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Oscillations in Chemical Systems. 13.[1] A Detailed Molecular Mechanism for the Bray–Liebhafsky Reaction of Iodate and Hydrogen Peroxide

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Abstract: Under certain conditions, the iodate-catalyzed decomposition of hydrogen peroxide (Bray–Liebhafsky reaction) takes place by alternating between dominance by nonradical process I ($2IO_3^- + 5HOOH + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O$) and by radical process II ($I_2 + 5HOOH \rightarrow 2IO_3^- + 2H^+ + 4H_2O$). The latter process is accompanied by a greatly enhanced evolution of oxygen, and the stoichiometry of this stage is better written as XII ($I_2 + 11HOOH \rightarrow 2IO_3^- + 3O_2 + 2H^+ + 10H_2O$). Concentrations of intermediate iodine-containing species switch between quite different pseudosteady states, depending upon which process is dominant. Although both processes I and II (or XII) are almost irreversible, I is favored kinetically in the absence of radicals because the O–O bond in hydrogen peroxide is sluggish to rupture by nucleophilic attack. On the other hand, thermodynamic arguments indicate that iodine-containing radicals can reduce hydrogen peroxide by 1-equiv processes that do break the O–O bond, but many of them will not oxidize it by hydrogen abstraction. Rapid switching between pseudosteady states occurs because iodous acid (HOIO) reacts with iodate to form $\cdot IO_2$ radicals that produce more iodous acid in an autocatalytic process. Elementary oxygen is essential to the oxidation of iodine atoms, and this fact contributes in making the mathematical steady state unstable with respect to oscillations. We have used these observations to develop a detailed mechanism that explains virtually all that is known about the Bray–Liebhafsky reaction, and is consistent with the available thermodynamic and kinetic information and with the analogous chemistry of chlorine and bromine. This mechanism also conforms to a pattern consistent with the other known mechanism of a chemical oscillator. We have also developed a system for classifying reactants and intermediates in chemical oscillators and have suggested some principles that may be helpful in elucidating biochemical control mechanisms in living organisms.

Historical Background

The first example of a homogeneous oscillating chemical reaction was reported by Bray[2] over 50 years ago, after studies of the iodate-catalyzed decomposition of hydrogen peroxide. Work on this reaction prior to 1972 has been reviewed briefly by Nicolis and Portnow.[3]

The oscillating phenomenon and the various component reactions were examined extensively by Bray and Liebhafsky[4-11] in the early 1930's. These studies, without benefit of modern instrumentation, have been well substantiated by more recent work, but neither the data nor the extent of chemical theory was sufficient to permit definitive mechanistic conclusions. After a scientific career devoted to subjects other than chemical kinetics, Liebhafsky has recently re-examined the system by previously unavailable techniques.[12-23] The reaction has also been studied experimentally by Peard and Cullis,[24] Vavilin and Zhabotinsky,[25,26] and Degn.[27] The latter author identified radical and nonradical component processes completely consistent with our subsequent independent conclusions.[28]

Because oscillatory homogeneous reactions are so dramatic and this example seemed for so long to be unique (at least for solution chemistry), it is not surprising that attempts were made to discount the very existence of the phenomenon. Thus Rice and Reiff[29] maintained that oscillations were absent if the hydrogen peroxide had been carefully distilled to eliminate dust and stabilizers, but they did not provide enough information to establish that they were examining compositions where others have observed oscillations. Peard and Cullis[24] admitted that oscillations existed, but ascribed the phenomenon to entrainment of iodine by the evolving gas. However, they failed to make the calculations which would have proved to them iodine could not have been removed rapidly enough even if the oxygen had been in saturation equilibrium with crystalline iodine. Their attempt to show that the final gas volume was greater than that of the oxygen to be expected from the hydrogen peroxide demonstrates they failed to recognize the evolved oxygen also contained water vapor! Shaw and Pritchard[30] maintained that light was necessary to induce oscillations, but this claim has been refuted.[28,31] Efforts to invoke effects of decomposition inhibitors in commercial hydrogen peroxide[29,30] have been disposed of by the observation of Degn[27] that oscillations occur in a system prepared from crystalline sodium peroxide and sulfuric acid.

Oscillations have now been observed in many laboratories

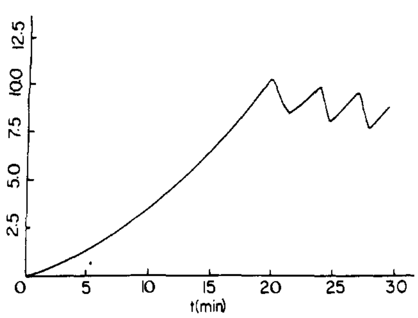


Figure 1. Spectrophotometric recording at 50 °C of iodine concentration in solution initially containing 0.104 M KIO_3, 0.490 M HOOH, and 0.047 M $HClO_4$. Note that at this low acidity the initial trace is concave up and oscillations commence immediately after the first maximum in iodine concentration.

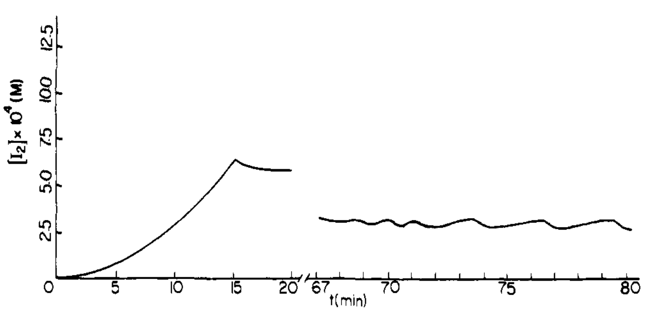


Figure 2. Spectrophotometric recording at 50 °C of iodine concentration in solution initially containing 0.104 M KIO_3, 0.490 M HOOH, and 0.059 M $HClO_4$. Note that at this high acidity the iodine concentration reaches a single initial maximum and there is a long second induction period before oscillations of small amplitude commence. The absolute iodine concentration is less than at lower acidity.

and have been followed visually,[2] calorimetrically,[15] manometrically,[2,14,15,24] spectrophotometrically,[15,27,28] and potentiometrically with electrodes specific to hydrogen ion,[15] iodide ion,[12,13,15,28] and dissolved oxygen.[28] The phenomenon indubitably exists, and the remaining challenge is to elucidate the mechanism at the molecular level.

Although early workers sometimes speculated about the sorts of processes that might generate the observed effects, they did not specify mechanistic details. Degn[27] first pointed out the free-radical nature of the reactions oxidizing iodine, but did not identify chemical species. Recently, Liebhafsky and co-workers[16,20,23] have made serious attempts to develop a mechanism, and a very rough proposal has been made by Schmitz.[32] These proposals are entirely nonradical and invoke intermediate species we consider unsubstantiated and implausible. We develop the argument below for an alternative explanation.

Net Chemical Change

Everybody has agreed that the system reacts by two overall processes designated I and II. Both of these processes are thermodynamically favored, and their net consequence is five times that of process III. It is the free energy change of process III that drives the oscillations. Note that only two of these three processes are stoichiometrically independent.

$$2IO_3^- + 5HOOH + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O \qquad \text{(I)}$$

$$I_2 + 5HOOH \rightarrow 2IO_3^- + 2H^+ + 4H_2O \qquad \text{(II)}$$

$$2HOOH \rightarrow O_2 + 2H_2O \qquad \text{(III)}$$

Processes I and II undoubtedly involve other iodine-containing species as intermediates. However, we shall demonstrate below that the system could not contain any known chemical species at concentrations stoichiometrically significant[33] compared to those of the species appearing in processes I and II. Therefore, net chemical change in the system can be described satisfactorily in terms of the extent of reaction by any two of these three processes or by any two linear combinations of those extents.

Experimental Constraints on Mechanism

Any proposed chemical mechanism must satisfy a body of experimental observations. Because this system exhibits such varied behavior, the development of a mechanism is complicated. However, this great variety also generates confidence that any mechanism consistent with that body of observation must be essentially valid. We attempt here to summarize the body of established experimental facts, each designated by e and followed by a number. Whether or not our mechanism stands the test of subsequent study, the mechanism ultimately validated must account for all of these assertions not disproved by further experiment. The discussion will frequently refer to figures from previous publications and will not attempt to illustrate all the varieties of behavior. The organization of topics requires that some important facts be stated more than once.

Significant Experimental Variables. The chemical composition of the system can be defined by the concentrations of the three substances KIO_3, HOOH, and $HClO_4$. Elementary iodine is a stoichiometrically significant[33] species derived from iodate, but the sum $[IO_3^-] + 2[I_2]$ may be considered constant during reaction of any system. Additional variables known to affect behavior are temperature, pressure of the gas into which the evolved oxygen is escaping, illumination with light, rate of stirring, and bubbling of nitrogen or oxygen through the solution. Obviously we do not have detailed information about effects of varying each of the above quantities for all possible combinations of the others.

Observable Quantities. We have followed $[I_2]$ spectrophotometrically and have followed $[I^-]$ and $[O_2]$ potentiometrically with specific electrodes. We have not developed equipment to make spectrophotometric and potentiometric measurements simultaneously, but Liebhafsky et al.[15] have done so. His research group has also measured oscillations in pH[15] and in temperature[15] and has measured rate of gas evolution;[14] the latter measurements can be integrated over time and combined with $[I_2]$ measurements to determine total consumption of hydrogen peroxide. In the subsequent discussion, we shall use $[O_2]$ to denote instantaneous concentration of dissolved oxygen and $[O_2]_{tot}$ to denote total oxygen produced by the net chemical change since the start of the experiment.

Nature of Oscillations in $[I_2]$. Figures 1 and 2 illustrate spectrophotometric traces of iodine concentration for two solutions at differing acidities. Several points deserve attention.

(e1) If no iodine is present initially, $[I_2]$ rises from zero to a maximum.

(e2) The trace during this rise is concave up.

(e3) When the maximum is reached, $d[I_2]/dt$ changes sign almost discontinuously and repeats this behavior at subsequent maxima and minima. This "saw-toothed" behavior is also illustrated in several previous publications, such as Figure 2 of ref 20.

(e4) When $d[I_2]/dt < 0$ (process II dominant), the absolute magnitude of the slope is several times that when $d[I_2]/dt > 0$ (process I dominant). Ratios of the order of five or ten are not uncommon.

(e5) At low acidities, oscillations commence immediately after the first maximum in $[I_2]$.

(e6) At low acidities, amplitudes and periods are very sensitive to factors like ease of escape of oxygen, but positive values

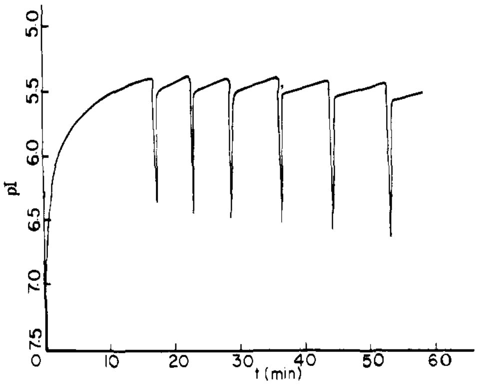


Figure 3. Potentiometric recording at 50 °C with an iodide specific electrode in a solution initially containing 0.432 M KIO_3, 0.490 M HOOH, and 0.055 M $HClO_4$. Note that at this low acidity (for such a high iodate concentration) the maxima in −pI are sharp just before switching. Chart speed was too slow to reveal detailed structure at low iodide concentration, but references to such recordings are provided in the text.

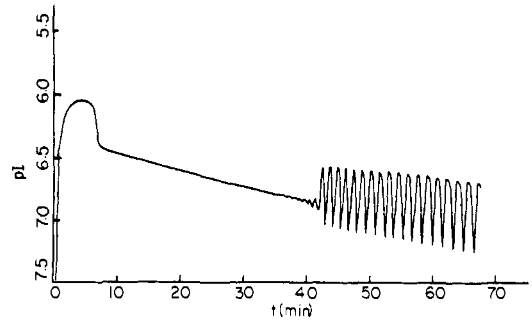


Figure 4. Potentiometric recording at 50 °C with an iodide specific electrode in a solution initially containing 0.432 M KIO_3, 0.490 M HOOH, and 0.071 M $HClO_4$. Note the rounded first maximum and second induction period. When oscillations commence, maxima are rounded and switch less sharply than at lower acidity.

of $d[I_2]/dt$ are insensitive to those same factors. This observation supports our general impression that amplitudes and periods are easy to measure, but are not particularly useful for elucidating mechanisms of chemical oscillators.

(e7) At higher acidities, oscillations commence only after a second induction period, during which $[I_2]$ has drifted down from the first maximum. Liebhafsky[6,20] has referred to this second induction period as smooth catalysis of hydrogen peroxide decomposition. This behavior is well illustrated in Figure 2.

(e8) Liebhafsky[6,20] asserts that $[I_2]$ is directly proportional to [HOOH] during the second induction period.

(e9) After the first maximum in $[I_2]$, successive maxima (or minima) usually tend to be at decreasing concentrations. We have occasionally seen trends of increasing concentration, but are uncertain whether changing oxygen pressure or some other effect might have been responsible.

Nature of Oscillations in $[O_2]$. Traces obtained with an oxygen-sensitive electrode have been shown previously.[28]

(e10) If $[O_2]$ denotes *dissolved* oxygen, values of $d[O_2]/dt$ reverse sign sharply at about the same time that values of $d[I_2]/dt$ do so.

(e11) The value of $d[O_2]/dt$ is strongly positive at the same time that $d[I_2]/dt$ is negative. This sign of coupling is unanticipated in view of the stoichiometries of processes I and II.

(e12) The maximum in $[O_2]$ is slightly rounded, and visual observation indicates it is reached a few seconds before $[I^-]$ begins its rapid rise; we believe this rise in $[I^-]$ coincides with the reversal of $d[I_2]/dt$ from negative to positive.

Nature of Oscillations in $[I^-]$ and in [HOI]. Figures 3 and 4 illustrate potentiometric traces of log $[I^-]$ for two systems differing in acidity.

(e13) The value of $[I^-]$ undergoes almost discontinuous switches between high and low values that differ by factors of the order of ten. We have every reason to believe these switches coincide with reversals in signs of $d[I_2]/dt$. Other good examples of the shape of pI traces can be found in Figure 3 of ref 13 and in Figure 1 of ref 20.

(e14) The value of $[I^-]$ tends to drift up at least during much of the time when it is in the high condition and during all of the time when it is in the low condition.

(e15) At low acidity, a system in the high $[I^-]$ condition rises to a rather sharp maximum and then falls rapidly as $d[I_2]/dt$ changes from positive to negative.

(e16) At high acidity, a system in the high $[I^-]$ condition rises to a rounded maximum, and $[I^-]$ falls appreciably before it starts its rapid drop.

(e17) The minimum in $[I^-]$ always comes immediately after its sharp drop, and the value then rises slowly until the sudden sharp rise that we believe coincides with $d[I_2]/dt$ changing from negative to positive.

(e18) If the system exhibits a second induction period (smooth catalysis), $[I^-]$ goes over a gently rounded maximum before the sudden drop that coincides with the maximum in $[I_2]$.

(e19) During oscillation, successive maxima (and minima) in $[I^-]$ drift downward at high acidity, but may perhaps drift upward at low acidity.

(e20) Because the hydrolysis equilibrium of iodine is rapidly established,[34] the product $[HOI][I^-]$ changes only slowly. Therefore, [HOI] switches magnitude at the same time as $[I^-]$ does, moving in the opposite direction, but by about the same factor.

Effect of Acidity on Behavior. Variations in $[H^+]$ have more effect on the behavior of this system that do variations in any other species. For systems about 0.10 M in KIO_3 at 50 °C, we found it difficult to get oscillations much outside the range from 0.04 to 0.06 M in $HClO_4$. Even within this rather narrow range there are large qualitative differences in behavior, and we refer to regions of high and low acidity as above and below about 0.05 M. It is obviously somewhat fortuitous that the oscillatory behavior was ever discovered.

Figure 5 illustrates values of $d[I_2]/dt$ for the rising and falling portions of oscillating curves like those in Figures 1 and 2. These observations were made as we were becoming aware of the effects of constraining the escaping oxygen, and those constraints were not always exactly reproduced. The data for $d[I_2]/dt > 0$ and for high acidity are both reproducible and reliable. The data for $d[I_2]/dt < 0$ at low acidity are very sensitive to oxygen pressure in the flask and these preliminary results should not be regarded as absolute values. However, the trends shown in Figure 5 are unmistakable.

At *low* acidities:

(e21) Values of $[I^-]$ rise to sharp maxima before a sudden drop.

(e22) Values of $[I_2]$ oscillate through large amplitudes that are irreproducible and sensitive to changing conditions. If oxygen can escape freely, $[I_2]$ may build up so much that solid element precipitates.

(e23) Oscillations commence immediately after the first maximum in $[I_2]$, and there is no second induction period.

(e24) The system is very sensitive to light and changes in oxygen pressure.

(e25) If the system is outside the range in which oscillations are possible, process I is dominant and the concentration of iodine increases until saturation.

At *high* acidities:

(e26) The system exhibits a second induction period (smooth catalysis of peroxide decomposition).

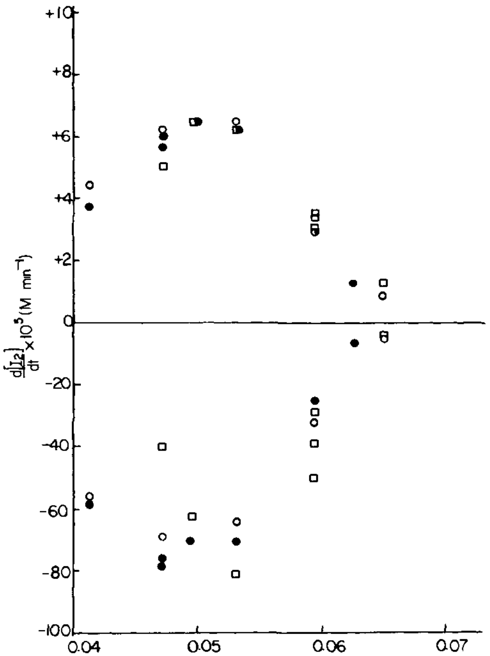


Figure 5. Rates of iodine formation and consumption (in 10^{-5} M min^{-1}) measured spectrophotometrically in stirred cells at 50 °C for oscillating solutions initially containing 0.104 M KIO_3 and 0.490 M HOOH. Open squares refer to runs in which the cell was loosely covered with a watch glass; this system would not oscillate for 0.0413 M $HClO_4$. Filled circles refer to runs in which the cell was fitted with a stopper and capillary tube. Open circles refer to runs in which the cell was stoppered with a file scratch on the stopper to provide a vent. Notice that the scale for negative rates is ten times that for positive rates. Negative rates (process II dominant) show more scatter than positive rates (process I dominant). At highest acidities, negative rates are a little less than ten times those of positive rates, and at lowest acidities negative rates are a little more than ten times those of positive rates. Restricting oxygen escape increases the negative rate at low acidity and may even slightly decrease it at intermediate acidity.

(e27) Values of $[I^-]$ go through rounded maxima.

(e28) The system is almost insensitive to light and changing oxygen pressure.

(e29) If the system is outside the range in which oscillations are possible, $[I_2]$ rises to a single low maximum and then decreases slowly, while the system exhibits smooth catalysis with process II dominant.

Effect of Hydrogen Peroxide on Behavior. We have usually worked in the range of initial hydrogen peroxide concentrations between about 0.1 and 0.5 M and call those limits low and high, respectively. Oscillations can be generated with concentrations outside these limits, and the system is not particularly sensitive to this variable.

(e30) When process I is dominant, $d[I_2]/dt$ is very nearly proportional to [HOOH].

(e31) When process II is dominant, the absolute magnitude of $d[I_2]/dt$ tends to increase with increasing [HOOH], but the effect is less than linear.

(e32) Increasing [HOOH] lengthens the second induction period when it is observed and can create a second induction period in systems that would not exhibit it at lower [HOOH].

Effect of Iodate on Behavior. Of the major reactants, it is iodate that generates the whole zoo of chemical species responsible for the dramatic kinetic behavior in this system. However, variations in iodate concentration tend to have rather little effect on that behavior. We usually worked at about 0.10 M KIO_3.

(e33) We find that $d[I_2]/dt$ is proportional to $[IO_3^-]/(1 + b[IO_3^-])$ when that slope is positive (process I dominant). Liebhafsky[6] found direct proportionality when the product iodine was continuously removed by shaking with carbon tetrachloride.

(e34) Increasing $[IO_3^-]$ has a small positive effect on the absolute magnitude of $d[I_2]/dt$ when that slope is negative (process II dominant).

(e35) Increasing $[IO_3^-]$ shortens the second induction period observed at high acidity.

Effect of Oxygen Pressure. Previous efforts to explain this system have assumed that oxygen was the inert product of irreversible processes I and III. During spectrophotometric observations of a very low acidity solution in an almost unstoppered cell, we found iodine oscillations of large amplitude corresponding to a range of several-fold in concentration. Sometimes the observations were even complicated by the precipitation of solid iodine. When the unstoppered cell was fitted with a ground glass stopper that had been scratched with a file to provide a small vent, the amplitudes of oscillations dramatically decreased even though rates of change of iodine concentration remained virtually the same. Solid iodine no longer appeared.

Our first effort to explain these observations postulated that a reactive intermediate was being vented with the oxygen much as Peard and Cullis[24] tried to explain oscillations. The vapor pressure of iodine was too low to be responsible, and HOI was implicated. However, further reflection about rates of diffusion and gas solution at interfaces made it difficult to explain the rate effects as due to changes in anything except the concentration of dissolved oxygen. Very different effects of purging the solution with oxygen and with nitrogen confirmed that the effect was chemical and not due to physical entrainment by evolving gas.

Subsequent studies of the oxygen effect were made in a closed flask fitted with a vent tube that could be inserted to any desired depth in a column of manometric fluid such as water or mercury. The flow of oxygen through the vent prevented any diffusion of vapor from the manometric fluid back to the flask. Increasing the pressure at which oxygen gas escapes will both increase the concentration of oxygen at the saturation equilibrium and slow equilibration with escaping bubbles by decreasing their size and surface area. Both effects increase the concentration of dissolved oxygen in the reacting solution.

In section S1 of the supplemental material accompanying the microfilm edition of this journal, we report some qualitative observations mostly concerned with the oxygen effect. We summarize here the facts any valid mechanism should explain.

(e36) Changing oxygen pressure has little effect when process I is dominant.

(e37) Increasing oxygen pressure tends to promote process II.

(e38) At low acidities, increased oxygen pressure increases the frequency of oscillation.

(e39) Oxygen has less effect at high acidity, but a sufficient pressure can sometimes hold a solution in smooth catalysis when it would oscillate at a lower pressure.

(e40) As might be anticipated, flushing with nitrogen gas has an effect opposite to that of increasing oxygen pressure.

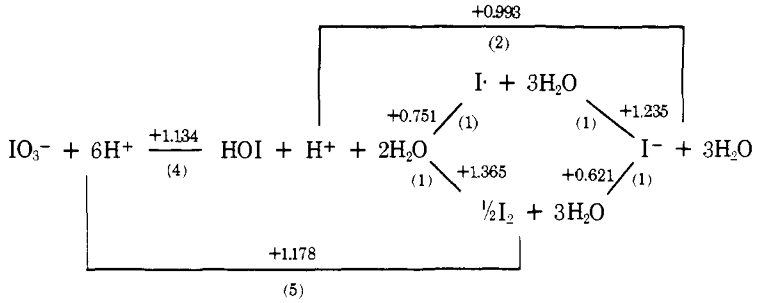
Effect of Light on Behavior. The qualitative effects of light have already been reported.[28] Light tends to resemble oxygen by promoting process II, but by having little effect on process I.

(e41) At low acidity, the solution is quite sensitive to visible light, which increases the frequency of oscillation.

(e42) At high acidity, light can throw an oscillating solution into smooth catalysis with process II dominant.

Kinetics of Process I. Liebhafsky[6] studied the reduction of iodate by hydrogen peroxide (process I) while preventing complicating side reactions by removing the product iodine with carbon tetrachloride as rapidly as it formed. He found the rate in M/s at 50 °C was given by eq 1. An "induction period"

Chart I. Established Reduction Potentials at 25 °C for Oxyiodine System



of a few minutes preceded attainment of the full rate.

$$2\frac{d[I_2]}{dt} = -\frac{d[IO_3^-]}{dt}$$
$$= (4.3 \times 10^{-6} + 2.15 \times 10^{-4}\,[H^+])[IO_3^-][HOOH] \quad (1)$$

(e43) Fact (e2) above indicates that the rate changes appreciably during a time in which none of the concentrations in eq 1 changes significantly, and furthermore, the changes in concentration that do occur should alter the rate in a direction *opposite* to that observed. Therefore, the kinetics of eq 1 are not sufficient to describe process I dominance in a system that is potentially subject to oscillation.

(e44) Light and oxygen pressure have little effect on the kinetic behavior when process I is dominant; we believe that component steps of process I are nonradical.

Kinetics of Process II. Liebhafsky[7] also studied the oxidation of iodine by hydrogen peroxide (process II) under conditions such that there should have been little simultaneous contribution from process I. Reaction was very slow unless iodate and acid were also present The observations were complicated by induction periods, but the rate during any single experiment could usually be described by eq 2. A good representative value of k_{II} at 0 °C was 5×10^{-4} s^{-1}, but it depended somewhat upon concentrations of other species. His rather scattered data indicated that k_{II} increased with increasing [IO$_3^-$], decreased with increasing [HOOH], and showed little trend with changing [H$^+$].

$$-d[I_2]/dt = k_{II}[I_2] \quad (2)$$

(e45) Our own studies of the condition of process II dominance in an oscillating system indicate that k_{II} decreases slightly with increasing [H$^+$] and increases slightly with increasing [HOOH] and [IO$_3^-$]. The system differs from that studied by Liebhafsky,[7] and effects of those variables are rather small in both systems.

(e46) Process II is probably free radical in type. It is accelerated by light[28] and oxygen and is inhibited by free-radical traps.[27]

Kinetics of Smooth Catalysis. (e47) Liebhafsky and Wu[20] report that the ratio [I$_2$]/[HOOH] remains essentially constant in a system subject to smooth catalytic decomposition of hydrogen peroxide.

Stoichiometric Constraints on Mechanism

No chemist can ever prove that a particular molecular mechanism is a *unique* explanation of a finite set of macroscopic observations.[35] He can often prove that a hypothetical mechanism is *not* consistent with those facts. He may also impose additional constraints on permissible mechanisms and demonstrate with considerable confidence that within the limits imposed by those constraints there is one and only one interpretation consistent with the known facts. Such an approach depends critically upon the method of Holmes,[36] and it is only within this framework that any mechanism is ever claimed to be validated. Any person wishing to challenge such a mechanism must then show either that additional hypothetical mechanisms are also consistent with the constraints or that the constraints themselves should be modified. In this section and the next, we select the constraints assumed to be imposed by chemical stoichiometry and thermodynamics.

As a result of over a century and a half of iodine chemistry, we assume as a constraint that no still unknown compound of this element is sufficiently stable that it can become stoichiometrically significant[33] in our system.

For reasons that will become apparent, we shall distinguish species with even and odd numbers of electrons. The five even-electron iodine-containing species we assume to be of mechanistic importance are IO$_3^-$, HOIO, HOI, I$_2$, and I$^-$. This listing includes only one species from each oxidation state, and we assume proton transfers to and from oxygen and iodine are always rapid. We therefore do not specifically invoke species like HOIO$_2$ and OIO$^-$, which may be present to the extent of several percent compared to IO$_3^-$ and HOIO, respectively. For the same reason, we do not specifically invoke IOH$_2^+$ even though its concentration in our acidic solutions is actually greater[18,37] than that of HOI.

We also invoke three odd-electron iodine-containing species ·I, ·IO, and ·IO$_2$; each is well established or is analogous to radical oxides of lighter halogens. The odd-electron species HO· and HOO· are well established. Peroxyiodine radicals such as ·OOI, ·OOIO, and ·OOIO$_2$ seem to be necessary to explain some of the observations; the species ·OOI and ·IO$_2$ are not the same. We admit the radical ·IO$_3$ may be present, but do not find it necessary to explain the data.

The above listing assumes we can ignore known iodine(VII) species such as IO$_4^-$ and H$_5$IO$_6$. It also ignores even-electron oxides like I$_2$O$_2$, I$_2$O$_4$, etc., even though they may be transient intermediates in this system. The known species I$_3^-$ is in negligible concentration compared to I$_2$ and is also ignored.

Because our analysis maintains that all iodine-containing species with oxidation number +1 are in rapid equilibrium, it ignores the hydrated cation I$^+$ invoked by Liebhafsky and Wu.[20] We also ignore oxygenated species containing more than one iodine atom, such as H$_2$I$_2$O$_3$ and H$_3$I$_3$O$_5$, invoked by Matsuzaki et al.[23] and IOI and IO$_2$I invoked by Schmitz.[32] Such species of unspecified structure were proposed as intermediates by Skrabal[38] to explain kinetic orders, but there is no evidence that they could exist for more than a molecular vibration.

Thermodynamic Constraints on Mechanism

Reduction potentials at 25 °C for the oxyiodine system are shown in Chart I. The data are derived from Latimer,[39] and the standard state of I$_2$ is ideal 1 *m* solution. Entries are in volts/equivalent (abbreviated V), and figures in parentheses are the numbers of equivalents involved in each of the indicated processes. The potentials involving ·I assume the (concentration) equilibrium constant for dissociation of the element in water is the same as in gas phase; this assumption is valid for saturated hydrocarbon solvents.[40,41] Spitz and Liebhafsky[21] have recently determined the potential of the iodate-iodine

Chart II. Reduction Potentials at 25 °C for Oxygen–Water System

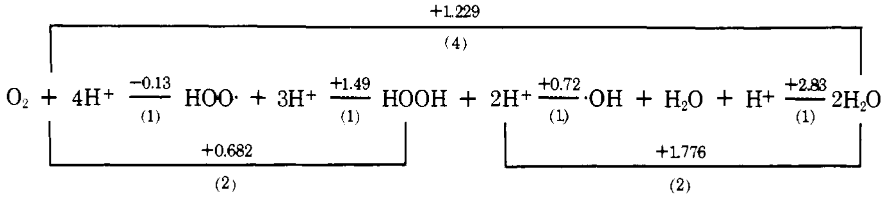
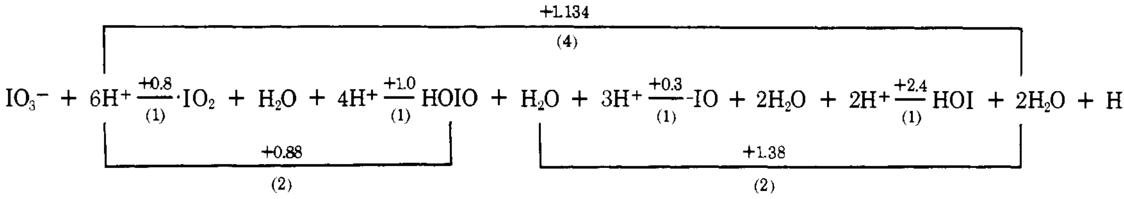


Chart III. Estimated Reduction Potentials at 25 °C for the Iodine(V) to Iodine(I) System



couple against *crystalline* element as 1.1942 V at 25 °C and 1.1863 V at 50 °C; this result agrees within 0.001 V with that in Chart I.

Latimer[39] potentials for the oxygen-hydrogen peroxide-water system at 25 °C are shown in Chart II. Each of the radical species is unstable to disproportionation, and hydrogen peroxide is unstable to disproportionation by a 2-equiv, but not a 1-equiv, process. A comparison of the overall potentials in Charts I and II reveals that the iodate-iodine couple is almost ideal to catalyze the disproportionation of hydrogen peroxide. This fact was clearly recognized by Bray.[2,42]

The entries in Charts I and II refer to 25 °C, where the most extensive data are available. Most studies of oscillations in this system have been conducted at 50 °C. The available evidence indicates that relative potentials would not be seriously different at the upper temperature. Equilibria for most of the component reactions will lie far to the same direction at both temperatures.

The entries in Chart I are not extensive enough to cover the component reactions that need to be considered. A complete set would be possible if we knew potentials for the three disproportionation reactions IV, V, and VI.

$$2HOIO \rightleftarrows IO_3^- + HOI + H^+ \qquad E_{IV}° \ (2) = 2x \qquad (IV)$$

$$2 \cdot IO_2 + H_2O \rightleftarrows IO_3^- + HOIO + H^+ \qquad E_V° \ (1) = 2y \qquad (V)$$

$$2 \cdot IO + H_2O \rightleftarrows HOIO + HOI \qquad E_{VI}° \ (1) = 2z \qquad (VI)$$

In section S2 of the supplementary material accompanying the microfilm edition of this journal, we attempt to make rough estimates of x, y, and z based on analogies with the chemistry of the lighter halogens and some bond energy values. As a result of this analysis, we assign the following values.

$$x = 0.25 \text{ volt/equiv} \qquad (3)$$

$$y = 0.1 \text{ volt/equiv} \qquad (4)$$

$$z = 1.1 \text{ volts/equiv} \qquad (5)$$

Although these assignments must be regarded as very tentative, the similarity in corresponding values for chlorine and bromine permits us to hope that x and y are known to within about 0.1 V. The much greater uncertainty in z has very little effect on mechanistic possibilities. On the basis of these estimates, the more extensive potentials in Chart III have been prepared.

Permissible Component Reactions

As a further constraint on our mechanism, we propose that net chemical change in the system is a consequence of elementary processes[33] involving no more than two reactant species (except for rapid proton exchange equilibria and perhaps water molecules) and in which no element changes oxidation state by more than 2 equiv. Given these additional constraints, we can effectively identify the various reaction types that could contribute to the mechanism.

Those types are summarized in Table I. The generalized equations involve species like $\cdot IO_j$ and $HOIO_j$, where j may be 0, 1, or 2. For this nomenclature, $HOIO_{-1}$ is equivalent to $H^+ + I^-$. The symbol k may be used for another oxyiodine species, and the generalization $HO_m\cdot$ may have m equal to 1 or 2.

The reaction types in Table I are very schematic. In section S3 of the supplemental material accompanying the microfilm edition of this journal, we list the detailed reaction possibilities and show the thermodynamic constraints determining the directions in which they will occur. We also discuss mechanistic implications and kinetic information on specific elementary processes when available. The comments here summarize only information essential to the mechanism as finally developed. The essential steps in that mechanism are presented in Table II.

The four possible A type reactions have been numbered according to the number of oxygen atoms in the transition state. All are essential to the mechanism as finally developed. They involve either hydrolysis of elementary iodine or oxygen atom transfer between two iodines. Rate data summarized in the supplemental material indicate each reaction is at least as fast as its analogue in oxybromine chemistry.

The three possible B type reactions involve direct reduction of an oxyiodine acid with oxygen formation. The reactions probably involve intermediate peroxy acids formed by nucleophilic attack of peroxide on iodine. The "induction period" reported by Liebhafsky[6] to precede attainment of the rate of eq 1 suggests a few minutes are necessary to establish the steady state of the $OOIO_2^-$ intermediate for reaction B2. However, the rapid hydrolysis A1 equilibrium of iodine[34] indicates that the HOOI intermediate for reaction B0 rapidly establishes its steady-state concentration. The oxygen molecule can then be generated by an electronic rearrangement that reduces the oxidation state of iodine by 2 equiv. The heavy iodine atom presumably facilitates the electron spin flip to produce the triplet-oxygen product. The isotopic studies of Cahill and Taube[50] make it almost certain that the original O-O bond of the peroxide remains intact throughout these oxidations.

The three possible C type reactions involve direct oxidation of an iodine species by hydrogen peroxide and are all strongly favored thermodynamically. The mechanism would require breaking the O-O bond by a nucleophilic attack, perhaps on

Table I. Generalized Possible Reaction Types

(A)	$HOIO_j + HOIO_k \to HOIO_{j-1} + HOIO_{k+1}$	
(B)	$HOIO_j + HOOH \to HOIO_{j-1} + O_2 + H_2O$	
(C)	$HOIO_{j-1} + HOOH \to HOIO_j + H_2O$	
(D)	$\cdot IO_j + HOOH \to HOIO_j + HO\cdot$	
(E)	$\cdot IO_j + HOOH \to HOIO_{j-1} + HOO\cdot$	
(F)	$\cdot IO_j + O_2 + H_2O \to HOIO_j + HOO\cdot$	
(G)	$\cdot IO_j + H_2O \to HOIO_{j-1} + HO\cdot$	
(H)	$HO_m\cdot + HOOH \nearrow H_2O + HOO\cdot$	$m = 1$
	$\searrow O_2 + H_2O + HO\cdot$	$m = 2$
(I)	$\cdot IO_j + HOIO_k \nearrow HOIO_{j-1} + \cdot IO_{k+1}$	
	$\searrow HOIO_j + \cdot IO_k$	
	$+ HOOH \to H_2O + \cdot IO_{j+1}$	
(J)	$\cdot IO_j + HOIO_k \to HOIO_{k-1} + \cdot IO_{j+1}$	
	$+ \cdot IO_k \to \cdot IO_{k-1} + \cdot IO_{j+1}$	
(K)	$\cdot IO_j + O_2 \to \cdot OOIO_j$	
(L)	$\cdot OOIO_j + HOIO_k \to HOIO_{k+1} + \cdot IO_{j+1}$	
(M)	$\cdot IO_j + \cdot OOIO_k \to \cdot IO_{k+1} + \cdot IO_{j+1}$	
	$+ HOO\cdot \to HO\cdot + \cdot IO_{j+1}$	
(N)	$HOIO_j + HOIO_k \to \cdot IO_{j+1} + \cdot IO_k + H_2O$	
(O)	$R_\alpha\cdot + R_\beta\cdot \rightleftarrows$ even-electron products	
(P)	$O_2(aq) \rightleftarrows O_2(g)$	

Table II. Important Elementary Processes in the Mechanism

$HOI + I^- + H^+ \rightleftarrows I_2 + H_2O$	(A1)
$HOIO + I^- + H^+ \to 2HOI$	(A2)
$IO_3^- + I^- + 2H^+ \rightleftarrows HOIO + HOI$	(A3)
$2HOIO \to IO_3^- + HOI + H^+$	(A4)
$HOI + HOOH \to I^- + O_2 + H^+ + H_2O$	(B0)
$\cdot IO + HOOH \to HOIO + HO\cdot$	(D1)
$\cdot IO_2 + HOOH \rightleftarrows IO_3^- + H^+ + HO\cdot$	(D2)
$HOO\cdot + I_2 \to I^- + O_2 + H^+ + \cdot I$	(−Fi)
$HO\cdot + HOOH \to H_2O + HOO\cdot$	(H1)
$\cdot I + O_2 \rightleftarrows \cdot OOI$	(K0)
$\cdot OOI + I^- + H^+ \to HOI + \cdot IO$	(L0)
$IO_3^- + HOIO + H^+ \to 2\cdot IO_2 + H_2O$	(N2)
$2HOO\cdot \to HOOH + O_2$	(O1)
$O_2(aq) \rightleftarrows O_2(g)$	(P)

an OOH_2 species in tautomeric equilibrium with HOOH. Iodide ion does react in just this way, but the discussion in the supplemental material shows the reaction is too slow to be important in our system. The oxy acids HOI and HOIO are presumably weaker nucleophiles that react even slower. Therefore, 2-equiv reactions with hydrogen peroxide tend to reduce iodine species, not because of any thermodynamic factors, but because C type oxidations are so slow kinetically.

Reaction types D-G all involve 1-equiv interactions between the oxyiodine and oxyhydrogen systems. The reactions in Table I are all written with oxyiodine radicals on the left and oxyhydrogen radicals on the right. However, because O_2 is the weakest 1-equiv oxidant in our system and HO· is the strongest, the F and G reactions all go irreversibly in the opposite direction to those in Table I. We regard the −G reactions as unimportant in our system because any hydroxyl radicals that are formed are irreversibly removed by hydrogen peroxide. Most of the −F reactions also seem to be unimportant. They would involve an HOO· radical contributing a hydrogen atom to break an I-O bond, and the evidence from H reactions suggest this kind of process is mechanistically implausible even when strongly favored thermodynamically. However, the −Fi reaction of HOO· with I_2 molecule is essential to our mechanism.

With regard to D and E reactions, the data in the supplemental material indicate that ·IO radicals can be both oxidized and reduced by hydrogen peroxide; we shall see below that kinetic factors seem to require that they are more likely to be oxidized. The I and IO_2 radicals can also be oxidized by hydrogen peroxide, but will not be reduced by it; the preferential oxidation of $\cdot IO_2$ is very important to the mechanism. Another way to summarize the same information is to say that HO· radicals can oxidize all even-electron iodine containing species (except iodate) and will reduce none, while HOO· can, in principle, reduce all even-electron iodine species (except iodide) and can also oxidize I^- and HOIO. Although we initially considered that at least one −E reaction of HOO· was required, none has been retained in the mechanism as finally developed.

The two possible H reactions involve oxyhydrogen radicals with hydrogen peroxide. Reaction with hydroxyl (HO·) is rapid and irreversible. Reaction with perhydroxyl (HOO·) is also irreversible, but it is slow. Because HOO· does not easily transfer a hydrogen atom to rupture the O-O bond in hydrogen peroxide, we feel justified in rejecting for kinetic reasons the −F reactions of oxyiodine species as mentioned briefly above.

Ten possible I reactions involve oxyiodine radicals and even-electron iodine-containing species. They are listed in section S3 of the supplemental material, and the discussion there indicates why they are kinetically unimportant in our system.

Reaction types D-I cover all possible 1-equiv processes involving oxyhydrogen and oxyiodine species other than peroxyiodine radicals. The discussion below will show why these reactions are unable to explain the experimental observations within the constraints imposed above and why ·I radicals must be oxidized to ·IO radicals without passing through HOI as an intermediate. The discussion in section S3 of the supplemental material indicates why reactions of types K and L are selected and types J and M are rejected as contributing to that process.

Because all species present in significant concentration contain even numbers of electrons, reactions of types N and O are necessary to create and destroy the radical species. The discussion in section S3 of the supplemental material indicates how we selected the reactions of these types that seem to be most important mechanistically.

Because K type reactions appear to be important, dissolved oxygen is a reactant present at a concentration comparable to that of I_2. The rate of release to the gas phase can therefore affect the dynamic behavior of the solution, and reaction P must be included.

Table I illustrates a rich variety of possibilities in this system. Before we attempt to select the individual elementary processes capable of accounting for the experimental observations, we should consider the specific constraints imposed by the existence of oscillations in a chemical system.

Characterization of Chemical Oscillators

Classification of Reacting Species. Chemical oscillators constitute a small but complicated and potentially important class of reactions. As mechanisms are elucidated, we should look for common characteristics that may help in the understanding of other systems. As a working hypothesis, we suggest that it may be useful to classify reacting species as major, phase-determining, or coupled, and that subclassifications are sometimes possible.

The *major reactants* either change irreversibly to generate the free-energy change that drives the oscillations, or (if they are catalyst species) their cyclic variations are only small fractions of their total concentrations. An approximate description of the system will regard their concentrations as almost constant during the period of a single oscillation. A specification of the concentrations of all major reactants will be sufficient to determine whether or not a particular system will undergo near-limit cycle oscillations in concentrations of other species and will also determine the trajectory, amplitude, and period of those oscillations. However, because major reactants do not change significantly during a single oscillation,

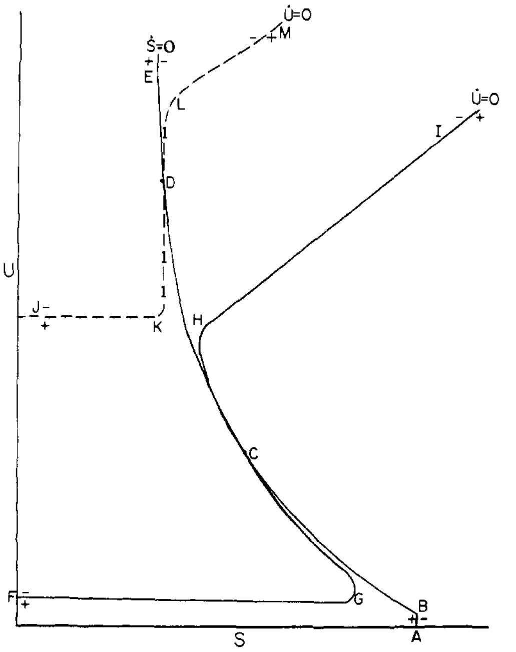


Figure 6. Composition space for stable (S) and unstable (U) phase-determining intermediates. Curve ABCDE is for $\dot{S} = 0$ and moves monotonically to the left with increasing U. Curve FGCHI for $\dot{U} = 0$ is three valued in U for some regions of S values, and the steady state C may be unstable with respect to limit cycle oscillations around it. Curve JKDLM for $U = 0$ generates a steady state at D that must be stable to minor perturbations.

their concentrations reveal nothing about the phase within a single period.

Each oscillating system will have at least two *phase-determining intermediates* (previously[43] called reference reactants), whose concentrations are sufficient to define the position of the system along the trajectory of its oscillations. Concentrations of phase-determining intermediates may vary by major fractions, but absolute ranges will be much smaller than the concentrations of at least some of the major reactants. In order to define the position of any *mechanical* oscillator along its trajectory, at least one coordinate and one momentum must be specified independently. Because the thermodynamic state and dynamic behavior of a *chemical* system are simultaneously defined in principle by stating the activities of all components, the chemical system has no analogue of a momentum independent of a coordinate. Therefore, the concentrations of at least two species must be assigned independently to define the phase of a chemical oscillator.

It will always be advantageous if a chemical oscillator can be approximated with only two phase-determining intermediates, and the trajectory is then confined to a phase plane defined by the two concentrations. Most previous theoretical models of oscillators have been restricted to two species, so trajectories could be described in just such a plane. It will be helpful to search for similar approximations to describe real systems, but it may not always be possible to find them.

At least when a system contains only two phase-determining intermediates, it is useful to classify them further as *stable* and *unstable.* Figure 6 illustrates a hypothetical system for which S and U represent concentrations of stable and unstable intermediates, respectively. Let S and U be time derivatives whose values at any point are defined by the kinetic behavior of the system. Because negative concentrations are impossible, and because the system is presumed stable to explosion under all conditions, the curves $S = 0$ and $U = 0$ must each separate regions of positive and negative values with signs as shown, and these curves must intersect at least once. For the stable intermediate, every point on $S = 0$ must satisfy eq 6. Therefore, if U is arbitrarily maintained constant, S will approach a steady state that will then be stable to fluctuations.

$$(\partial \dot{S}/\partial S)_U < 0 \tag{6}$$

If the situation is as shown in Figure 6, then eq 7 is valid at the steady state defined by the intersection of the curves. This steady state is unstable to fluctuations in U at constant S, and it may also be unstable to fluctuations under the kinetic equations defining the system. In other words, simultaneous satisfaction of eq 6 and 7 at the steady state is necessary but not sufficient to ensure that steady state is unstable with respect to an oscillatory limit cycle trajectory around it. Further discussion of this analysis of oscillatory systems will be presented in a manuscript to be submitted to the *Journal of Chemical Physics.*

$$(\partial \dot{U}/\partial U)_S > 0 \tag{7}$$

The reactant species that are neither major nor phase determining are classified as *coupled intermediates* (previously[43] called derived reactants). Their concentrations will generally be very much less than those of the phase-determining intermediates, and they will respond rapidly as the system moves along the trajectory of an oscillation. Because of this rapid response, concentrations of coupled intermediates cannot be varied independently from those of phase-determining intermediates, but are coupled to them. Just as the phase rule depends upon the number of independent chemical components in an equilibrium system but is not constrained by which species are considered components, so it may sometimes be rather arbitrary which species are designated as phase determining and which as coupled. However, the distinction can usually be based on stoichiometric significance.[33]

It apparently is a frequent characteristic of chemical oscillators that at least some of the coupled intermediates are also *switched.* The mathematical steady state of the system is a point in the phase space defined by the concentrations of the phase-determining intermediates, and the oscillatory trajectory passes around that unstable steady state. As that trajectory is traversed, the small concentration of a coupled intermediate will often exist in a pseudosteady state until a set of conditions is attained when it switches dramatically to a different pseudosteady state. The switching requires some sort of feedback mechanism in the reactions of the switched intermediate, and the examples discovered to date involve either initiation or cessation of the opportunities for autocatalytic growth. The switching of the coupled intermediate between two pseudosteady states will create the conditions that cause one of the phase-determining intermediates to reverse the direction of its change in concentration. Therefore, the time dependence of a phase-determining intermediate will often exhibit a "saw-toothed" appearance as the direction of the change of concentration reverses almost discontinuously at the maximum and minimum values (see Figures 1 and 2).

Some people may be dissatisfied with the classification into major, phase-determining, stable, unstable, coupled, and switched species as developed here. The classifications are approximations, and mathematicians can devise many mechanisms that fail entirely to obey these criteria. We use them solely because of the empirical observation that they fit those two chemical oscillators for which reasonably detailed chemical mechanisms seem to be known. We suggest this as a useful way to discuss chemical oscillators, unless a system that violates its principles is discovered.

Application to Previous Examples. The above classification can be illustrated by application to a few examples. Those unfamiliar with the mechanisms discussed can find them in the cited references or in a recent review.[55]

The Lotka[56] mechanism was the first proposal for a chemical oscillator and involves two phase-determining intermediates and no coupled intermediates. At the steady state, the expressions in eq 6 and 7 are both zero, and the intermediates are neither stable nor unstable. This mechanism does not generate true limit cycle oscillations.

The Brusselator[57,58] mechanism also involves two phase-determining intermediates and no coupled intermediates. The species Y is stable, but the $\dot{X} = 0$ curve passes through a maximum and then traverses a region in which any steady state for the system may be unstable. Although this mechanism can model limit cycle oscillations, it is not generally applicable to closed systems.[59]

The Oregonator[60] mechanism involves three intermediate species and conforms to the above analysis. The species Z is a stable phase-determining intermediate that attains a stable steady-state value if X and Y are arbitrarily held constant. The species X is a coupled intermediate that undergoes dramatic switches of 10^5-fold between two pseudosteady states. These switches occur at precisely those times when $\dot{Z}$ very rapidly changes sign. The species Y, to which X is coupled, is an unstable phase-determining intermediate. For a particular value of Z, there may be three different values of Y for which $\dot{Y} = 0$. If the system will neither explode nor generate negative concentrations, $\dot{Y} > 0$ for sufficiently small Y and $\dot{Y} < 0$ for sufficiently large Y. Then $(\partial\dot{Y}/\partial Y)_Z < 0$ for the largest and smallest of the three $\dot{Y} = 0$ points. However, it is greater than zero at the intermediate point. If this point is the steady state of the system, it may be unstable, so that a fluctuation in Y will cause the system to leave the steady state and execute limit cycle oscillations about it. We do not know whether it is significant that for this model the switched intermediate is coupled to the unstable phase-determining intermediate, but switching occurs when there is a change of sign in the rate of the reaction of the stable intermediate.

The Oregonator is designed as a simplified model for the mechanism of the Belousov-Zhabotinsky reaction.[43] In that mechanism potassium bromate and malonic acid are major reactants that are irreversibly depleted, and the total amount of cerium ion catalyst (approximated by cerium(III)) is invariant during a run and can also be regarded as a major reactant. If the concentration of malonic acid is so great that elementary bromine cannot accumulate in the system, the two phase-determining intermediates are cerium(IV) (stable) and bromide ion (unstable); the oscillations in these species are saw-toothed, as in Figure 3 of ref 43. The other bromine-containing species are at much lower concentrations and are coupled to the phase-determining intermediates; at least $HBrO_2$ and $\cdot BrO_2$ are also strongly switched. At lower malonic acid concentrations (as in Figures 1 and 2 of ref 43), elementary bromine accumulates during periods of cerium(IV) production,[61] and description of the system requires three phase-determining intermediates. Time dependence of bromide ion concentration now resembles that of a switched intermediate, and it may be that simple saw-toothed behavior of a phase-determining intermediate is not necessary, unless the system can be approximated by only two phase-determining intermediates.

Application to the Bray-Liebhafsky Reaction. Hydrogen peroxide is the only true major reactant in the system that we are considering here, but the iodate and hydrogen ion catalyst species vary little in concentration and can be considered major reactants, just as the cerium(III) catalyst is so considered in the Belousov-Zhabotinsky reaction.

The most logical chemical to designate as a phase-determining intermediate is elementary iodine. The spectrophotometric recordings in Figures 1 and 2 exhibit the saw-toothed behavior consistent with that designation (e3). All of the Liebhafsky[6,7] observations on the kinetics of formation and destruction indicate that iodine is a stable intermediate that is formed when it is at low concentration and is destroyed at a rate that increases when its concentration exceeds a critical steady-state value.

Table III. Equilibrium and Rate Constant Estimates

Reaction		Equilibrium constant[a]		Rate constant[b]
A1		3.8×10^{12} M^{-2}	(25 °C)	3.1×10^{12} M^{-2} s^{-1}
	(50 °C)	2.43×10^{11}		
A2		1.5×10^{13} M^{-1}		2×10^{10} M^{-2} s^{-1}
A3		1.9×10^{-4} M^{-2}	(25 °C)	1.43×10^{3} M^{-3} s^{-1}
				3.71×10^{3}
A4		8.0×10^{16} M		2×10^{9} M^{-1} s^{-1}
B0		3.3×10^{10} atm	(25 °C)	37 M^{-1} s^{-1}
				108
D1		5.8×10^{6}		
D2		0.020 M		
–Fi		233 M atm		
H1		4.5×10^{22} M^{-1}	(25 °C)	4.5×10^{7} M^{-1} s^{-1}
K0		>1 atm^{-1}		
L0		>20 M^{-1}		
N2		4.2×10^{-4} M^{-1}		7×10^{4} M^{-2} s^{-1}
O1		2.4×10^{27} M^{-1} atm	(25 °C)	7.5×10^{5} M^{-1} s^{-1}

[a] At 25 °C unless otherwise indicated. [b] At 50 °C unless otherwise indicated.

The remaining species, I^-, HOI, HOIO, and all radicals, are present at much lower concentration than elementary iodine and would be expected to behave as coupled intermediates. The recordings in Figures 3 and 4 demonstrate that I^- (and therefore also HOI) undergoes switching at critical times during a cycle (e13).

Elementary oxygen is the only intermediate species other than iodine that can oscillate with an amplitude a significant fraction of 10^{-3} M. The oxygen-electrode recording in Figure 3 of ref 28 exhibits the saw-toothed behavior consistent with a phase-determining intermediate (e10), and changes in oxygen pressure substantially affect chemical behavior (e37–39). The argument then leads by the method of Holmes[36] to the unanticipated conclusion that *oxygen is the unstable phase-determining intermediate in the Bray-Liebhafsky reaction.* Mechanistic justification for that conclusion is provided below.

It is interesting to note for both the Belousov-Zhabotinsky and the Bray-Liebhafsky reactions that the stable phase-determining intermediate is derived from a catalyst species, that the concentration of the stable intermediate decreases with increasing concentration of the unstable one, and that the switching of pseudosteady states of coupled intermediates occurs simultaneously with reversal of the direction of change in the stable intermediate. It is premature to speculate as to whether these coincidences are accidental or whether they reflect characteristics that will be general for chemical oscillators.

Validation of Mechanism

Reaction types A-P in Table I include almost all we consider conceivable within the constraints imposed above. As a result of the thermodynamic and kinetic evidence discussed in section S3 of the supplemental material, many of these conceivable reactions could be rejected as unimportant in this system. Table II contains the list of elementary processes we have retained as important for reaction in the dark, and Table III contains the pertinent equilibrium data at 25 °C. Table III also summarizes measured or estimated rate constants discussed in more detail in the supplemental material. As is pointed out there, many of the rate constants show a pattern very similar to that for analogous oxybromine reactions.[43]

We shall now attempt to demonstrate that the proposed mechanism is indeed consistent with the observations. The demonstration is complicated because not all rate constants

Table IV. Compositions and Kinetic Behavior of Systems at 50 °C

	Process I dominant		Process II (or XII) dominant
$[H^+]$, M		0.05	
[HOOH], M		0.5	
$[IO_3^-]$, M		0.1	
$[I_2]$, M		0.001	
$[I^-]$, M	1.4×10^{-6}		1.2×10^{-7}
[HOI], M	6.0×10^{-8}		7.4×10^{-7}
[HOIO], M	9×10^{-10}		6×10^{-8}
$d[I_2]/dt$, M s^{-1}	6.4×10^{-7}		-1.3×10^{-5}
$d[O_2]_{tot}/dt$, M s^{-1}	3.2×10^{-6}		3.9×10^{-5}

are known and not all concentrations of interest can be measured directly. However, the argument can be carried far enough to provide great confidence that the essential features of the mechanism are understood. Some of the detailed argument is presented in the supplemental material accompanying the microfilm edition of this journal and is only summarized here.

Kinetics of Observable Rates. As has already been pointed out, the state of the system can be uniquely specified at any time by giving concentrations of the major and phase-determining species HOOH, H^+, IO_3^-, I_2, and perhaps O_2; all other chemical species are coupled to these.

The quantities $[I_2]$, $[I^-]$, and $[O_2]$ can be monitored continuously by spectrophotometric or potentiometric techniques. Gas volume measurements give $[O_2]_{tot}$, the total amount of oxygen produced, and [HOOH] can then be calculated at any time. Because only the major and phase-determining species are stoichiometrically significant,[33] the values of $[I_2]$ and $[O_2]_{tot}$ are the only possible measurements giving *independent* information about net chemical change. As was pointed out in the section on Net Chemical Change, these two measurements will not permit us to obtain separate rates for the three processes I, II, and III. The equations below show the relations imposed by stoichiometry.

$$d[I_2]/dt = v_I - v_{II} \tag{8}$$

$$d[O_2]_{tot}/dt = 5v_I + v_{III} \tag{9}$$

An examination of the mechanism in Table II shows that during the transition between IO_3^- and I_2 every iodine atom passes through HOIO as an intermediate and precisely half of them pass through I^- to I_2. We should also note that all intermediate iodine species are stoichiometrically insignificant[33] and that the equilibrium of A1 is established on a short time scale compared to that for net chemical change in the system. Then eq 10 and 11 become valid approximations. In these equations, $v_{a \rightarrow b}$ is the net rate at which iodine atoms in oxidation state a are converted to those in state b.

$$d[I_2]/dt = \tfrac{1}{2}v_{5 \rightarrow 3} = v_{3 \rightarrow -1} \tag{10}$$

$$[I_2] = K_{A1}[H^+][HOI][I^-] \tag{11}$$

If no radical processes are significant, eq 10 and 11 plus an expression for $v_{3 \rightarrow 1}$ are sufficient to define reaction rates and concentrations of HOIO, HOI, and I^- in terms of rate and equilibrium constants and the concentrations of HOOH, H^+, IO_3^-, and I_2 only. If radicals are also kinetically significant, it is useful to add eq 12, where v_N and v_O are the total rates by which pairs of radicals are created and destroyed, respectively.

$$v_N = v_O \tag{12}$$

Mechanism of Process I. We have already discussed evidence that process I is nonradical (e44). Then only A and B type reactions in Table II are applicable, and the stoichiometry of process I is generated by 2(A3) + 2(A2) + 5(B0) + A1. The more complete mechanistic possibilities are presented in section S4 of the supplementary material accompanying the microfilm edition of this journal, and the specific selections of Table II are justified.

Given this mechanistic sequence, the following are obtained.

$$\frac{d[I_2]}{dt} = \frac{1}{5}\frac{d[O_2]_{tot}}{dt} = \tfrac{1}{2}k_{A3}[H^+]^2[IO_3^-][I^-] \tag{13}$$

$$[HOIO] = \frac{k_{A3}}{k_{A2}}[H^+][IO_3^-] \tag{14}$$

$$[HOI] = \frac{2.5k_{A3}[H^+]^2[IO_3^-][I^-]}{k_{B0}[HOOH]} \tag{15}$$

$$[I^-] = \sqrt{\frac{k_{B0}[HOOH][I_2]}{2.5K_{A1}k_{A3}[H^+]^3[IO_3^-]}} \tag{16}$$

This mechanistic interpretation seems to be in virtually quantitative agreement with measurements on systems in which process I is dominant. The kinetics are those to be expected if the rate-determining step is A3, which initiates the Dushman[46] reaction, and these equations generate rates of half-order in both $[IO_3^-]$ and [HOOH]. Liebhafsky[6] observed first-order dependence in both when he removed product iodine with carbon tetrachloride, but those conditions do not lead to oscillation. Under the Liebhafsky[6] conditions, B2 had replaced A3 as the rate-determining step. Our less than first-order dependence on $[IO_3^-]$ (e33) is not inconsistent with some half-order contribution. We obtained nearly first-order dependence in [HOOH] (e30), but again might have had some contribution from B2. As is pointed out in the supplemental material, B2 and A3 make equal contributions to iodate reduction when $[I^-]/[HOOH]$ is about 5×10^{-7}. Because $[I^-]$ increases as $[I_2]$ is formed, spectrophotometric plots like Figures 1 and 2 will be mildly concave up during the induction period (e2). Most of the oxygen in such a system is produced by B0, and this reaction maintains $[I^-]$ about 1000 times above the equilibrium expected for existing I_2 and IO_3^- concentrations.

In Table IV the first column contains our estimates of the composition and kinetic behavior of a system with $[H^+]$ a little below 0.05 M, [HOOH] about 0.5 M, $[IO_3^-]$ about 0.1 M, and $[I_2]$ about 0.001 M with process I dominant; such a system should be approaching, but have not quite reached, the switching condition. The compositions in the first column of Table IV are computations based on rate and equilibrium constant data by Liebhafsky and discussed in sections S4 and S6 of the supplemental material, but our own less precise measurements of $[I^-]$ and of $d[I_2]/dt$ are entirely consistent with those computations.

Mechanism during Process II Dominance. Process II is radical (e46) and has many complicating possibilities. The reasons for selecting the specific steps of Table II are presented in sections S5 and S7 of the supplemental material. Alternative mechanistic possibilities are also discussed there.

If photochemical generation of radicals is excluded, the sequence N2 + 2(D2) + 2(H1) generates the net stoichiometry of process VII. This process is thermodynamically favored even though it produces a pair of radicals, although some of the component steps have slightly negative $E°$ values. Combination with the radical termination process (O1) generates the stoichiometry of process VIII.

$$HOIO + 4HOOH \rightarrow IO_3^- + H^+ + 3H_2O + 2HOO\cdot \tag{VII}$$

$$HOIO + 3HOOH \rightarrow IO_3^- + O_2 + H^+ + 3H_2O \tag{VIII}$$

The sequence −Fi + K0 + L0 + D1 + H1 generates the stoichiometry of radical-catalyzed process IX. This sequence is chosen in order to regenerate the HOIO consumed in initiation process VII and to provide catalysis by the HOO· radicals generated in that process.

$$I_2 + 2HOOH \rightarrow HOIO + HOI + H_2O \qquad (IX)$$

In order to describe net chemical change in the system, we must also generate sequences that convert the HOI and HOIO of process IX into stoichiometrically significant species. The sequence B0 + A1 generates the stoichiometry of process X, and the sequence 2(A4) + X generates that of process XI.

$$2HOI + HOOH \rightarrow I_2 + O_2 + 2H_2O \qquad (X)$$

$$4HOIO + HOOH \rightarrow 2IO_3^- + I_2 + O_2 + 2H^+ + 2H_2O \qquad (XI)$$

If chains are long, the sequence of 4(IX) + 2(X) + XI generates the stoichiometry of process XII as the net chemical change in a system with process II dominant.

$$I_2 + 11HOOH \rightarrow 2IO_3^- + 3O_2 + 2H^+ + 10H_2O \qquad (XII)$$

If chains are shorter, net chemical change can be determined by combining the radical generating and destroying sequences (which consume HOIO) with the radical sequence that produces the HOIO consumed in radical formation. However the sequence of 2(VII) + 2(IX) + X + 2(O1) generates precisely the stoichiometry of process XII also. Because of this peculiar coincidence, the stoichiometry of net chemical change in the system is given by process XII, independent of chain length!

Process XII is the net stoichiometry predicted (but not yet verified) when process II is dominant, and its stoichiometry is actually that of II + 3(III). Because radical conditions generate the stoichiometry of process XII during the oxidation of iodine, we can see why oxygen is evolved so rapidly when iodine is oxidized, even though the simple stoichiometry of process II produces no oxygen whatsoever (e11). If step A2 competes significantly with A4, the oxygen produced during iodine oxidation will exceed even that predicted by the stoichiometry of process XII.

By an argument developed in section S6 of the supplemental material, we have estimated rate constants for all of the even-electron processes. The last column in Table IV shows the nature of the solution of the first column when it has switched to process II dominance. The value of $d[I_2]/dt$ is based on our experimental estimate, and [HOI] is computed from it with the use of k_{B0}. The value of $[I^-]$ is then computed with K_{A1}. The calculations of [HOIO] follow from the material in section S6. It is interesting that [HOIO] only switches by about a factor of 100 between the two conditions; this is appreciable but much less than the factor of 10^5 for the corresponding switch in the Belousov-Zhabotinsky reaction.[43]

Generalized Kinetics. The preceding section explains how the proposed mechanism leads to the stoichiometry by which iodine is oxidized to iodate. More specific kinetic equations can now be written by noting that eq 10 is equivalent to the two equations $d[I_2]/dt = -\frac{1}{2}d[IO_3^-]/dt$ and $d[HOIO]/dt = 0$. Then we can write the equations

$$\frac{d[I_2]}{dt} = \tfrac{1}{2}k_{A3}[H^+]^2[IO_3^-][I^-] - \tfrac{1}{2}k_{N2}[H^+][IO_3^-][HOIO] - \tfrac{1}{2}k_{A4}[HOIO]^2 \qquad (17)$$

$$k_{A3}[H^+]^2[IO_3^-][I^-] - k_{A2}[H^+][HOIO][I^-] + (2\theta - 1)k_{N2}[H^+][IO_3^-][HOIO] - 2k_{A4}[HOIO]^2 = 0 \qquad (18)$$

These equations tacitly treat A3 and N2 as irreversible and should use net rates if they are not. The quantity θ is the probability that an $\cdot IO_2$ radical that is formed by step N2 and does not react by the reverse of that step will initiate the sequences of IX + ½ (X) that produces an HOIO molecule. Of course, θ will be a function of various concentrations and may be greater than or less than unity. If iodine can be photochemically oxidized by hydrogen peroxide in solutions containing little iodate ion, θ can be estimated.

Elementary iodine is in the mobile equilibrium of reaction A1, and the amount of iodine available to that equilibrium can change only if HOI is reduced by step B0 or if I^- is oxidized. Then we obtain eq 19. The derivation assumes that every $\cdot IO_2$ radical that reacts by step D2 initiates step H1, every $HOO\cdot$ radical reacting by step −Fi initiates the sequence of process IX, and step O1 is thus the only significant radical recombination reaction. To the extent that those assumptions are not valid, the equation will need to be modified.

$$d[I_2]/dt = k_{B0}[HOOH][HOI] - k_{A3}[H^+]^2[IO_3^-][I^-] - k_{A2}[H^+][HOIO][I^-] - 2\theta k_{N2}[H^+][IO_3^-][HOIO] \qquad (19)$$

Finally, we note that oxygen is produced only by step B0 and we obtain the equation

$$d[O_2]_{tot}/dt = k_{B0}[HOOH][HOI] \qquad (20)$$

The equilibrium of eq 11 and dynamic eq 17-20 are sufficient in principle to define the entire observable kinetic behavior of the system and to calculate the concentrations of all nonradical species at any time, provided θ is known as a function of the stoichiometrically significant species H^+, HOOH, IO_3^-, and I_2. In practice, we have found such a problem sufficiently formidable that we have satisfied ourselves with qualitative arguments to demonstrate the basic validity of the mechanism. It is helpful to refer to eq 21, obtained by a trivial manipulation of eq 11.

$$\frac{d[I^-]}{dt} = \frac{1}{K_{A1}[H^+][HOI]}\left\{\frac{d[I_2]}{dt} - \frac{[I_2]}{[HOI]}\frac{d[HOI]}{dt}\right\} \qquad (21)$$

Further Details during Process I Dominance. If the terms in k_{N2} and k_{A4} are neglected in eq 17-20, we recover eq 13-16, which have already been shown to be quantitatively valid when only process I is important. However, as the system approaches a switch to process II dominance, the simple kinetics are modified. While $d[I_2]/dt$ does not change greatly because a single term in eq 17 remains dominant, eq 21 shows that $[I^-]$ may go through a maximum earlier than $[I_2]$ does if $d[HOI]/dt$ is sufficiently positive.

Increased $[H^+]$ increases [HOIO] according to eq 14 and therefore increases the rate of N2 as the square of acidity. The influence of acid on step L0 will also serve to increase θ. Especially if θ is in the neighborhood of 0.5, small changes in acidity can therefore exert grossly magnified effects on the magnitudes of the k_{N2} terms. At low acidities, [HOI] and [HOIO] will increase rather slowly until the system reaches the switching condition discussed below, and $[I^-]$ will also continue to increase almost until the switching condition is reached (e15,21). If the acidity is greater, $d[HOI]/dt$ will be great enough that $[I^-]$ will go through a maximum well before switching is attained (e16,27). Because increased [HOOH] also will tend to increase θ, the first maximum in $[I^-]$ is particularly rounded when the system goes into a second induction period of smooth catalysis before any oscillations commence (e18).

Further Details during Process II Dominance. The situation is considerably more complicated when radical (e46) process XII is dominant. We have already shown how the stoichiometry of the process generates considerable amounts of oxygen at the same time that iodine is being oxidized (e11). The increase in radical reactions initiated by step N2 will cause [HOIO] and [HOI] to increase (e20) and $[I^-]$ to be less (e13) than when process I is dominant. Because I_2 is being consumed, [HOI] and [HOIO] will both be decreasing, but eq 21 shows that if $d[HOI]/dt$ is sufficiently negative then $d[I^-]/dt$ may be positive; this is always the situation in the oscillating systems we have observed (e14,17). If the system is in the smooth catalysis of the second induction period, $d[I^-]/dt$ may be negative.

We cannot account for all of the kinetic observations during this condition. Because increased [HOOH] increases θ, we can explain the dependence of $d[I_2]/dt$ on this variable (e31), but we are surprised that the effect of $[IO_3^-]$ is not larger (e34). Because acidity has so much effect on the qualitative behavior of the pI traces, we are also surprised it has so little effect on $d[I_2]/dt$ (e45).

Mechanism during Smooth Catalysis. The system sometimes goes through a single maximum in $[I_2]$ and then enters a nonoscillatory situation in which the concentration of iodine is determined by those of the three major reactants. During this condition, eq 22 should be substituted into eq 17 and 19 where $[I_2]_{ss}$ is the steady state concentration. It is probably a good enough approximation to use $d[I_2]/dt = 0$ for this condition.

$$\frac{d[I_2]}{dt} = \left(\frac{\partial[I_2]_{ss}}{\partial[HOOH]}\right)_{[IO_3^-],[H^+]} \frac{d[HOOH]}{dt} \tag{22}$$

This smooth catalysis condition arises because there is so much hydrogen peroxide that θ is large, radical chain lengths are long, and $[I^-]$ does not increase enough to switch the system out of process II dominance. In accordance with this interpretation, increased [HOOH] will lengthen the second induction period (e32), while increased $[IO_3^-]$ will speed up hydrogen peroxide consumption and shorten the second induction period (e35). Because increased hydrogen peroxide increases θ, the concentration of iodine at the time of switching is less at greater [HOOH], and this fact is consistent with the claim of Liebhafsky and Wu[20] that $[I_2]$ and [HOOH] are proportional during smooth catalysis (e8,47).

Effects of Acidity on Rate. The Bray–Liebhafsky reaction is very dependent upon acidity. Oscillations only occur when the pH is within less than 0.2 units of 1.3. The pK of iodic acid, $HOIO_2$, is[21,64] 0.78 at 25 °C and 0.95 at 50 °C, and the pK of iodous acid, HOIO, can be estimated[65] to be about 2. Hypoiodous acid, HOI, is not significantly ionized, but 50% protonation occurs[18,37] at a pH of about 2.9. Rates of many of our reactions will depend strongly upon pH, and any interpretation of acidity effects will have strong overtones of rationalization.

Acidity clearly promotes the radical oxidation of iodine by process XII, and this fact is consistent both with initiation step N2 and the possibility that radical propagating step L0 is partially in competition with termination. The effect on initiation step N2 explains why the systems at higher acidity are less sensitive to parallel radical initiation by light (e24,28), and the effect on (L0) explains why systems at high acidity are less sensitive to changes in oxygen pressure (e24,28). The increased rate of initiation N2 at high acidity also explains why the $[I^-]$ traces are more rounded as conditions for ending process I dominance are approached (e21,27).

Effects of Light and Oxygen. A number of other experimental observations can also be rationalized. The above discussion has accounted for the effects of changes in the concentrations of major reactants. Light can also influence behavior by increasing the rate of radical formation, and oxygen can promote steps K0 and L0 and thereby increase θ. At high acidity, radical formation due to step N2 will already be rapid, and step L0 will be facilitated sufficiently that other steps determine the chain length; therefore light and oxygen will be more important at low acidity than at high acidity (e6,24,41). Oxygen will have little effect on rate when nonradical process I is dominant (e36), will promote radical process XII (e37), will increase the frequency of oscillation at low acidity when process I is dominant most of the time (e38), and will inhibit oscillations at high acidity by maintaining the system in the radical condition of smooth catalysis (e39). It is not surprising that flushing the system with nitrogen opposes oxygen effects (e40) and that exposure to light exerts effects similar to increased oxygen pressure (e42).

Mechanism of Switching. One of the most dramatic features of this reaction involves the almost discontinuous changes in sign of $d[I_2]/dt$ and $d[O_2]/dt$ as the system switches between dominance by two very different reactions (e3,10). Our experience with the Belousov–Zhabotinsky reaction[43] suggests that this kind of switching can occur if some intermediate is formed by processes that are zero and first (autocatalytic) order in its concentration and is destroyed by processes that are first and second order. The species X in the Oregonator[60] model is just such an intermediate.

Examination of eq 18 suggests that HOIO also can function as such an intermediate. When process I is dominant, we can neglect the term in k_{A4} and write an approximate expression for $[HOIO]_{small}$. When process II is dominant, we can neglect the term in k_{A3} and write an approximate expression for $[HOIO]_{large}$. Switching will occur whenever $[I^-]$ passes the critical value of eq 25.

$$[HOIO]_{small} = \frac{k_{A3}[H^+]^2[IO_3^-][I^-]}{k_{A2}[H^+][I^-] - (2\theta - 1)k_{N2}[H^+][IO_3^-]} \approx \frac{k_{A3}}{k_{A2}}[H^+][IO_3^-] \tag{23}$$

$$[HOIO]_{large} = \frac{(2\theta - 1)k_{N2}[H^+][IO_3^-] - k_{A2}[H^+][I^-]}{2k_{A4}} \approx \frac{(2\theta - 1)k_{N2}}{2k_{A4}}[H^+][IO_3^-] \tag{24}$$

$$[I^-]_{crit} = \frac{(2\theta - 1)k_{N2}}{k_{A2}}[IO_3^-] \tag{25}$$

This explanation is in at least qualitative agreement with the observations. When process I is dominant, the system can be described by $[HOIO]_{small}$ and the concentration of iodine steadily builds up. Because the comparatively inert HOO· radicals must react with iodine to initiate its oxidation, θ will steadily increase until the system goes critical and the concentration of iodous acid switches to $[HOIO]_{large}$. The rate constants in Table III suggest that the two concentrations differ by a factor of about 100. This large concentration promotes radical formation by N2, and radical process II (or rather XII) becomes dominant with consumption of iodine. This consumption of iodine reduces θ until the critical condition is again attained, and the system switches back to process I dominance. Because θ is smaller at high radical concentrations when termination by O1 is more important, the switch from XII to I dominance will take place at a smaller $[I^-]$ than does that from I to XII dominance (Figures 3 and 4).

In section S7 of the supplemental material accompanying the microfilm edition, we point out why the switching phenomenon requires that HOO· radicals react by reducing iodine molecules (−Fi) rather than by oxidizing iodide ion (−E0).

Instability of Steady State. Even the above discussion of mechanistic complications is not sufficient to explain why the system oscillates instead of going to a stable steady state in which the concentration of HOIO is intermediate between the extremes of eq 23 and 24! That explanation requires a consideration of the effect of oxygen concentration on $d[I_2]/dt$.

Figure 7 contains a number of plots of $d[I_2]/dt$ against $[I_2]$ at constant oxygen pressure. At low iodine concentrations, process I is dominant and the positive rate increases slowly with increasing $[I_2]$ (e2). As iodine increases, θ grows and radical oxidation of iodine becomes more and more important until the switching condition is attained, and the system moves almost discontinuously to net iodine consumption by process XII with simultaneous increase in oxygen production. The experiments of Liebhafsky[7] suggest that the (negative) rate is now proportional to $[I_2]$ by eq 2. Curve a in Figure 7 has been drawn for this behavior.

If the oxygen concentration is increased, the equilibrium K0 and the rate of step L0 are increased so that θ is larger and the rate of process XII is also larger. Therefore, increased oxygen concentration would have little effect for positive $d[I_2]/dt$, but will shift to the left of the curve in regions where process XII is significant. Because gas evolution process P has a finite rate constant, homogeneous oxygen concentration will be monotonically related to the rate of oxygen formation in the solution. The continuous curves a to f in Figure 7 are each drawn for constant oxygen concentrations corresponding to those that would be steady states for the $d[I_2]/dt$ values marked with the same letters on the axis. The dashed curve in Figure 7 gives $d[I_2]/dt$ as a function of $[I_2]$ for the condition that oxygen is at the steady-state concentration corresponding to the rates of reaction in the system. The dashed curve in Figure 7 crosses the axis with a positive slope, demonstrating that the steady state is unstable to perturbations that couple oxygen production to the change in iodine concentration, even though the same steady state is stable to perturbations that maintain constant oxygen concentration.

Application of the proposed mechanism to Figure 7 explains a number of the experimental observations. If concentrations of H^+ and HOOH are large, the rate of radical process XII is also large, the concentration of I_2 at the steady state is small, and the concentration of dissolved oxygen is large. Because of the high oxygen concentration, the equilibrium of K0 is shifted to the right so that most iodine atoms are peroxidized and small changes in oxygen concentration have little effect on the rate of step L0 or on θ. Therefore, the continuous curves at different oxygen concentrations in Figure 7 will be close together, and the dashed curve will cross the axis with a steep slope that may not even be positive. Under such conditions, the steady state will be stable, and the system will exhibit the smooth catalysis of the second induction period (e26). As hydrogen peroxide is consumed by that catalysis, the oxygen concentration decreases, the spacings between continuous curves in Figure 7 increase, the steady state becomes unstable, and the second induction period is followed by oscillation (e7). The length of that second induction period is lengthened by increased initial concentration of hydrogen peroxide (e32) and is shortened by increased iodate (e35).

If the acidity is low, the rate of radical process XII is less, and the concentration of I_2 is greater at the steady state. Because rates are less, oxygen concentrations are also less, the probability that reaction L0 will take place before chain termination is less, and the system will be more dependent on oxygen concentration with corresponding increased separation of the continuous curves in Figure 7. Then the system that has reached the steady state will go into oscillation without a second induction period at the hydrogen peroxide concentrations we employed (e5,23), and the amplitudes of the oscillations will be greater than at higher acidities (e22).

At sufficiently low acidities, process I will remain dominant until the solution becomes saturated with iodine, and the system will not attain oscillations (e25).

It is useful to show that Figure 7 is indeed consistent with the analysis that developed Figure 6, if $[I_2]$ is equated to S and $[O_2]$ is equated to U. Curves a to f in Figure 7 represent increasing oxygen concentration, and they cross the axis at steadily smaller concentrations of I_2. Therefore, the ABCDE curve for $\dot{S} = 0$ in Figure 6 has a negative slope and is monotonic. The AB segment corresponds to saturation with solid iodine and is not a region of oscillations. As S gets smaller, $\dot{S} = 0$ occurs at greater U with the slope getting steeper, corresponding to decreasing intervals at which curves cross the axis in Figure 7.

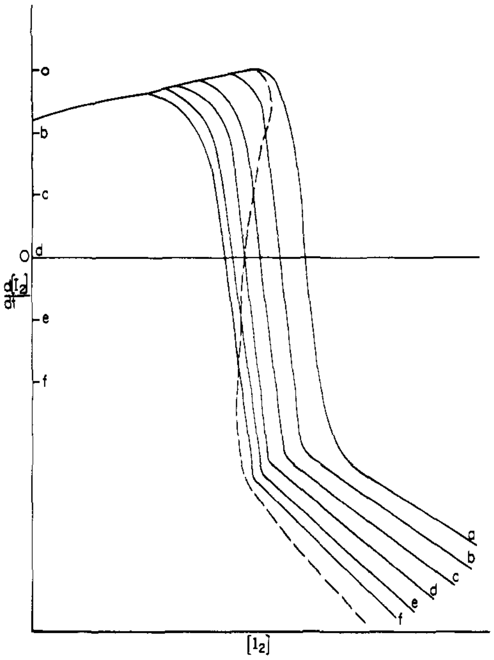


Figure 7. Curves a to f are plots of $d[I_2]/dt$ against $[I_2]$ for constant oxygen concentrations to be expected at steady states for $d[I_2]/dt$ values designated a to f on axis. Dashed curve is the plot for a system in which oxygen concentration responds rapidly enough to maintain its steady-state value for instantaneous rate of change of iodine. Note that when $d[I_2]/dt = 0$ the dashed curve has a positive slope, so that a fluctuation along that curve that changes $[I_2]$ will change the rate in a direction to amplify that fluctuation and to make the steady state unstable.

When $S \gg 0$, the steady-state $[O_2]$ is small and increases very little with increasing $[I_2]$, the FG portion of the continuous $U = 0$ curve in Figure 6 is almost horizontal. When $S \ll 0$, oxygen is produced rapidly by process XII, and U is large for the HI portion of the continuous $U = 0$ curve in Figure 6. The rapid transition from G to H takes place when S is not greatly different from zero, and the steady state at point C exhibits just the characteristics necessary for instability.

The dashed curve JKDLM corresponds to a system at high acidity and high [HOOH] where the $S = 0$ curve is so steep that the $\dot{U} = 0$ curve does not have a negative slope at the steady-state point D. Such a system would be in the smooth catalysis of a second induction period and would not oscillate until the crossing point had moved down closer to C.

The above arguments are primarily qualitative in nature, but they account so well for so many specific features of the mechanism that our interpretation could hardly be in major error.

Discussion

Summary of Mechanism. It is probably useful to summarize here the mechanism as developed. When sufficient iodide ion is present, iodate is reduced by hydrogen peroxide by a sequence involving four steps.

$$IO_3^- + I^- + 2H^+ \rightarrow HOIO + HOI \qquad (A3)$$

$$HOIO + I^- + H^+ \rightarrow 2HOI \qquad (A2)$$

$$HOI + HOOH \rightarrow I^- + O_2 + H^+ + H_2O \qquad (B0)$$

$$HOI + I^- + H^+ \rightleftarrows I_2 + H_2O \qquad (A1)$$

Steps A3 and A2 have the net effect of reducing IO_3^- to HOI. Step B0 regenerates the I^- necessary for that reduction and maintains $[I^-]$ much greater than it would be in the absence of hydrogen peroxide. The rapid hydrolysis equilibrium

A1 is far enough to the right that virtually all of the reduced iodine is present as I_2.

If these steps are combined so that there is no net change in the concentrations of stoichiometrically insignificant intermediate species, the sequence 2(A3) + 2(A2) + 5(B0) + A1 generates the stoichiometry of process I.

$$2IO_3^- + 5HOOH + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O \tag{I}$$

Although hydrogen peroxide is also thermodynamically capable of oxidizing iodine to iodate, all direct oxygen transfer reactions are slow. Therefore, nonradical processes cause net reduction of iodate to iodine by process I, and additional catalyzed nonradical decomposition of hydrogen peroxide is of negligible importance. If no radicals are present, $[HOIO] = (k_{A3}/k_{A2})[H^+][IO_3^-]$ and is a few times 10^{-10} M.

Although nonradical reactions cause net reduction of iodate, the radicals $\cdot I$ and $\cdot IO_2$ can be oxidized by hydrogen peroxide, but cannot be reduced by it. Therefore, radical processes cause net oxidation of iodine to iodate. In the dark, reaction N2 is the only one that can produce radicals at a significant rate. Steps D2 and H1 follow rapidly, and the net result is the formation of $HOO\cdot$ radicals by process VII. Note that one HOIO molecule is consumed for each pair of radicals produced.

$$IO_3^- + HOIO + H^+ \rightarrow 2\cdot IO_2 + H_2O \tag{N2}$$

$$\cdot IO_2 + HOOH \rightarrow IO_3^- + H^+ + HO\cdot \tag{D2}$$

$$HO\cdot + HOOH \rightarrow H_2O + HOO\cdot \tag{H1}$$

$$HOIO + 4HOOH \rightarrow IO_3^- + H^+ + 3H_2O + 2HOO\cdot \tag{VII}$$

The relatively inert $HOO\cdot$ radicals will ultimately recombine by step O1 if they do not participate in a step that generates another kind of radical.

$$2HOO\cdot \rightarrow HOOH + O_2 \tag{O1}$$

Each of the radical species has only one principal reaction with nonradical species; such a reaction must necessarily generate another radical. A sequence of five of these reactions is necessary to generate a chain by which the initial HOO is regenerated, and the net chemical change of process IX is simultaneously accomplished.

$$HOO\cdot + I_2 \rightarrow I^- + O_2 + H^+ + \cdot I \tag{$-$Fi}$$

$$\cdot I + O_2 \rightleftarrows \cdot OOI \tag{K0}$$

$$\cdot OOI + I^- + H^+ \rightarrow HOI + \cdot IO \tag{L0}$$

$$\cdot IO + HOOH \rightarrow HOIO + HO\cdot \tag{D1}$$

$$HO\cdot + HOOH \rightarrow H_2O + HOO\cdot \tag{H1}$$

$$I_2 + 2HOOH \rightarrow HOIO + HOI + H_2O \tag{IX}$$

Let θ be the efficiency with which a radical formed by step N2 initiates the chain sequence of process IX. Termination by radical-radical reactions like step O1 will be in competition with the completion of process IX, and in most of our solutions θ probably differs from unity by a factor much less than ten. When θ is less than 0.5, process I will be dominant because iodate reacts by step A3 more rapidly than it does by step N2. However, θ will be increased by increases in the concentrations of both I_2 and O_2. Whenever process I increases $[I_2]$ until θ sufficiently exceeds 0.5, the net effect of VII + 2(IX) will cause [HOIO] to increase autocatalytically in spite of destruction by step A2. As [HOIO] increases, second-order process A4 becomes more important, and the system approaches a steady state in which $[HOIO] = [(2\theta - 1)k_{N2}/2k_{A4}][H^+][IO_3^-]$, which is a few times 10^{-8} M.

$$2HOIO \rightarrow IO_3^- + HOI + H^+ \tag{A4}$$

If step A2 is neglected, and if all of the other processes are combined in such a way that there is no net formation or destruction of stoichiometrically insignificant species, the net stoichiometry of process XII is generated.

$$I_2 + 11HOOH \rightarrow 2IO_3^- + 3O_2 + 2H^+ + 10H_2O \tag{XII}$$

When $[I_2]$ has increased enough for θ to exceed 0.5, the autocatalytic increase in [HOIO] and the accompanying increase in [HOI] from process IX will both act to reduce $[I^-]$ by reactions A1 and A2, and reduction of iodate by process I will become less important at the same time that the oxidation of iodine by process XII is becoming more important. We would normally expect such a situation to generate a stable steady-state concentration of iodine such that processes I and XII go at equal rates, and the net effect is the catalyzed decomposition of hydrogen peroxide. Precisely such a situation occurs in solutions with high concentrations of acid and hydrogen peroxide. However, at lower concentrations of these species, the steady state becomes unstable because of the time lag associated with the equilibration of step P. This equilibration apparently involves a time constant of the order of min^{-1} even in well-stirred solutions.

$$O_2(aq) \rightleftarrows O_2(g) \tag{P}$$

When process I is dominant, $[I_2]$ increases until θ exceeds 0.5. The rapid onset of process XII then increases the concentration of dissolved oxygen and further increases θ, so that it remains above the critical value even though $[I_2]$ is being decreased by the dominance of process XII. Eventually, $[I_2]$ decreases enough that θ falls to near 0.5 in spite of the high concentration of dissolved oxygen, and the steady state for process XII can no longer be maintained. As the system switches back to dominance by process I, the excess of dissolved oxygen is vented and $[I_2]$ must again increase appreciably before θ exceeds 0.5 and process XII can regain dominance. Oscillations will thus proceed with net destruction of hydrogen peroxide.

Potential Validity of Mechanism. The mechanism we have developed is quite complicated, and many people will argue that it can have little claim to uniqueness for interpreting the facts. In contrast, we assert that the great complexity of this system is an asset for establishing the uniqueness of our mechanism. We have observed a wealth of unusual experimental detail and have accommodated it directly to a small number of elementary processes consistent with the independent thermodynamic and kinetic evidence. Moreover, the rate and equilibrium parameters we find necessary for treating this oxyiodine system correlate well with what is known about oxybromine and oxychlorine chemistry.

There are remarkably few loose ends! We have tried to consider all conceivable thermodynamically allowed processes consistent with the general stoichiometric constraints we imposed. As we tried to accommodate the various possibilities to observed experimental detail, we have been amazed again and again as all possibilities except one became untenable, and that one remained clearly consistent with what was known. The mechanism as presented in Table II is clearly oversimplified in that O1 is the only radical termination step that has been included. In section S5 of the supplemental material, we admit the possibility that $-$A3 as well as A4 contributes to iodate formation during process II dominance, although the subsequent quantitative discussion of rate constants makes such a contribution unlikely. Otherwise, we see no alternative elemontary processes that are even moderately attractive! Such a large body of experimental detail is simultaneously consistent with our explanation that we doubt that the true molecular mechanism can differ significantly from what has been proposed here.

Implications for Peroxide Chemistry. This whole complicated structure is driven by the free-energy change from the disproportionation of hydrogen peroxide to oxygen and water. The complexities are possible only because certain processes that are thermodynamically allowed are kinetically slow. The mechanism as elucidated has emphasized a number of facts about this peculiar material.

Various possible reactions can be classified as to whether hydrogen peroxide is oxidized or reduced. They can also be classified as to whether or not species derived from hydrogen peroxide have an even number of electrons at all times, and the even-electron reactions can be further classified as to whether the peroxide behaves as a nucleophile or as an electrophile.

When hydrogen peroxide is reduced to water, the O-O bond must be broken. When hydrogen peroxide is oxidized to oxygen, the O-O bond might be broken, but need not be. The isotopic studies of Cahill and Taube[50] demonstrate that it usually is not broken whether the process involves an even or an odd number of electrons.

When hydrogen peroxide behaves as an electrophile, it is necessarily reduced with rupture of the O-O bond. Iodide ion and other monatomic even-electron reducing agents must certainly react in this way, perhaps attacking an OOH_2 tautomer of HOOH. However, we find this reaction is rather slow kinetically, even though it is strongly favored thermodynamically.

The oxy acids and oxy anions of many elements can also oxidize or reduce hydrogen peroxide by even-electron processes. When the peroxide is oxidized, it is hardly conceivable that two hydrogens are abstracted in a concerted process that simultaneously reverses an electron spin to form triplet oxygen. It appears, rather, that the hydrogen peroxide behaves initially as a nucleophile to displace a water molecule and form a peroxy acid intermediate. Thus, $HOIO_2$ presumably first forms $HOOIO_2$, which then tautomerizes and decomposes to HOIO + O_2 with both oxygens coming from the original peroxide. In the section on permissible component reactions, we mention kinetic evidence by Liebhafsky[6] that suggests just such an intermediate in reaction B2.

When hydrogen peroxide is reduced by an oxy anion like $HOSO_2^-$, it might conceivably function either as an electrophile, as it does with iodide ion, or as a nucleophile. The isotopic studies of Halperin and Taube[66] demonstrate that for this particular example the reaction is XIII. This observation seems to require that the hydrogen peroxide functions first as a nucleophile even with this strong reducing agent. The peroxy species $HOOIO_2$ and $HOOSO_2^-$ are isostructural. The potentials are such that the iodine compound might go either to $I^{3+} + O_2$ or to I^{7+}; the first products are more favored and are observed. The heavy iodine may help this result by catalyzing the change of electron spin so that triplet oxygen is produced before the complex has time to rearrange. The sulfur compound might conceivably go to an unknown S^{2+} species or to the observed S^{6+}, and thermodynamics probably determines the outcome.

$$HSO_3^- + HO^*O^*H \rightarrow HSO_2O^*{}_2^- + H_2O \quad \text{(XIII)}$$

We conclude that when hydrogen peroxide reacts in an even-electron process, it will preferentially behave as a nucleophile in the initial step, even though it is ultimately reduced rather than oxidized.

Hydrogen peroxide may be oxidized by an odd-electron reagent that abstracts a hydrogen atom and may be reduced by one that breaks the O-O bond with formation of HO· radical. The potentials in Chart II demonstrate that only a very strong 1-equiv oxidant can oxidize hydrogen peroxide, while the reduced form of a much weaker oxidant can reduce it. Thus Fe^{2+} can reduce hydrogen peroxide by direct attack,[67] even though Fe^{3+} cannot oxidize it. We find similarly that ·I and $\cdot IO_2$ radicals are thermodynamically capable of reducing hydrogen peroxide, and at least the latter must do so in our mechanism; however, they are incapable of oxidizing it. Although ·IO radicals are capable, in principle, of both oxidizing and reducing hydrogen peroxide, the reduction must be kinetically favored if our mechanism is to be acceptable.

Like other radicals, H atoms can reduce hydrogen peroxide with HO radical formation.[63] However, HOO radicals do not function in this way[52] in spite of a favorable potential. Nevertheless, the discussion in section S7 of the supplemental material indicates that HOO· can act as a 1-equiv reductant to rupture the I-I bond, even though it does not react this way at a reasonable rate with the HO-OH bond. It may be significant that only in the I_2 case can the reaction be accomplished by simple electron transfer from HOO· without simultaneous physical transfer of a proton.

In summary, hydrogen peroxide reacts preferentially as a nucleophile rather than as an electrophile with even-electron reagents, but the final products of reaction may correspond to either oxidation or reduction, depending upon the chemistry of the reagent involved. With odd-electron reagents, reduction to form HO· radical is generally favored over hydrogen abstraction to form HOO· radical even when both are possible. These facts are vital to the mechanism developed here and suggest that there may be other systems where these peculiar mechanistic preferences can use the stored energy of hydrogen peroxide to chemical advantage.

Implications for Other Chemical Oscillators. Now that both the Belousov-Zhabotinsky[43] and the Bray-Liebhafsky oscillators are understood, we can begin to generalize the reaction features to look for when developing similar systems. It appears that for any chemical oscillator, the system must permit two net processes which generate different final products and both of which are thermodynamically favored. One and only one of these processes can go at a reasonable rate by even-electron processes, and the other must be facile when odd-electron reagents are present. Finally, if the system is to switch repeatedly between dominance by one or the other of the two processes instead of going to a stable steady state, the radical process must be turned on rapidly by an autocatalytic buildup of the appropriate reactants and the pseudosteady state so formed must evolve for a while before it can switch back again.

We believe these principles will have general applicability to chemical oscillators. We also believe they will apply to the biochemical processes in living organisms, where control mechanisms will once or repeatedly switch between alternative types of behavior. If the system is confined to the first-row elements with the s and p orbitals of conventional organic chemistry, free-radical processes are usually energetically prohibitive and are unlikely as components of biochemical processes. The transition elements from the third row of the periodic table use d orbitals and can undergo odd-electron reactions much more easily. It is tempting to suggest that enzymes employing trace amounts of transition metals will be important to the processes of biochemical control for starting and stopping major avenues of chemical activity.

Concluding Remarks

The argument as presented has relied heavily upon the method of Holmes.[36] That method makes for excellent fiction, but its application to science is always suspect because we can never be sure we have indeed eliminated all other possibilities. Such an uncertainty actually applies even to the most firmly established molecular mechanism, and our confidence will always be a matter of degree. We have tried here to impose clearly defined stoichiometric and thermodynamic constraints and to relax them only as far as was necessary in order to obtain an acceptable mechanism. Thus, we at first imposed a constraint that no free radical could change its oxidation state by more than 1 equiv in a single elementary process, and we found it was then impossible to accommodate the experimental facts. Reaction types J, L, and M were considered only because it was impossible to exclude them. We had almost completed writing the manuscript before we realized the phenomenon of switching permitted us to say cleanly that HOO· radicals reacted by reducing iodine molecules −Fi and not by oxidizing iodide ions −E0.

Many other examples could be cited. The development of this mechanism has been a tortuous process. Often the whole effort seemed ready to collapse like a house of cards. A truly intractable experimental fact could still destroy the whole structure. We can only assert that many, many hours of search have been unable to locate that fact!

The postulating of chemical mechanisms has justifiably developed a bad reputation because many very fanciful mechanisms have been proposed on the basis of small amounts of experimental fact and without regard for other available information. We believe the solution for this problem is not to abandon hope of understanding chemical mechanisms, but to apply to a system all potentially relevant information that can be obtained from valence theory, stoichiometry, redox potentials, bond energies, and kinetic behavior in related systems. Precisely because these chemical oscillators are so complex, the wealth of available information makes it easier to reject false mechanistic hypotheses. This is the second time[43] that after protracted consideration and very many blind alleys we have come upon a mechanism that suddenly accommodated a large number of previously mystifying observations. When such a situation arises, the transition is so sharp that it removes any doubt as to the basic validity of the interpretation so developed.

Chemical reactions can involve very complicated combinations of elementary processes. However, most of those processes can be classified into relatively few categories, such as electron transfers, atom abstractions, nucleophilic displacements, homolytic and heterolytic bond scissions, etc. An ever growing body of information exists about energetics and rates of such processes. Techniques are also being developed[33] for showing how consecutive and competitive combinations of reversible and irreversible elementary processes can generate the observable manifestations of net chemical change in real systems. The success in elucidating the mechanisms of chemical oscillators shows we no longer need fear to examine a complicated system. It is our hope that the present paper will suggest some techniques that may help to fit complicated chemical reaction mechanisms into a truly unified science of chemical theory.

Additional Information. After this manuscript had been completed, we learned from Dr. Gidon Czapski[68] that the reduction potential of O_2 to HOO· is probably −0.037 V instead of −0.13 V as reported here. The changes that would result from using the revised figure would not be sufficient to justify the work of revising the entries in the tables.

Experimental Section

Materials. Analytical Reagent KIO_3 (Mallinckrodt) was recrystallized before use. Inhibitor-free 30% hydrogen peroxide (Mallinckrodt) was used; its absolute concentration was determined by titration with standardized permanganate. The only other reagent was analytical reagent $HClO_4$; its absolute concentration was also determined by titration. All solutions were made in triply distilled water.

Analytical Procedures. Iodine was followed spectrophotometrically with a Cary 14 recording spectrophotometer in a 10-mm quartz cell thermostated at 50.0 ± 0.2 °C. Measurements were made at 465 nm. The absolute value of iodine concentration was calibrated with solutions in which a known amount of iodide was added to an excess of iodate in 0.05 M perchloric acid. The molar extinction coefficient of iodine in this system was 740 M^{-1} cm^{-1}. When the Bray reaction was being followed spectrophotometrically, solutions were stirred with a small magnetic stirrer. Especially at low acidities, behavior was quite sensitive to the way in which the cell was stoppered.

Iodide ion was followed potentiometrically with an Orion Model 94-95 ion specific electrode in conjunction with an Orion Model 90-02-00 double junction reference electrode and an Orion Model 1400 IONALYSER. The signal was applied to a Leeds and Northrop Speedomax recorder, which could accept two inputs when oxygen was simultaneously followed. The system was calibrated with iodide solutions of known concentration.

The concentration of dissolved oxygen was also followed potentiometrically with a Beckman Oxygen Macro Electrode briefly described previously.[28]

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Supplementary Material Available: Many of the details of our mechanistic arguments have only been summarized above, but are presented in sections S1 to S7 (41 pages). Ordering information is given on any current masthead.

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A Simple Theoretical Molecular Orbital Model for Five-Membered Heterocycles

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Abstract: A one-electron MO approach is utilized to discuss the physical properties of heteroaromatic five-membered rings (C_4H_4X). The observed changes in geometry, resonance energy, and PE spectra as X is varied are adequately rationalized. The question of d-orbital participation when X is a second period element is discussed. In most cases, it is found that d-orbital participation is not necessary for the qualitative rationalization of trends, although its presence cannot be excluded. The electophilic substitution patterns in these molecules as well as their benzo derivatives are discussed along the same lines.

The physical and chemical properties of C_4H_4X heteroaromatic five-membered rings change dramatically as the heteroatom X is changed from a first row element to a second row element.[2a] It has been suggested that participation of empty, low-lying d orbitals in the case of the second row element can account for the observed differences. Longuet-Higgins has utilized a molecular orbital (MO) model including d orbitals in order to rationalize the difference between thiophene and furan.[3] However, dramatic changes are also noted as the heteroatom is changed from an element in one column of the periodic table to an element of the adjacent column but same row.[2b] Obviously, these changes cannot be explained by invoking d-orbital participation. In this paper, we wish to present a one-electron MO (OEMO) approach with neglect of overlap that is capable of explaining the differences observed in five-membered ring heteroaromatic compounds. In particular, we wish to compare the chemical and physical properties of furan and thiophene, a case where the heteroatom is changed from one row to another, and to make the analogous comparison between furan and pyrrole, a case where the heteroatom is changed from one column to another. The approach should only be used when comparing heteroaromatics that are similar, e.g., furan vs. thiophene and furan vs. pyrrole, but not pyrrole vs. thiophene.

The model consists of the π MO's of butadiene interacting with the heteroatom lone pair atomic orbital (AO). The typical interaction diagram (for furan) is shown in Figure 1. We have labeled the orbitals as symmetric (S) or antisymmetric (A) with respect to a mirror plane that bisects the five-membered ring. The interaction between the lowest filled MO of the butadiene fragment and the p_z AO of X results in neither stabilization nor destabilization, since overlap has been neglected. Consequently, the primary interaction of interest is between the lowest unfilled MO (LUMO) of the butadiene fragment and the p_z AO of the heteroatom. This interaction results in net stabilization given by the expression[4]

$$\mathrm{SE} = H_{ij}{}^2/\Delta\epsilon \tag{1}$$

where SE is the stabilization energy, H_{ij} is the off-diagonal matrix element of the interacting MO's, i.e., $\int \phi_i H \phi_j \, d\tau$, and $\Delta\epsilon$ is the difference between the unperturbed energies of the interacting MO's. The matrix element will be approximated in the usual manner, that is,[5]

$$H_{ij} = kS_{ij} \tag{2}$$

where S_{ij} is the overlap integral between ϕ_i and ϕ_j and k is a constant. The stabilization energy is then

$$\mathrm{SE} = k^2 S_{ij}{}^2/\Delta\epsilon \tag{3}$$

Using this simple model we shall now investigate the chemical and physical differences between furan and thiophene and between furan and pyrrole.

Ground-State Geometries

The ground-state geometries of furan,[6] thiophene,[7] and pyrrole[8] are shown below. The C(1)-C(2) bond length in furan is considerably shorter than in thiophene or pyrrole. Likewise,