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

The dependence of the orientation of the principal component $A_{\parallel}(\mathrm{N})$ upon bending at the radical site is given in Figure 9. The deviation of the $A_{\parallel}(\mathrm{N})$ 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 $A_{\parallel}(\mathrm{N})$ 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 $A_{\parallel}(\mathrm{N})$ from the normal direction to the NO bond will be. On another hand, the NH component of the $\mathbf{a}_H$ 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.

Registry No. 1, 41578-59-0; H_2NO, 14332-28-6.

The Oscillatory Briggs–Rauscher Reaction. 1. Examination of Subsystems[1]

Stanley D. Furrow*[2a,b] and Richard M. Noyes*[2a]

Contribution from the Departments of Chemistry, University of Oregon, Eugene, Oregon 97403, and Pennsylvania State University, Berks Campus, Reading, Pennsylvania 19608.

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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 $\cdot IO_2$ 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 → yellow → black → colorless. The frequency is a few times per minute, and the transition from yellow to black is particularly sharp. Shakhashiri[4] 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. Cooke[8] 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 Observations[9]

The Iodate–Peroxide Subsystem. The definitive study of this reaction was by Liebhafsky.[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.

$$2IO_3^- + 5H_2O_2 + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O \qquad (A)$$

Even with his best efforts to remove iodine, Liebhafsky[10] observed a stoichiometry that required (A) to be accompanied by some induced disproportionation of hydrogen peroxide according to (B).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (B)$$

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[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.

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[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. *Nouv. J. Chim.* **1979**, *3*, 247–253.

[7] De Kepper, P. Dr. es Sci. Thesis, Universitê de Bordeaux, 1978.

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

[9] Details of procedures are described at the end of the second paper of this series.

[10] Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 896–911.

0002-7863/82/1504-0038\$01.25/0

The initial rate of (A) is first order in $[IO_3^-]$ and in $[H_2O_2]$ and less than first order in $[H^+]$. 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 $[H^+] = 0.1$ M, $[IO_3^-] = 0.05$ M, and $[H_2O_2] = 1$ 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 Gyani[12] find they are several fold less efficient than iron salts. At concentrations comparable to those in a Briggs–Rauscher[3] oscillator, we found destruction of hydrogen peroxide to be less than 0.1%/h.

The Iodate–Manganous Subsystem. The reduction potential of the $IO_3^-(aq)/I_2(aq)$ 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 $[Mn^{2+}]$ and in $[H_2O_2]$ and is zero order in $[IO_3^-]$ when $[IO_3^-] > 0.02$ M. He reports a maximum rate when $[H_2SO_4]$ 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 $[H_2O_2]$ just as reported by Cooke.[8b] At $0.05 \text{ M} < [H^+] < 0.15$ M and $[IO_3^-] > 0.02$ M, we found the rate was nearly independent of $[IO_3^-]$ as claimed by Cooke. However, at $[H^+] < 0.05$ M our rate was first order in $[IO_3^-]$. Cooke[8b] found little rate dependence on $[Mn^{2+}]$ at low $[IO_3^-]$ and first order in $[Mn^{2+}]$ at $[IO_3^-] = 0.022$ M. We found dependence on $[Mn^{2+}]$ to be slightly greater than first order at $[IO_3^-] = 0.015$ M and nearly second order at $[IO_3^-] = 0.05$ M. Plots of log (rate) vs. log (concentration) were not linear, and the results clearly cannot be represented by a simple rate law.

At 25 °C with $[H_2SO_4] = 0.076$ M and $[IO_3^-] = 0.0215$ M, the Cooke[8b] rates in M s^{-1} can be summarized over a modest interval by eq 1.

$$d[I_2]/dt = ((8 \pm 2) \times 10^{-3})[Mn^{2+}][H_2O_2] \tag{1}$$

For the conditions $5 \times 10^{-4} \text{ M} < [Mn^{2+}] < 5 \times 10^{-3}$ M, $0.0125 \text{ M} < [IO_3^-] < 0.125$ M, and $0.2 \text{ M} < [H_2O_2] < 0.5$ M, our observations can be summarized by eq 2.

$$d[I_2]/dt = 0.24 \pm 0.05[Mn^{2+}]^2[H_2O_2]/[H^+] \tag{2}$$

At $[Mn^{2+}] = 0.0022$ M and $[H^+] = 0.15$ 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

$$\alpha = \frac{\Delta[O_2] - 5\Delta[I_2]}{2.5\Delta[I_2]} \tag{3}$$

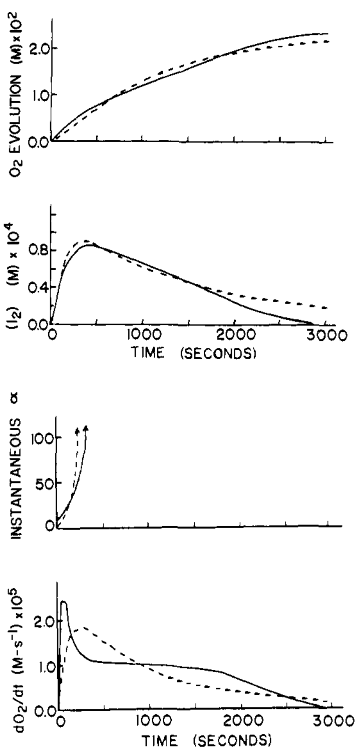

Figure 1. Experimental observations (full curves) and computations based on Table I (dashed curves) for stoichiometric parameters in a subsystem with initial composition $[IO_3^-]_0 = 0.015$ M, $[H_2O_2]_0 = 0.050$ M, $[Mn^{2+}]_0 = 0.0020$ M, and $[H^+]_0 = 0.10$ M. Meanings of instantaneous concentration 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 $[I_2]$ reaches a maximum.

Initial values of α were always at least 4. They increased with increasing $[IO_3^-]$, with decreasing $[H_2O_2]$, and with decreasing $[Mn^{2+}]$. 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, $[I_2]$ 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.

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \tag{C}$$

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 (A) + (C) = 5(B). Reaction C is essential to understanding the oscillatory Bray–Liebhafsky[11] reaction. We shall see below that it need not be invoked in order to explain most features of the Briggs–Rauscher[3] reaction.

The Manganese(III)–Peroxide Subsystem. Solutions of uncomplexed manganese(III) rapidly disproportionate with precipitation of MnO_2. However, pyrophosphate, $P_2O_7^{4-}$, 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

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

at pH $\simeq 1$.[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

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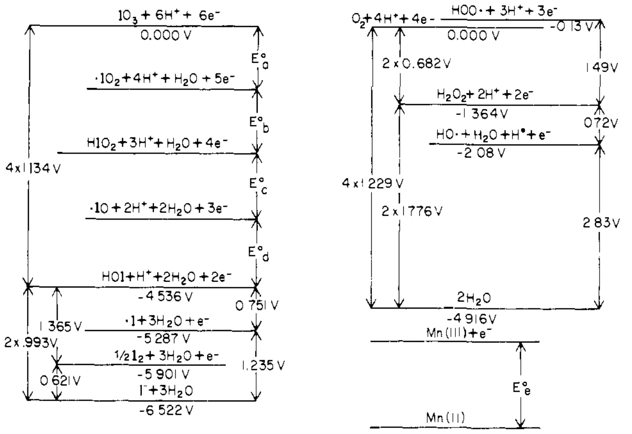

Figure 2. Free energy changes in volt equivalents for various half-reactions in the iodine, oxygen, and manganese subsystems.

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 oxyiodine[16] and peroxide systems. The numerical values are taken from Latimer[13] with the standard state for I_2 based on ideal 1 m solution. Sharma and Noyes[15] 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), $E_e°$, 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 HIO_2 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 IO_3^- with Mn^{2+} 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 processes[16] 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

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

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

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

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

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

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

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

Step I5 initiates radical processes; it is well precedented 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

$$IO_3^- + H^+ + H_2O_2 \rightarrow HIO_2 + O_2 + H_2O \qquad (D)$$

that the rate is first order in $[H_2O_2]$ 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 HIO_2 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 processes[16] 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)

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

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

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

Steps D4 and D5 mean that I_2 and IO_3^- are in competition for the strongly reducing species HOO·. The mechanism as developed in Scheme II is thus consistent with the observation of Liebhafsky[10] that in the iodate-peroxide subsystem the extent of reaction B could be greatly reduced if I_2 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 I_2, 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 I_2. The mechanistic possibilities are even less uniquely defined than for the other reactions, but Scheme III lists some pseudo elementary processes[16] that might account for the observed behavior. Others are conceivable. Some of the reasons for selecting specific

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

(16) Except for consideration of both I_2 and ·I, we have included only one species representing each oxidation state of iodine. Selections of IO_3^-, $\cdot IO_2$, HIO_2, ·IO, HOI, and I^- assumed them to be dominant species under the experimental conditions. Other species like $H_2IO_3^+$, 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 $\cdot IO_2$ and ·IO should be scavenged too rapidly to form the dimers I_2O_4 and I_2O_2. We have ignored polynuclear oxyacids like $H_2I_2O_3$ 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	3.1×10^{12} M^{-2} s^{-1}	2.2 s^{-1} [a]
I2	2.0×10^{9} M^{-2} s^{-1}	90 M^{-1} s^{-1}
I3	1.4×10^{3} M^{-3} s^{-1}	2.8 M^{-1} s^{-1}
I4	1.0×10^{4} M^{-1} s^{-1}	0.86 M^{-2} s^{-1}
I5	1.9×10^{4} M^{-2} s^{-1}	1.0×10^{9} M^{-1} s^{-1} [a]
U1	coupled to U2 and D5	
U2	2.5×10^{9} M^{-1} s^{-1}	
U3	coupled to U4	
U4	3.0×10^{8} M^{-1} s^{-1}	
D1	37 M^{-1} s^{-1}	
D4	3.5×10^{5} M^{-2} s^{-1}	
D5	2.0×10^{7} M^{-1} s^{-1}	
O1	4.5×10^{7} M^{-1} s^{-1}	
M1	1.0×10^{4} M^{-1} s^{-1} [a]	2.0×10^{8} M^{-1} s^{-1}
M2	3.2×10^{4} M^{-1} s^{-1}	6.4×10^{2} M^{-1} s^{-1} [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

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

$$\cdot IO_2 + HOI \rightarrow HIO_2 + \cdot IO \qquad (I6)$$

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

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

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

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

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

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

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

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

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 ·I and ·IO as flow-through[18] 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 $\cdot IO_2$, ·IO, ·I, HOO·, HO·, and $Mn(OH)^{2+}$. 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 oscillators[1] suggests that the Briggs–Rauscher[3] oscillator should involve switching between two pseudo-stationary states. One of those states would involve large $[I^-]$ and small $[HIO_2]$, and oxidation state would never change except by 2 equivs in a single step. The other state would involve small $[I^-]$ and large $[HIO_2]$ 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 $[HIO_2]$ provided $[I^-]$ 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 $[I^-]$ 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 $[I_2]$, the subsystem is not an oscillator. It can become an oscillator only if $[I^-]$ can be increased enough for step I2 to control the autocatalytic production of HIO_2.

Permissible Hydroxyl Radical Reactions. As Figure 2 demonstrates, the HO· 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 is[19] 4.5×10^7 M^{-1} s^{-1}. No bimolecular reaction in solution can have a rate constant greater than about[20] 10^{10} M^{-1} 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.

$$HO\cdot + HOI \rightarrow H_2O + \cdot IO \qquad (U5)$$

We have also somewhat arbitrarily neglected step M4. The

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

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, we[22] 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

$$\cdot IO_2 + H_2O_2 \rightarrow HIO_2 + HOO\cdot \qquad (Dx)$$

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

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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 HO· or Cl· 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 $\cdot IO_2$, the oxidant is sluggish at abstracting a hydrogen atom regardless of the thermodynamic driving force.

When these principles are applied to the present system, $\cdot IO_2$ reacts only slowly or not at all by step Dx and preferentially abstracts an electron from Mn^{2+} while simultaneously or subsequently 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.

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The Oscillatory Briggs–Rauscher Reaction. 2. Effects of Substitutions and Additions[1]

Stanley D. Furrow*[2a,b] and Richard M. Noyes*[2a]

Contribution from the Departments of Chemistry, University of Oregon, Eugene, Oregon 97403, and Pennsylvania State University, Berks Campus, Reading, Pennsylvania 19608.

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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, iodinates 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 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 $[HOI] + 2[I_2] + [I^-]$, but it may increase the $[I^-]/[HOI]$ ratio enough that $[I^-]$ actually increases.

The previous paper[1] 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

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

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

an autocatalytic increase of $[HIO_2]$. 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 Rauscher[3] have shown that addition of malonic acid to such a subsystem can create an extremely effective oscillator. Our experience with bromate-driven oscillators[4] suggests that during a portion of each cycle $[I^-]$ 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 HOO· and particularly HO·. (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 $[I^-]/[HOI]$. (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 hypoiodous 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-

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

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