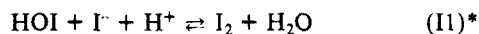
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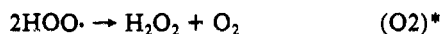
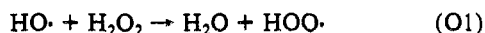
reduction of this element with no change in average oxidation number. A DOWN step involves reduction of an iodine species and oxidation of an oxygen species. An UP step involves oxidation of an iodine species by an oxygen species. MANGANESE and CARBON steps are in addition to the original Liebhafsky¹¹ classification.

Scheme I. Elementary Processes Postulated in the Briggs-Rauscher⁴ System

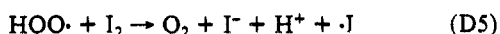
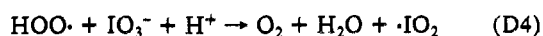
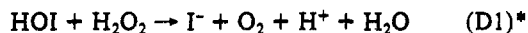
IODINE Steps



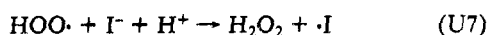
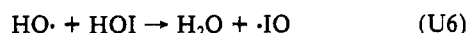
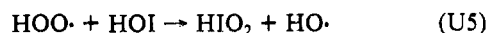
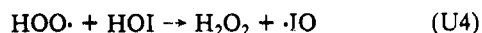
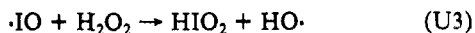
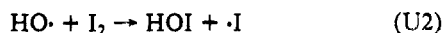
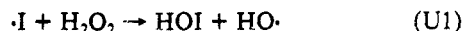
OXYGEN Steps



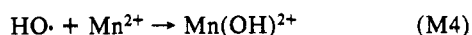
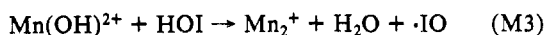
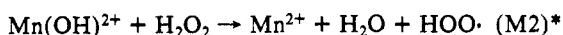
DOWN Steps



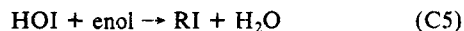
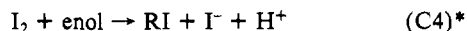
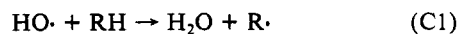
UP Steps



MANGANESE Steps



CARBON Steps



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

Table I. Initial Composition Assumed for Computations

$[\text{H}_2\text{O}_2] = 1.1 \text{ M}$	$[\text{Mn}^{2+}] = 0.004 \text{ M}$
$[\text{IO}_3^-] = 0.019 \text{ M}$	$[\text{MA}] = 0.013 \text{ M}$
$[\text{H}^+] = 0.057 \text{ M}$	

been indicated with an asterisk (*). We believe these eleven steps are sufficient to generate the behavior observed in the Briggs-Rauscher⁴ (but not necessarily in the Bray-Liebhafsky¹¹) system. The objective of this paper is to demonstrate that a plausible set of equilibrium and rate constants can generate oscillations.

Conditions for Computations

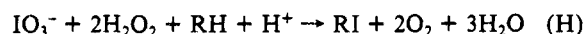
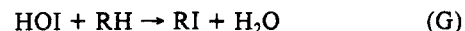
Table I lists the concentrations of major reactant species which were maintained constant during our model computations. Roux and Vidal⁷ made a particularly careful experimental study in which they continuously added these five species to a stirred reactor and maintained their concentrations almost invariant 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_{12} is comparable to that estimated²³ 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 $\text{Mn}(\text{OH})^{2+}$. This restriction was imposed to simplify the selection of rate constants; the kinetic observations reported in the first paper³ suggest reversibility of step M1 may need to be included in more exact modeling.

The three remaining rate constants k_{15} , k_{-15} , and k_{14} 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



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 $\cdot\text{IO}_2$ can be calculated from steady-state expression 1. Let q be the fraction $2k_{15}[\text{H}^+][\text{IO}_3^-][\text{HIO}_2] = k_{M1}[\text{Mn}^{2+}][\cdot\text{IO}_2] + 2k_{-15}[\cdot\text{IO}_2]^2$ (1) of $\cdot\text{IO}_2$ (formed by step I5) that reacts by step M1 rather than by step -I5. Let v_{15} be the net rate of step I5. Then

$$q = \frac{k_{M1}[\text{Mn}^{2+}]}{k_{M1}[\text{Mn}^{2+}] + 2k_{-15}[\cdot\text{IO}_2]} \quad (2)$$

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(19) Of course no rate constant in either direction for an elementary process should exceed that for a diffusion-controlled reaction.

$$v_{I_2} = \frac{1}{2}v_{M_1} = qk_{15}[H^+][IO_3^-][HIO_2] \quad (3)$$

These relations lead to the steady-state expression

$$d[HIO_2]/dt \approx 0 \approx k_{13}[H^+]^2[IO_3^-][I^-] + \\ [qk_{15}[H^+][IO_3^-] - k_{12}[H^+][I^-]][HIO_2] - 2k_{14}[HIO_2]^2 \quad (4)$$

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

$$[HIO_2]_n \approx (k_{13}/k_{12})[H^+][IO_3^-] \quad (5)$$

$$[HIO_2]_r \approx (qk_{15}/2k_{14})[H^+][IO_3^-] \quad (6)$$

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

$$[I^-]_c = (qk_{15}/k_{12})[IO_3^-] \quad (7)$$

We made the arbitrary assumptions that when the system switches from the nonradical to the radical path, $[HIO_2] = 10[HIO_2]_n$, and that when it switches from the radical to the nonradical, $q = 0.01$. These two conditions led to the values of k_{15} and k_{-15} 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_{14} 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_{14} 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 Vidal⁷ 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 Vidal⁷ observe a factor of only about 5. Because of the hard transition we encountered when varying k_{14} , 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_{14} 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 Vidal⁷ 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 Vidal⁷ 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 com-

Table II. Rate Constants Available from Experiment

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

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

Table III. Rate Constants Assigned for Computations

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

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

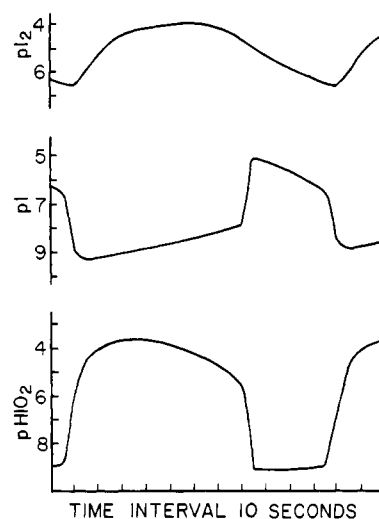


Figure 1. Computed time dependence of three intermediate species computed with rate constants from Tables II and III while concentrations of major species were held constant at the values from Table I. These results can be compared with Figure 4 in ref 7.

putations 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.

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-Liebhaufsky reaction showed²⁰ 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-Liebhaufsky¹² 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.

Effects of Various Organic Substrates. Our second paper¹ 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

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

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.

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

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 paper³ 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 overshoot 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-Rauscher⁴ 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 Oregonator²² 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 FKN²³ mechanism for the Belousov²⁴-Zhabotinsky²⁵ 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 assigned²⁶ to the ostensibly simpler iodate-peroxide¹² 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.

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(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.

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(25) Zhabotinsky, A. M. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 392-395.

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A Mechanistic Study of Oscillations and Bistability in the Briggs–Rauscher Reaction

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Abstract: A ten-step mechanism has been developed for the Briggs–Rauscher system which contains iodate, hydrogen peroxide, malonic acid, and manganese(II) in acidic solution. The model is qualitatively identical with, though it differs quantitatively from, that proposed independently by Noyes and Furrow. It also bears strong similarities to the mechanistic suggestions of Cooke. Extensive numerical simulations of the reaction in a flow reactor show that the model predicts the observed topology of the “cross-shaped phase diagram” in which both bistability and oscillations appear as the input flows of the reactant species are varied. The observed hysteresis in the steady-state iodine concentration as a function of I_2 flow and a variety of other dynamic behavior are also calculated in agreement with experiment. The remaining discrepancies between theory and experiment appear to result from an overestimation in the model of the stability of the nonradical steady state. A possible remedy for this problem is suggested.

The Briggs–Rauscher (BR) reaction,¹ in which the acidic oxidation of malonic acid by a mixture of hydrogen peroxide and iodate is catalyzed by manganous ion, is best known as the most visually impressive of the chemical oscillators. Under appropriate conditions and with the addition of a starch indicator, at room temperature a stirred batch solution goes through 15 or more cycles of colorless–gold–blue before expiring as a purplish solution with a strong odor of iodine.

The BR reaction, however, exhibits a far richer collection of nonlinear dynamic phenomena than simple oscillation. In a flow reactor, complex oscillations² as well as multiple stable states³ accompanied by a variety of bifurcation and hysteresis phenomena have been observed.^{2,4}

The BR system was discovered some 8 years ago and is a hybrid of two other chemical oscillators, the Belousov–Zhabotinskii (BZ)⁵ and the Bray–Liebhafsky (BL) reactions,⁶ for which detailed mechanisms have been proposed and numerically evaluated.^{7,8} It is therefore surprising that until quite recently there had been no quantitative and very little qualitative discussion of the mechanism of the BR reaction.

Cooke⁹ has studied the BR and related systems experimentally and has made a number of mechanistic suggestions based on his results. No quantitative comparison between theory and experiment was carried out. More recently, Furrow and Noyes¹⁰ have conducted a systematic study of the reaction, investigating the kinetics of the reacting species taken two and three at a time. These authors have proposed a skeleton mechanism and have estimated rate constants for the elementary steps in that mechanism. They have also reported a single numerical simulation^{10c}

with their model which shows that it can indeed give rise to oscillations.

In this paper, we use a broad range of experimental data obtained mainly, but not exclusively, under flow conditions, to guide the construction of a mechanism for the BR reaction. Although we approach the problem from a rather different point of view, we have independently arrived at a mechanism similar to that of Cooke and nearly identical with that of Furrow and Noyes. We have carried out extensive calculations with our mechanism in an attempt to simulate not only the oscillatory behavior, but the multistability, hysteresis, and bifurcation phenomena as well. We find qualitative agreement with nearly all of the observed phenomena and quantitative agreement with some. Most of the discrepancies which remain between our calculations and the experimental results can be attributed to a single weakness of the model—its exaggeration of the stability of the nonradical steady state of the system. We suggest how the mechanism might be augmented to correct this failing.

Modifications of the BR system in which malonic acid is replaced by related organic species^{1,9,11} are also known to oscillate. In particular, Furrow¹¹ has carried out a careful study of the BR reaction with methylmalonic acid and has found a significant lengthening of the oscillation period over that of the malonic acid system. By introducing Furrow's experimentally determined rate parameters for the methylmalonic acid–iodine reaction at the appropriate point in our model, we show that it indeed predicts the observed increase in the period of oscillation.

Experimental Studies

Since the initial study of Briggs and Rauscher¹ in 1973, the BR system has been the subject of a variety of investigations.

Cooke⁹ has looked at the BR reaction and the related system with malonic acid replaced by acetone under batch conditions. He has studied the dependence of the period and of the redox potential trace on the concentrations of the constituent species. He has also examined the behavior of the inorganic components (hydrogen peroxide, iodate, manganese) and the effect of Cu(II) and Cl[−] ions on these reactions.

Furrow and Noyes^{10a,b} have also attempted to simplify the BR system by examining several subsystems in some detail in a batch configuration. They first probe the set of inorganic reactions and then consider the role of various organic substrates as replacements for malonic acid in an effort to elucidate the mechanisms of the component reactions.

The most extensive experiments on the BR system have been carried out by De Kepper et al.^{2,4,12} in a continuous-flow stirred-tank reactor (CSTR). These more phenomenologically oriented studies probed a portion of the phase diagram in the constraint space defined by iodate, hydrogen peroxide, malonic acid, temperature, and residence time. A

(1) Briggs, T. C.; Rauscher, W. C. *J. Chem. Educ.* **1973**, *50*, 496.

(2) (a) De Kepper, P.; Pacault, A.; Rossi, A. C. R. *Hebd. Acad. Sci., Ser. C* **1976**, *282C*, 199–204. (b) Pacault, A.; De Kepper, P.; Hanusse, P.; Rossi, A. *Ibid.* **1975**, *281C*, 215–220. (c) De Kepper, P.; Pacault, A. *Ibid.* **1978**, *286C*, 437–441.

(3) We employ the term “stable state” to mean a dynamic state to which the system will return after a small perturbation. Such states may be either steady (concentrations constant) or oscillatory (concentrations vary periodically).

(4) Pacault, A.; Hanusse, P.; De Kepper, P.; Vidal, C.; Boissonade, J. *Acc. Chem. Res.* **1976**, *9*, 439–445.

(5) Belousov, B. P. “Ref. Radiats. Med., 1958”; Medgiz: Moscow, 1959; p 145. Zhabotinsky, A. M. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 392–395.

(6) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262–1267. Liebhafsky, H. A. *Ibid.* **1931**, *53*, 896–911.

(7) Edelson, D.; Noyes, R. M.; Field, R. J. *Int. J. Chem. Kinet.* **1979**, *11*, 156–164.

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

(9) (a) Cooke, D. O. *Inorg. Chim. Acta* **1979**, *37*, 259–265. (b) *Int. J. Chem. Kinet.* **1980**, *12*, 671–681. (c) *Ibid.* **1980**, *12*, 683–698.

(10) (a) Furrow, S. D.; Noyes, R. M. *J. Am. Chem. Soc.*, part 1 in this issue. (b) *Ibid.*, part 2 in this issue. (c) Noyes, R. M.; Furrow, S. D. *Ibid.*, part 3 in this issue.

(11) Furrow, S. D., *J. Phys. Chem.*, submitted for publication.

(12) (a) De Kepper, P. Ph.D. Thesis, Bordeaux, France, 1978. (b) De Kepper, P., unpublished observations.

wealth of spectacular phenomena was revealed.

Different types of simple and complex oscillations as well as transitions among these and various steady states were observed. The responses monitored in these experiments were the absorbance at 460 nm, a measure of the I_2 concentration in the reactor, and the potential of a platinum electrode, primarily sensitive to the iodide concentration.

Roux and Vidal¹³ carried out a single experiment in which the outputs of different sensors were fed into a computer for further analysis. Simultaneous oscillations of $[I^-]$, $[I_2]$, $[I_3^-]$, [iodomalonic acid], and $[O_2]$ are reported.

It is these flow experiments, and in particular their determination of the regions of the constraint space in which the system exhibits oscillations in connection with a neighboring region of bistability between two steady states, that we shall employ as the primary test of our mechanism. We shall occasionally refer to the results of batch experiments as well when they provide a relevant comparison between theory and experiment.

Construction of the Mechanism

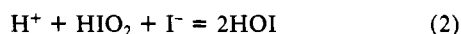
Choice of Reactions. Briggs and Rauscher¹ note the presence of manganese (or cerium) and malonic acid in both BR and BZ reactions and suggest that the similarity between the two reactions results from the role of malonic acid as a halogen consumer and halide producer in both systems. Roux and Vidal,¹³ on the basis of a careful analysis of the rates of production and consumption of various halogen-containing species in the oscillating BR system in comparison with the BZ and BL oscillators, conclude that the similarity between the BR and BZ systems is even more fundamental. They also observe that while MA serves as the major source of halide in the BZ reaction, in the BR system it appears to serve primarily as a halogen sink.

Extensive studies of the BZ¹⁴ and BR^{12,15} reactions in a stirred tank reactor (CSTR) reveal further parallels in their dynamic behavior. Most strikingly, under appropriate conditions both systems exhibit a region of bistability between two different steady states, regions in which each state is uniquely stable and a region of oscillations, all of which are linked in a characteristic "cross-shaped phase diagram".¹⁵ In both reactions, the steady states differ in their halide concentrations by several orders of magnitude. In the BZ reaction, the low halide state is recognized¹⁵ as being dominated by radical processes. The low halide BR state is characterized by a high I_2 concentration and an increase in the rate of O_2 evolution suggesting, by analogy with Noyes and Sharma's analysis of the BL reaction, a rapid decomposition of H_2O_2 via a radical process.

In both systems large amplitude oscillating states show complex secondary small amplitude oscillations about the low halide pseudo steady state.² Furthermore, transitions from the high halide state to the oscillatory state show subcritical bifurcation¹⁷ on increasing the malonic acid flow in both the BR and BZ reactions.^{12,14b,15}

These resemblances in the dynamic behavior suggest that our skeleton mechanism should contain a series of steps which mimic the essential steps of the FKN mechanism¹⁶ which has been so successful in predicting a wealth of phenomena in the BZ system.

The FKN mechanism contains five reactions which summarize the chemistry of the principal bromine-containing species in the BZ reaction, Br^- , Br_2 , $HOBr$, $HBrO_2$, BrO_2 , and BrO_3^- . To characterize the iodine chemistry in the BR system, we adopt the same set of five elementary steps (eq 1–5) with bromine replaced by iodine.



(13) Roux, J. C.; Vidal, C. "Synergetics - Far from Equilibrium"; Pacault, A., Vidal, C., Eds.; Springer-Verlag: Berlin, 1979; pp 47–50.

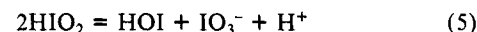
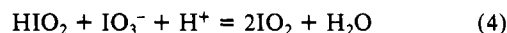
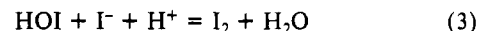
(14) (a) De Kepper, P.; Rossi, A.; Pacault, A. *C. R. Hebd. Acad. Sci., Ser. C* **1976**, 283C, 371–375. (b) De Kepper, P.; Boissonade, J. *J. Chem. Phys.* **1981**, 75, 189–195.

(15) Boissonade, J.; De Kepper, P. *J. Phys. Chem.* **1980**, 84, 501–506.

(16) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, 94, 8649–8664.

(17) Marsden, J.; McCracken, M. "The Hopf Bifurcation and its Applications"; Springer-Verlag: New York, 1977.

(18) Graziani, K. R.; Hudson, J. L.; Schmitz, R. A. *Chem. Eng. J.* **1976**, 12, 9.



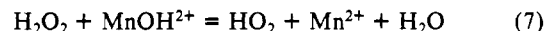
Along with a number of other authors,^{9,10a} we have observed that the slow decomposition of hydrogen peroxide by iodate is greatly accelerated by the presence of manganous salts. The oxidation of H_2O_2 by iodine-containing species should thus involve $Mn(II)$ and $Mn(III)$ through a radical process. This view is also consistent with Briggs and Rauscher's observation¹ that oscillations may occur in the absence of a metal ion catalyst, but only at greatly increased $[H_2O_2]$ and $[H^+]$.

The key radical species in the FKN mechanism is BrO_2 , which leads to the autocatalytic production of $HBrO_2$. A similar autocatalytic production of HIO_2 can be obtained in our mechanism by introducing reaction 6.¹⁹

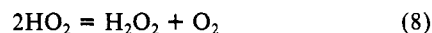


In the BZ reaction with both cerium and manganese, oscillations amounting to 10% or more of the initial catalyst concentration have been observed.^{14,16} Experiments on the BR reaction have failed to detect changes in the $Mn(II)$ concentration or measurable amounts of $Mn(III)$, even using paramagnetic resonance techniques sensitive to 0.3% changes in $[Mn(II)]$.^{12b}

The regeneration of $Ce(III)$ in the BZ reaction results from the oxidation of malonic acid and its derivatives by $Ce(IV)$.¹⁶ The analogous reaction in the BR system is apparently too slow to yield $Mn(II)$ at a significant rate and whatever $Mn(III)$ does form must be reduced in a rapid reaction probably with H_2O_2 , which is present in high concentration. We thus add to our mechanism reaction 7 as the simplest step of this type. While further radicals

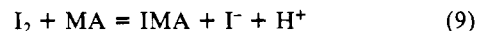


such as OH , IO , etc. might be postulated, the simplest chain-termination step consistent with the stability of the various radical species is

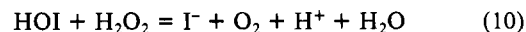


Preliminary calculations using eq 1–8 confirmed that this set of reactions does give rise to bistability under appropriate flow conditions. We were thus assured that our initial estimates of the rate constants and the dynamic structure of this part of our model were compatible with a key experimental phenomenon.

In order to obtain oscillations as well as bistability, it is necessary to introduce a means of regenerating iodide, one of the principal oscillatory species in the BR reaction. The equilibrium constants for reactions 2 and 3 are such that the reverse reactions cannot serve as major sources of I^- . An obvious source of iodide is the iodination of malonic acid

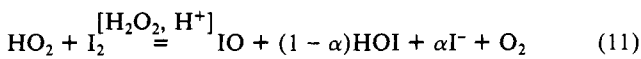


where MA and IMA represent malonic and iodomalonic acids, respectively. An analogous step provides the major source of bromide in the BZ reaction. A second iodide-producing reaction



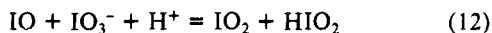
was also introduced. While hydrogen peroxide surely interacts with other iodine species as well, reaction 10 is probably the most significant such reaction under the usual reaction conditions.

Several other steps such as



and

(19) We write the manganic species as $MnOH^{2+}$, since the equilibrium constant for the hydrolysis reaction $Mn^{3+} + H_2O = MnOH^{2+} + H^+$ is 0.93 M at 25 °C (Davies, G.; Kirschenbaum, L. J.; Kustin, K. *Inorg. Chem.* **1968**, 7, 146–154). At a typical $[H^+]$ for the BR system of 5×10^{-2} M, we have $[Mn(OH)^{2+}]/[Mn^{3+}] \approx 20$.



were introduced in the early stages of this work as a convenient way of summarizing several possible radical pathways. Since inclusion of these reactions increased the complexity of the model, both in terms of the number of equations and the number of independent species, without producing better agreement between the calculated and experimental results, these steps were dropped from the mechanism.

We are thus left with the ten steps ((1)–(10)). As we discuss in the next section, rate constants for these steps were chosen where possible from experimental data in the literature. The remaining parameters, k_2 , k_4 , k_5 , and k_6 , were then varied in an attempt to optimize agreement with two major dynamical features: (a) the cross-shaped phase diagram¹⁵ in which bistability and oscillations give way to unique steady states as input species concentrations are varied, and (b) the “inverse regulation” of iodine²⁰ in which the I_2 concentration in the reactor drops dramatically as the iodine flow is increased above a critical value.

Values of Rate Constants. Having chosen what we believe to be a plausible set of component reactions, we now require a rate law and corresponding rate constants for each of these steps in order to simulate numerically the experimental data. We discuss sequentially each of the steps ((1)–(10)) in our mechanism with respect to its rate expression.

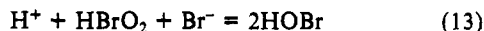
Reaction 1. This reaction constitutes the initial step in the Dushman reaction²⁰ and has been studied experimentally by Furuichi and Liebhafts²¹ at an iodide concentration of 10^{-9} M maintained by addition of AgI and AgNO₃. Using a quasi-empirical rate law of the form

$$v_1 = -d[\text{IO}_3^-]/dt = k_1[\text{H}^+]^2[\text{I}^-][\text{IO}_3^-] \quad (V1)$$

they obtain a value of $k_1 = 1.43 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$ at 25 °C. Noyes and Furrow^{10c} employ the same value. By working at such a low iodide concentration, Furuichi and Liebhafts were able to eliminate the effects of the term in the rate law for the Dushman reaction which is second order in $[\text{I}^-]$ and which presumably arises from more complex processes. Under the usual conditions for the BR reaction, $[\text{HIO}_2]$ and $[\text{HOI}]$ are sufficiently low that the reverse of reaction 1 may be neglected.

Reaction 2. Since no direct experimental measurement has been made of the rate of this reaction, a rate constant was estimated by analogy with the corresponding bromine chemistry.

The forward and reverse rate constants for reaction 13 are taken



in the FKN model⁷ as $2.0 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ and $5.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, respectively. These values have also been employed for reaction 13 by Bar-Eli and co-workers²² in several numerical investigations of bromate-containing systems. In their study of the BR reaction, Furrow and Noyes suggest rate constants $k_2 = 5.4 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ and $k_{-2} = 90 \text{ M}^{-1} \text{ s}^{-1}$ for reaction 2 in the IO_3^- – I_2O_2 – Mn^{2+} – H^+ subsystem and $k_2 = 2 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ for the full system. The latter value has also been employed in numerical simulation of the BL reaction.⁸

Since the experimentally determined rates for the iodine reactions in steps 1 and 3 are about 10^3 faster than those for the corresponding bromine reactions, it seems reasonable to expect that $k_2^{\text{HIO}_2} > k_2^{\text{HBrO}_2}$. We thus took the rate law for step 2 to be

$$v_2 = -d[\text{HIO}_2]/dt = k_2[\text{H}^+][\text{HIO}_2][\text{I}^-] \quad (V2)$$

with $k_2 = 2 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$. The numerical simulations did not show significant improvement when k_2 was changed or when a reasonable non-zero value of k_{-2} was included.

Reaction 3. This reaction was studied by Eigen and Kustin²³ using a temperature-jump technique. At 20 °C, the rate law was found to be

$$v_3 = -d[\text{HOI}]/dt = k_3[\text{H}^+][\text{HOI}][\text{I}^-] - k_{-3}[\text{I}_2] \quad (V3)$$

with $k_3 = 3.1 \times 10^{12} \text{ M}^{-2} \text{ s}^{-1}$ and $k_{-3} = 2.2 \text{ s}^{-1}$. Nearly identical values have been employed by Noyes and co-workers in their modeling of the BL and BR systems.^{8,10c}

Reaction 4. No experimental data are available for this reaction. The relative instability of IO_2 should make reaction 4 less favorable than its bromine equivalent, for which the forward and reverse rates in the FKN scheme⁷ are $7.3 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ and $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively. For reaction 4 in the BL system, Edelson and Noyes⁸ give $k_4 = 1.06 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ and $k_{-4} = 4.64 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 50 °C, while Sharma and Noyes²⁴ suggest $k_4 = 7 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ and $k_4/k_{-4} = 4.2 \times 10^{-4} \text{ M}^{-1}$. Furrow and Noyes^{10c} obtain values $k_4 = 1.5 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ and $k_{-4} = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in their model of the BR system and note that the features of the oscillation are very sensitive to these parameters.

We started from estimated values of $k_4 = 4 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$ and $k_{-4} = 1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in the rate law

$$v_4 = -\frac{d[\text{IO}_2]}{dt} = k_4[\text{H}^+][\text{IO}_3^-][\text{HIO}_2] - k_{-4}[\text{IO}_2]^2 \quad (V4)$$

We found that improved agreement between the simulations and experiment was obtained with $k_4 = 7.3 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. Note that because of the unknown potential of IO_2 , the equilibrium constant for this reaction is not known. The value chosen for k_{-4} does not significantly influence our results.

Reaction 5. The forward and reverse rates for bromous acid disproportionation in the FKN model are estimated⁷ as $4.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $2.0 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$, respectively. For reaction 5 in the BL system, Noyes and co-workers⁸ have suggested $k_5 = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_5 = 5.56 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-5} = 6.93 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$. In their first paper on the BR reaction, Furrow and Noyes^{10a} give $k_5 = 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-5} = 0.86 \text{ M}^{-2} \text{ s}^{-1}$. Their mechanistic study,^{10c} in which k_{-5} is set to zero, yields a value for k_5 of $45.3 \text{ M}^{-1} \text{ s}^{-1}$. This value appears rather low, and the $[\text{HIO}_2]$ concentrations obtained in that work do seem unrealistically high.

We found the effects of including k_{-5} to be negligible. Starting from an initial estimate of $k_5 = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, we obtained an optimal value of $k_5 = 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in the rate law

$$v_5 = -\frac{1}{2}d[\text{HIO}_2]/dt = k_5[\text{HIO}_2]^2 \quad (V5)$$

Reaction 6. The rate for this reaction was estimated from various radical-cation rate constants in the literature. The cerous– BrO_2 rate constant is given⁷ as $1.5 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$, while Field²⁵ estimates that the rate constant for IO_2 plus Fe^{2+} is about $10^5 \text{ M}^{-2} \text{ s}^{-1}$. Our calculations, in agreement with those of Noyes and Furrow,^{10c} suggest that $k_6 = 1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in eq V6 gives the

$$v_6 = -d[\text{IO}_2]/dt = k_6[\text{IO}_2][\text{Mn}^{2+}] \quad (V6)$$

best results. In view of the extremely low concentration of Mn(III), the reverse reaction has been neglected.

Reaction 7. The rate law, taken from Davies et al.,¹⁹ is

$$v_7 = -d[\text{MnOH}^{2+}]/dt = k_7[\text{MnOH}^{2+}][\text{H}_2\text{O}_2] \quad (V7)$$

with $k_7 = 3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Inclusion of the reverse reaction has no effect on the simulations.

Reaction 8. This reaction is essentially irreversible. Sharma and Noyes²⁴ value of $k_8 = 7.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in rate law V8 was

$$v_8 = -\frac{1}{2}d[\text{HO}_2]/dt = k_8[\text{HO}_2]^2 \quad (V8)$$

adopted. Edwards²⁶ gives $k_8 = 5.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, but so long as

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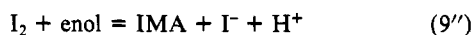
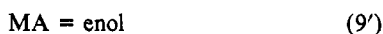
Table I. Steady State Species Concentrations^a

concn, M	I ₂	I ⁻	HIO	HIO ₂	IO ₂	Mn(III)	MA
SSI	6.13 × 10 ⁻⁷	2.94 × 10 ⁻⁸	2.69 × 10 ⁻¹⁰	3.18 × 10 ⁻¹⁰	2.60 × 10 ⁻¹⁰	9.85 × 10 ⁻¹³	1.49 × 10 ⁻³
SSII	7.42 × 10 ⁻⁴	6.85 × 10 ⁻⁹	1.38 × 10 ⁻⁶	1.55 × 10 ⁻⁶	7.40 × 10 ⁻⁷	2.8 × 10 ⁻⁹	9.93 × 10 ⁻⁴

^a Bistable composition with $[\text{IO}_3^-]_0 = 4 \times 10^{-2}$ M, $[\text{I}_2]_0 = 2.5 \times 10^{-6}$ M, all other constraints are as in Figure 1.

this reaction is rapid, the actual numerical value used is of little importance.

Reaction 9. This reaction takes place in two steps, enolization of the acid followed by iodination of the enol



where $\text{MA} \equiv \text{CH}_2(\text{COOH})_2$, $\text{enol} \equiv (\text{OH})_2\text{C} = \text{CHCOOH}$, and $\text{IMA} \equiv \text{CHI}(\text{COOH})_2$. By making a steady-state approximation on the enol,²⁷ one obtains a rate law of the form

$$v_9 = \frac{d[\text{I}_2]}{dt} = \frac{k_9' k_9'' [\text{MA}] [\text{I}_2]}{k_9' + k_9'' [\text{I}_2]} \equiv \frac{k_9 [\text{MA}] [\text{I}_2]}{1 + C_9 [\text{I}_2]} \quad (\text{V9})$$

Leopold and Haim²⁸ have studied reaction 9 and have obtained a somewhat more complex rate law. Furrow¹¹ has investigated this reaction under conditions closer to those of the BR system. Using his data, we obtain $k_9 = (5/2)16 \text{ M}^{-1} \text{ s}^{-1} = 40 \text{ M}^{-1} \text{ s}^{-1}$, where the 5/2 is a stoichiometric factor resulting from the presence of iodate and $C_9 = 10^4 \text{ M}^{-1}$. If malonic acid is replaced by methylmalonic acid, the experiments of Furrow¹¹ yield $k_9^{\text{MMA}} = (5/2)6.4 \text{ M}^{-1} \text{ s}^{-1} = 16 \text{ M}^{-1} \text{ s}^{-1}$ and $C_9^{\text{MMA}} = 10^5 \text{ M}^{-1}$.

Reaction 10. The importance of this essentially irreversible step in the hydrogen peroxide-iodine reaction has been shown by Liebhafsky,²⁹ who gives rate law V10 at 25 °C with $k_{10} = 37 \text{ M}^{-1} \text{ s}^{-1}$.

$$v_{10} = -d[\text{HOI}]/dt = k_{10}[\text{H}_2\text{O}_2][\text{HOI}] \quad (\text{V10})$$

Calculations

Method. The rate equations derived from eq V1-V10 were augmented by flow terms $k_0[\text{X}]_0 - k_0[\text{X}]$ for each species X, where k_0 is the flow rate (reciprocal of the residence time) and the input concentration $[\text{X}]_0$ is the concentration that species X would have if all the chemicals were combined in a single input flow without reaction. For each experimental simulation a set of initial concentrations in the reactor $[\text{X}]_i$, a flow rate k_0 and input concentrations $[\text{X}]_0$ had to be supplied. For tests of hysteresis behavior, a series of calculations was done in which a parameter (k_0 or an $[\text{X}]_0$) was varied and the $[\text{X}]_i$ values for each calculation were taken as the steady-state concentrations from the previous one.

The equations were integrated numerically by using Hindmarsh's version³⁰ of the Gear method³¹ for stiff differential equations. The equations are apparently quite stiff and, especially for high $[\text{MA}]_0$, the computing time required to attain a steady state was sometimes as long as 20–30 min for a single simulation on the Brandeis University PDP-10 computer.

Since no pH changes greater than 0.01 were observed experimentally, in the simulations $[\text{H}^+]$ was held fixed. The total manganese $[\text{Mn}^{2+}] + [\text{MnOH}^{2+}]$ and the total organic species $[\text{MA}] + [\text{IMA}]$ are also constants. We thus had nine variable concentrations in the model: $[\text{IO}_3^-]$, $[\text{I}^-]$, $[\text{I}_2]$, $[\text{HIO}_2]$, $[\text{HOI}]$, $[\text{IO}_2]$, $[\text{MnOH}^{2+}]$, $[\text{HOO}]$, and $[\text{MA}]$. Oxygen was treated as an inert product, though its concentration could be obtained if desired from the results of the simulations.

(27) Strictly speaking, under flow conditions the steady-state calculation must also take into account the rate of flow of the enol out of the reactor. However, the effect of this additional term is negligible so long as $k_0 \ll k_9'$. For the experiments under discussion in this work, k_0/k_9' is typically about 3×10^{-4} .

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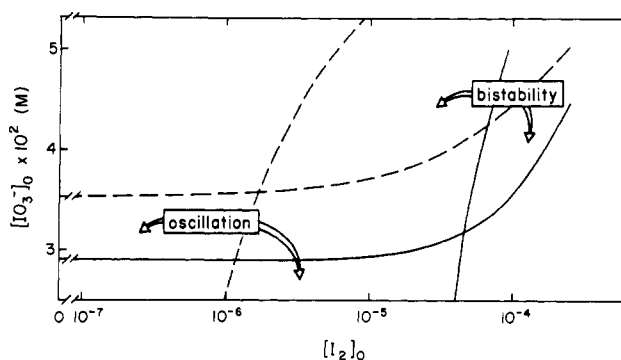


Figure 1. Experimental (—) and calculated (---) "cross-shaped phase diagram" in the $[\text{IO}_3^-]_0$ – $[\text{I}_2]_0$ constraint space. Other constraints held constant at $[\text{H}_2\text{O}_2]_0 = 0.33$ M, $[\text{CH}_2(\text{COOH})_2]_0 = 0.0015$ M, $[\text{H}^+]_0 = 0.056$ M, $[\text{Mn}^{2+}]_0 = 0.004$ M, residence time = 156 s, and $T = 25$ °C.

Results of Calculations. In Figure 1 we present the experimentally determined^{12,15} and calculated phase diagrams of the system in the $[\text{I}_2]_0$ – $[\text{IO}_3^-]_0$ constraint plane. Qualitatively, the calculation predicts the cross-shaped topology of the diagram. The position of the computed cross point, where the monostable, bistable, and oscillatory regions join, is in nearly quantitative agreement with the experimentally observed value for $[\text{IO}_3^-]_0$. However this point is shifted to an iodine flow nearly 30 times too small.

Another computed section of the phase diagram, this time in the $[\text{IO}_3^-]_0$ – $[\text{MA}]_0$ plane (Figure 2a), is compared with the corresponding experimental phase diagram^{12,15} (Figure 2b). The shape of the calculated and experimental plots differ significantly, though certain key features such as the dependence of the period on the malonic acid flow, are in good agreement. The model predicts that at certain $[\text{IO}_3^-]_0$ values, oscillations persist even as $[\text{MA}]_0$ is decreased to zero. This behavior has not been observed experimentally.

One remarkable feature of the BR reaction in a flow reactor is the inverse regulation of $[\text{I}_2]$. For a given set of values of the other constraints, at low iodine flows ($[\text{I}_2]_0$) the system attains a steady state (denoted SSII) in which the iodine concentration ($[\text{I}_2]_{\text{SSII}}$) considerably exceeds $[\text{I}_2]_0$, while at high values of $[\text{I}_2]_0$, the system reaches a steady state (SSI) in which $[\text{I}_2]_{\text{SSI}} < [\text{I}_2]_0$. This behavior is shown in Figure 3. Above a critical value of $[\text{I}_2]_0$ a transition occurs from SSII to SSI, directly or through an oscillatory region, so that an increase in the iodine input flow results in a net drop in the iodine concentration in the reactor!

As Figure 3 shows, the calculation gives semiquantitative agreement with the observed inverse regulation of iodine for both the steady state I_2 concentrations and locations of the SSII \rightarrow SSI transitions. However, at the other end of the hysteresis loop, where the system jumps from SSI to SSII as $[\text{I}_2]_0$ is decreased, the calculated transition points occur at values of $[\text{I}_2]_0$ much lower than observed, i.e., the model makes SSI much too stable.

We note that the slight overestimate of the calculated $[\text{I}_2]_{\text{SSII}}$ values could probably be corrected by including in the model the experimentally observed evaporation of iodine from the reactor. However, in view of the more serious discrepancies between theory and experiment, such "fine tuning" was not deemed justified.

The two steady states differ not only in the concentrations of I_2 , but in all other species concentrations as well. In Table I we list the concentrations of major species in the two steady states for a set of constraints in the bistable region near the cross point. SSI is characterized by lower concentrations of MnOH^{2+} and of all iodine containing species except I^- . This state, a true steady state in the flow system, corresponds to the nonradical pseudo

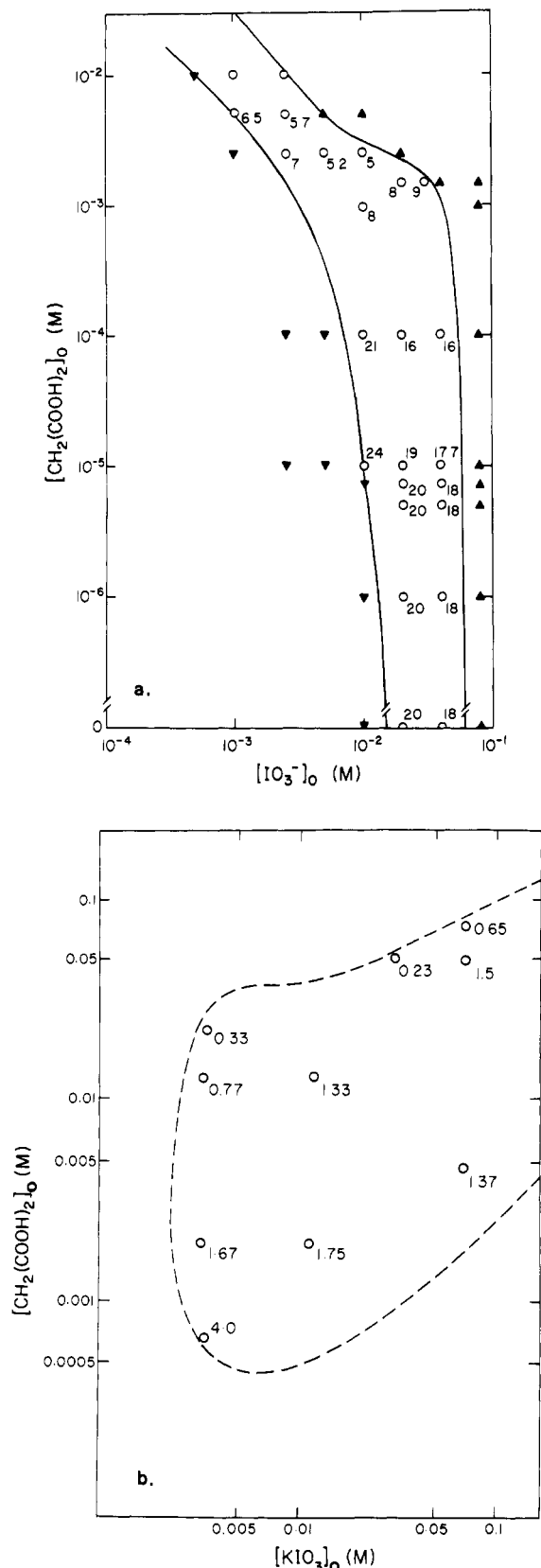


Figure 2. Computed (a) and experimental (b) phase diagram in the $[\text{CH}_2(\text{COOH})_2]_0$ - $[\text{IO}_3^-]_0$ constraint space with $[\text{I}_2]_0 = 0$, all other constraints as in Figure 1: ▼, SSII; ▲, SSII; ○, oscillations with period in minutes.

steady state referred to by Noyes and Furrow.^{10c} The radical steady state SSII shows concentrations of the radical species IO_2 and MnOH^{2+} roughly 4 orders of magnitude higher than in SSII. Figure 4 allows comparison between the concentration jump in the oscillatory state and the neighboring steady-state concentra-

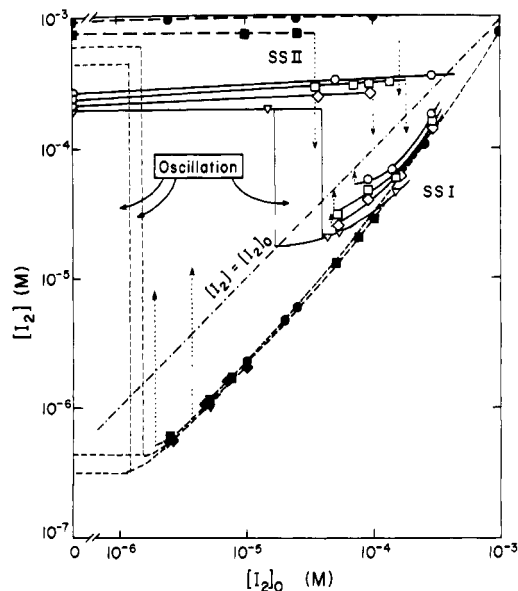


Figure 3. Calculated and experimental "inverse regulation" of iodine. Steady state iodine concentration $[\text{I}_2]$ vs. input-flow concentration $[\text{I}_2]_0$. Arrows indicate spontaneous transitions between states for different $[\text{IO}_3^-]_0$: 0.047 M, ● (calcd), ○ (exptl); 0.040 M, ■ (calcd), □ (exptl); 0.035 M, ◆ (calcd), ◇ (exptl); 0.030 M, ▼ (calcd), ▲ (exptl). All other constraints are as in Figure 1.

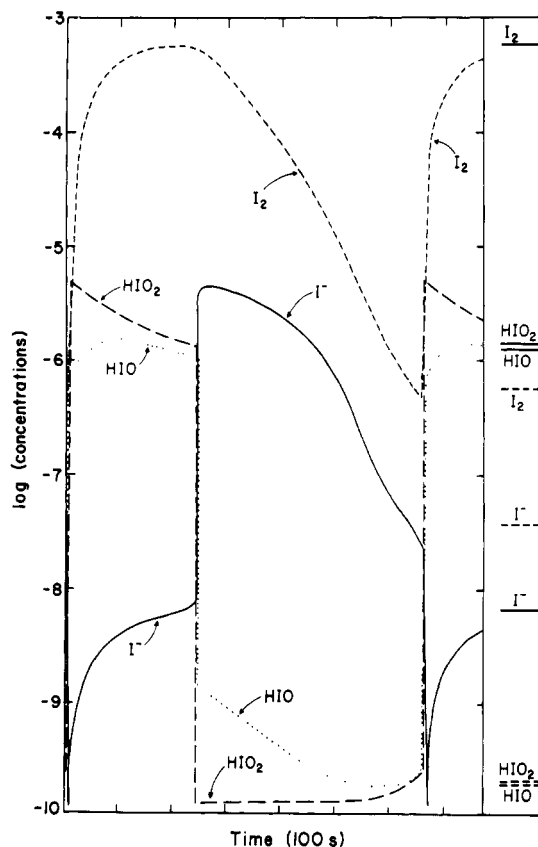


Figure 4. Computed oscillations of $[\text{I}^-]$, $[\text{I}_2]$, $[\text{HIO}]$, and $[\text{HIO}_2]$ for $[\text{IO}_3^-]_0 = 0.035 \text{ M}$ and $[\text{I}_2]_0 = 10^{-6} \text{ M}$ and in the right-hand column SSII (---) and SSII (—) concentrations of the same species for $[\text{IO}_3^-]_0 = 0.038 \text{ M}$ and $[\text{I}_2]_0 = 2.8 \times 10^{-6} \text{ M}$, a neighboring bistable composition. All other constraints are as in Figure 1.

tions in the bistable region. It clearly shows that during oscillations the system essentially jumps periodically between these steady-state critical values.

In Figure 5a we show a projection in the iodide sensitive electrode potential- $[\text{I}_2]$ response plane of the experimental limit cycle.¹² The corresponding calculated projection in the $[\text{I}^-]$ - $[\text{I}_2]$

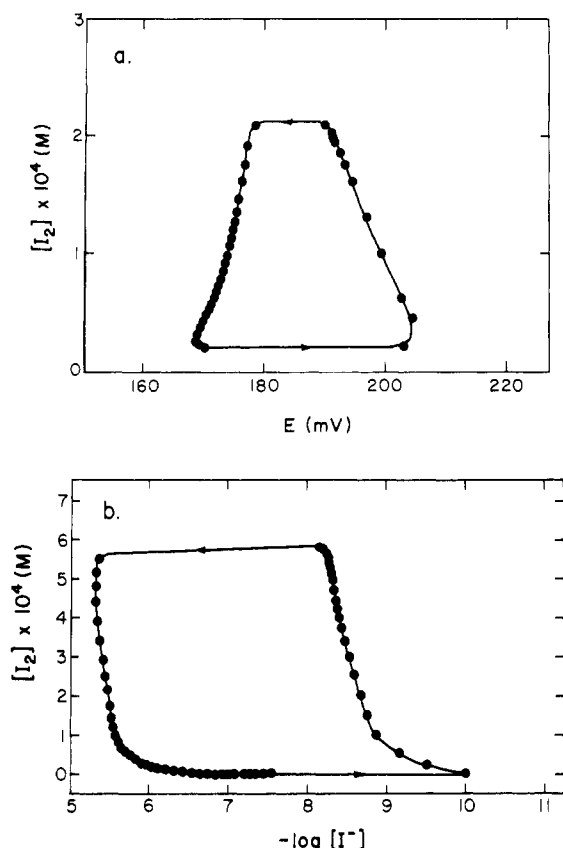


Figure 5. Projection of the limit cycle (a) in the $[I_2]$ -Pt electrode potential plane for the experimentally observed oscillating composition on Figure 1 and (b) in the $[I_2]$ - $[I^-]$ plane for a calculated oscillatory state on Figure 1. The time interval between points is 12 s.

plane is shown for comparison in Figure 5b. The points are equidistant in time to afford an idea of the relative rates of change at different points on the cycle, which further emphasizes the similarities between the computed and experimental projections of the limit cycle. Finally, if we compare our computed oscillograms of I^- and I_2 (Figure 4) with those derived by Roux and Vidal¹³ from their experimental data (although the conditions are not identical), we observe qualitative agreement between the experimental and calculated phases of these species. During a single period of oscillation, the iodine concentration reaches a maximum as iodide increases by several orders of magnitude. Then iodine decreases slowly with iodide, followed by a rapid increase in iodine as the iodide concentration suddenly drops by several orders of magnitude to a minimum. The iodide then increases slightly before undergoing a sharp increase as iodine again reaches its maximum concentration.

Variation of Rate Constants. A number of tests were made of the sensitivity of the model to changes in the expendable parameters. These variations in the k 's were carried out primarily for the conditions shown in the cross-shaped $[IO_3^-]_0$ - $[I_2]_0$ phase diagram section of Figure 1. Each rate constant was varied by a factor of at least 10.

Decreasing k_2 shifts the point of transition from the oscillatory state to SSII toward lower values of $[IO_3^-]$. Malonic acid and iodate consumption are increased and $[I_2]_{SSII}$ also increases significantly.

An increase in k_4 , the rate of disproportionation of the IO_2 radicals, somewhat surprisingly has little effect on the stability of SSII, though it does cause a decrease in $[I_2]_{SSII}$.

The model appears most sensitive to changes in k_5 and k_6 . As k_5 is increased, the transition from oscillations to SSII shifts to lower $[IO_3^-]_0$ and $[I_2]_{SSII}$ increases nearly proportionally to k_5 . Increasing k_6 also decreases the stability of the oscillatory state relative to SSII, thereby lowering the critical $[IO_3^-]_0$ for the transition. Higher k_6 values, however, tend to lower $[I_2]_{SSII}$ slightly.

Methylmalonic Acid. As noted above, the BR reaction with methylmalonic acid may be simulated by replacing the values of k_9 and C_9 for MA by Furrow's¹¹ corresponding values for MMA. Using the same conditions reported by Briggs and Rauscher² (no flow, $[IO_3^-]_i = 0.067$ M, $[MA]_i = 0.050$ M, $[Mn^{2+}]_i = 0.0067$ M, $[H_2O_2]_i = 1.20$ M, $[H^+]_i = 0.035$ M), we obtained oscillations with both the MA and MMA parameters. The periods of oscillation were $T_{MA} = 140$ s and $T_{MMA} = 400$ s. Experimentally, we observe an increase of a factor of about 6 on replacing malonic by methylmalonic acid.

Discussion

The mechanism presented here bears strong resemblances to the models of the BR system developed independently by Cooke⁹ and by Noyes and Furrow.¹⁰ Cooke's mechanistic discussion includes all of the steps in our model as well as a large number of additional reactions involving such radical species as I , IO , and OH . No rate constants are given, and no attempt is made at calculating any kinetic behavior. The steps of Noyes and Furrow's scheme are identical with ours, except that they treat reactions 9' and 9'' separately, so that the enol becomes an additional independent species.

While many of our rate constants, being experimentally determined, are the same as those used by Noyes and Furrow, we differ in the values chosen for several of the expendable parameters, most notably k_4 , k_{-4} , and k_5 . In spite of a difference of more than 4 orders of magnitude in k_5 , we have verified that our model does give oscillations under the conditions of Noyes and Furrow's calculation. We believe that the much lower concentrations of HIO_2 and IO_2 found in our simulations lie closer to the actual values.

Some insight into the behavior of the system may be gleaned by examining the velocities of the individual steps in the mechanism. We find, for example, that in all cases $v_2 < v_4$ when the system is in the nonradical steady state SSII, with the inequality reversed in SSII. Furthermore, the shift from high $[I^-]$, low $[I_2]$, and low radical concentrations to low $[I^-]$ and high concentrations of the other species occurs just as v_4 begins to exceed v_2 . Thus, the switching between the nonradical and radical regimes depends upon whether or not $[I^-]$ is high enough so that HIO_2 reacts preferentially in the nonradical step (2) rather than in the radical autocatalytic step (4). This switching takes place at a critical iodide value given by $[I^-]_c = (k_4/k_2)[IO_3^-] = (3.7 \times 10^7)[IO_3^-]$, which is consistent with the transition shown in Figure 4.

All the component reactions with the exception of (1) proceed more rapidly in the radical state (or the radical portion of the oscillation period) than in the nonradical state. Interestingly, in the radical regime, the order of some of the principal reaction velocities is $v_{10} > v_4 > v_2 > v_3 > v_9$, while in the nonradical state these velocities fall in exactly the opposite order, though they all drop by several orders of magnitude.

The rates of eq 4, 6, and 7 are very strongly coupled, with $v_6 = v_7 = \frac{1}{2}v_4$ at all times to an accuracy of better than 1%. This observation first suggested to us that either step 4 or step 6 was rate determining for the overall sequence (4) + 2((6) + (7)) or



However, testing this hypothesis showed that the reaction profile was sensitive to all three rate parameters k_4 , k_{-4} , and k_6 .

On further consideration, we recognized that the coupling of v_4 , v_6 , and v_7 implies only that $[MnOH^{2+}]$ and $[IO_2]$ maintain pseudo-steady-state values throughout the course of the reaction. Setting

$$d[IO_2]/dt = 0$$

we obtain

$$[IO_2]_{ss} = \frac{k_6[Mn^{2+}]}{4k_{-4}} \left[\left(\frac{1 + 16k_4k_{-4}[H^+][HIO_2][IO_3^-]}{k_6^2[Mn^{2+}]^2} \right)^{1/2} - 1 \right] \quad (15)$$

The rate of production of HIO_2 via process 14 may be written as

$$\frac{d[\text{HIO}_2]}{dt} = \frac{1}{2} \frac{d[\text{HOO}]}{dt} = \frac{1}{2} k_7 [\text{H}_2\text{O}_2] [\text{MnOH}^{2+}] = \frac{1}{2} k_6 [\text{Mn}^{2+}] [\text{IO}_2] \quad (16)$$

where the last equality results from setting $d[\text{MnOH}^{2+}]/dt = 0$. Two limiting cases arise, depending upon the relative sizes of the terms $16k_4k_{-4}[\text{H}^+][\text{HIO}_2][\text{IO}_3^-]$ and $k_6^2[\text{Mn}^{2+}]^2$ in eq 15. If step 4 is rate determining so that the latter term is much larger, then we find

$$[\text{IO}_2]_{\text{pss}} \approx (2k_4/k_6)[\text{H}^+][\text{HIO}_2][\text{IO}_3^-]/[\text{Mn}^{2+}] \quad (17)$$

and, substituting in (16)

$$d[\text{HIO}_2]/dt = k_4[\text{H}^+][\text{HIO}_2][\text{IO}_3^-] \quad (18)$$

The sequence then produces HIO_2 autocatalytically in a process also catalyzed by manganous ion. On the other hand if step 6 is ratedetermining, then the pseudo-steady-state value of iodine dioxide is given by eq 19 and 20, where $K_4 = k_4/k_{-4}$. We still

$$[\text{IO}_2]_{\text{pss}} \approx (K_4[\text{H}^+][\text{HIO}_2][\text{IO}_3^-])^{1/2} \quad (19)$$

$$d[\text{HIO}_2]/dt = \frac{1}{2} k_6 K_4^{1/2} [\text{Mn}^{2+}] ([\text{H}^+][\text{HIO}_2][\text{IO}_3^-])^{1/2} \quad (20)$$

have autocatalysis in HIO_2 but now of a lower order and catalyzed by manganous ion. On examining the values of the rate constants and species concentrations during the course of an oscillation or in the two steady states (see Table I), we observe that the relative magnitudes of the two terms in eq 15 are interchanged as the system switches from the radical to the nonradical regime. Thus neither approximation holds over the entire course of the reaction, and the only permissible "simplification" would be to combine eq 4, 6, and 7 into the single autocatalytic process (14) with a rate law derived from eq 15 and 16.

While the mechanism presented here succeeds in predicting many of the dynamic features of the system over a wide range of constraint values, several major discrepancies remain between theory and experiment in the BR system. Minor quantitative differences could probably be improved by further manipulation of the rate constants, but all the major qualitative disagreements appear to be attributable to a common problem which is unlikely to be resolved by additional refinement of the expendable parameters. A more drastic solution is required.

As we see in Figures 1 and 3, wherever there are large differences between the simulated and experimental dynamics of the

system, these discrepancies are associated with an overestimate of the region of stability of SSI; the model makes the nonradical state too stable. This is especially clear in the lower left part of Figure 3.

One way to destabilize the nonradical SSI in the calculation is to "push" the system toward the radical state by producing an appropriate chemical species. Although varying certain rate constants (e.g., increasing k_4 , decreasing k_5) will serve this purpose, this procedure also changes the system in other ways, destroying the agreement between simulation and experiment at other points. One highly suggestive result is that introducing an input flow of iodosous acid ($[\text{HIO}_2]_0 = 10^{-6} \text{ M}$) into the simulation decreases the range of stability of SSI and increases the iodine minimum in the oscillatory state without noticeably affecting the other calculated results. This observation suggests that augmentation of the mechanism by steps which produce HIO_2 at a sufficient rate without perturbing the rest of the model too greatly might resolve most if not all of the remaining discrepancies between theory and experiment. A possible candidate is



though the rate given by Liebhafsky in 1931³² for this reaction would make it much too slow to produce iodosous acid at the appropriate rate. Further experimental investigation of this reaction may be in order.

The validity of a model of such complexity is credible only if several major experimental features are reproduced. The fact that the mechanism presented here predicts not only oscillations but also bistability with the observed inverse regulation of iodine and the dependence of the period on malonic acid all suggest that this scheme does indeed account for the kinetic skeleton of the Briggs-Rauscher system. The computational effort involved has been considerable and important gaps remain, but in view of the agreement achieved both with experiment and with other models independently arrived at, it appears that mechanistic understanding of the Briggs-Rauscher reaction has taken a large step forward.

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Olefin Rearrangement Resulting from the Gas-Phase KrF Laser Photolysis of $\text{Cr}(\text{CO})_6$

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Abstract: We have found that irradiation of $\text{Cr}(\text{CO})_6$ -1-butene mixtures in the gas phase with a KrF laser (248 nm) results in the efficient (yield ~ 0.2) isomerization of 1-butene to 2-butene, in marked contrast to results in solution. The primary photochemical yield is independent of 1-butene pressure and of $\text{Cr}(\text{CO})_6$ pressure over wide pressure ranges. Secondary photochemical processes are also found, the importance of which depends upon 1-butene pressure. We also report yields of species $\text{Cr}(\text{CO})_m(\text{PF}_3)_{6-m}$ resulting from irradiation of $\text{Cr}(\text{CO})_6$ - PF_3 mixtures at 248 nm. At high dilution $[\text{Cr}(\text{CO})_6]_0/\text{PF}_3 = 2 \times 10^{-3}$, we find relative yields of 0.10, 0.14, 0.73, and 0.03 for $\text{Cr}(\text{CO})_2(\text{PF}_3)_4$, $\text{Cr}(\text{CO})_3(\text{PF}_3)_3$, $\text{Cr}(\text{CO})_4(\text{PF}_3)_2$, and $\text{Cr}(\text{CO})_5\text{PF}_3$, respectively. These results suggest a high degree of fragmentation following optical excitation at 248 nm. We present a reasonable kinetic model to explain the observed isomerization of butene in which a primary photofragment, probably $\text{Cr}(\text{CO})_3$ or $\text{Cr}(\text{CO})_2$, is the active species.

I. Introduction

It has long been recognized that the photoexcitation of metal carbonyl compounds may result in species which are active for photocatalytic or photoassisted processes.¹⁻³ For species of the

form $\text{M}(\text{CO})_m$ where M is a transition metal, it has generally been accepted that the primary photochemical process involves the

(1) M. S. Wrighton, *Chem. Rev.*, 74, 401 (1974).