A Generalized Mechanism for Bromate-Driven Oscillators Controlled by Bromide[1]

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Abstract: Concentrations of intermediates oscillate for five different classes of reaction involving oxidation of an organic substrate by acidic bromate. Class i involves a substrate like malonic acid that easily forms a bromide whose oxidation liberates bromide ion; the reaction requires a redox catalyst like cerous iron or ferroin. Class ii involves a derivative of phenol or aniline that can be oxidized to a quinoid species; no catalyst is necessary. Class iii involves a mixed substrate like acetone (that brominates without being oxidized) and tartaric acid (that oxidizes without bromination); the reaction requires a redox catalyst. Class iv involves an easily oxidizable substrate like oxalic acid and a redox catalyst; oscillations occur only if excess bromine is scrubbed with an inert carrier gas. Class v involves a system of class i to which silver nitrate has been added; the concentration of bromide ion no longer oscillates, but the potential of a platinum electrode does. A single generalized mechanism can explain oscillations in all five classes, and for each class we present a set of elementary processes generating the proper stoichiometry for oscillation. Class v exhibits some special features that will be treated in a subsequent publication. Substitution-labile species like ceric ion and substitution-inert ones like ferroin differ so much in behavior that it may become appropriate to split class i. Thermodynamic and kinetic constraints can also be generalized to rationalize the sensitivity of these systems to oscillation. A particularly significant kinetic constraint is that none of the oxidants can accomplish an elementary process that inserts an oxygen atom into a C–H bond. The basic mechanisms of bromate-driven oscillators are now understood, and refinements can be accomplished by quantitative studies of the effects of changing organic substrate and redox catalyst.

Introduction

It is over 20 years since Belousov[2] observed repeated oscillations in chemical composition during oxidation of citric acid by acidic bromate catalyzed by cerium salts. As a result of interest thus stimulated, workers in several laboratories have now identified five distinct classes of oscillating reactions each resulting from the oxidation of an organic substrate by acidic bromate:

(i) The "classical" Belousov[2]–Zhabotinsky[3] (BZ) designation is probably best reserved for metal ion catalyzed reactions in which the organic substrate can be brominated by an enolization mechanism and in which bromide ion is liberated when the resulting organic bromide reacts with the oxidized form of the catalyst. Körös et al.[4] identify two different kinds of catalysts. The oxidized forms of Ce(III) and Mn(II) are labile to ligand substitution and have reduction potentials of about 1.5 V. The oxidized forms of $Fe(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$ are inert to substitution and have reduction potentials of about 1.0–1.3 V. Kasperek and Bruice[5] list a number of aliphatic substrates that exhibit oscillations during cerous ion catalysis, but malonic acid has probably been studied more than any other. A detailed mechanism was first proposed by Field, Körös, and Noyes[6] (FKN), and the principal features of that mechanism are strongly supported by the modeling computations of Edelson.[7,8]

(ii) Körös and Orbán[9,10] have recently reported a class of oscillations that do not require any metal ion catalysts. The substrates presently known[10] are all derivatives of phenol or of aniline. They are easily brominated, but the resulting compounds do not react to form bromide ion. Oxidation products include quinones, quinone imines, and polynuclear aromatic compounds. Orbán, Körös, and Noyes[11] (OKN) have shown how these oscillations

can be explained by a rather minor modification of the FKN[6] mechanism for catalyzed oscillators, and Field[12] has conducted model calculations that support this proposal.

(iii) Rastogi, Singh, and Singh[13] have recently reported cerous-catalyzed oscillations with a mixed substrate of tartaric acid and acetone. Nosztieczius[14] reports similar results with oxalic acid and acetone and notes the absence of the induction period customary with cerous-catalyzed BZ[2,3] systems. Both tartaric and oxalic acids can be oxidized but do not brominate while acetone brominates but is not oxidized in the presence of the other compounds. These oscillations with mixed substrates cannot be accommodated to the FKN[6] mechanism in its original form, and some modification will be necessary.

(iv) Nosztieczius and Bódiss[15] have reported cerous-catalyzed oscillations with oxalic acid alone as substrate, provided elementary bromine is scrubbed from the solution by a stream of inert gas. This observation is also inconsistent with the original FKN[6] mechanism.

(v) The oscillations in the four classes above can be followed either visually with an oxidation–reduction indicator or electrochemically either with a platinum electrode or with an electrode specific to bromide ion. Nosztieczius[16] has recently reported that addition of silver nitrate to a "classical" BZ[2,3] system can temporarily suppress oscillations of a bromide-specific electrode while the potential of a platinum electrode still oscillates.
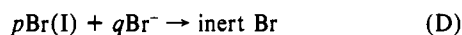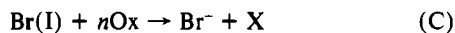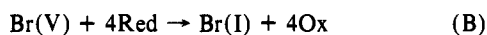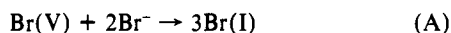
The first four of the above classes switch rapidly between conditions of relatively large and small concentrations of bromide ion whenever [Br⁻] passes through a certain critical value. The object of this paper is to show that oscillations in these four systems can all be explained by a generalized mechanism obtained by minor modification of the FKN[6] and OKN[11] mechanisms. We also present thermodynamic and kinetic justifications for the generalization. Although class v oscillations can also be explained by the same mechanism, switching is controlled by the concentration of hypobromous acid (HOBr) rather than by that of the bromide ion (Br⁻). Such control has not previously been invoked, and a detailed justification is best left for a subsequent manuscript.

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(14) Nosztieczius, Z. *Magy. Kem. Foly.* **1979**, *85*, 330.

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The Generalized Mechanism

The behaviors in these classes can all be described by invoking four component stoichiometric processes designated (A)–(D). In
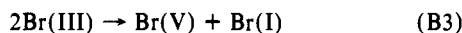
$$Br(V) + 2Br^- \rightarrow 3Br(I) \qquad (A)$$

$$Br(V) + 4Red \rightarrow Br(I) + 4Ox \qquad (B)$$

$$Br(I) + nOx \rightarrow Br^- + X \qquad (C)$$

$$pBr(I) + qBr^- \rightarrow inert\ Br \qquad (D)$$

these processes, roman numerals in parentheses refer to oxidation states of bromine such as HOBr, HBrO$_2$, BrO$_2\cdot$, and BrO$_3^-$ for I, III, IV, and V, respectively. Other notations are explained during discussion of specific processes.

Process (A) is the net consequence of two successive pseudoelementary processes A1 and A2. In the strongly acidic media

$$Br(V) + Br^- \rightleftarrows Br(III) + Br(I) \qquad (A1)$$

$$Br(III) + Br^- \rightleftarrows 2Br(I) \qquad (A2)$$
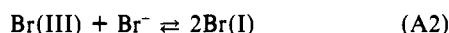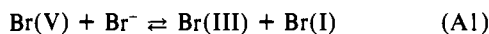
of classes i–iv, process A is virtually irreversible, although step A1 may be reversible at certain times during the oscillations. In class v reactions, the silver ion so depletes Br$^-$ that process A and the component steps may be driven from right to left.

Process B is the net consequence of three pseudoelementary processes. The overall process results from 2(B1) + 4(B2) + (B3).

$$Br(V) + Br(III) \rightleftarrows 2Br(IV) \qquad (B1)$$

$$Br(IV) + Red \rightleftarrows Br(III) + Ox \qquad (B2)$$

$$2Br(III) \rightarrow Br(V) + Br(I) \qquad (B3)$$

In all reaction classes except (ii), "Red" is the reduced form of a catalyst metal ion; in class ii it is the organic substrate itself. The oxidation state of "Ox" differs by one equivalent from that of "Red". Steps B1 and B3 are common to all reaction classes, the first being reversible and the other virtually irreversible. Step B2 may or may not be reversible, depending upon the oxidation potential of "Red".

Process C involves the reduction of HOBr to Br$^-$ with simultaneous oxidation of the organic substrate. It may be the consequence of many competing elementary processes, and species "X" designates a complicated mixture of compounds. The importance of the stoichiometric coefficient n is discussed below.

Process D converts bromine in oxidation state +1, 0 or –1 to a form that no longer contributes to processes A, B, or C. The stoichiometric coefficients p and q may each be 0 or 1, depending upon the oxidation state of "inert Br" in the system of interest. Of course they may not both be simultaneously zero.

## Permissible Stoichiometries for Reaction

A bromate driven system will not oscillate if the rate constants of processes C and D are very large.[17] However, in presently known systems those rate constants are far below the maximum permissible values. Steady states are then stable or oscillating, depending upon the stoichiometries of processes C and D rather than upon their rates. Such a conclusion is in agreement with the graph theory treatments developed by Clarke.[18]

The stoichiometric coefficient n in process C is identical with $2/f$ where f is the coefficient in the Oregonator[19] model. Stability calculations with that model[19,20] demonstrate that oscillations will be impossible unless n is between about 0.8 and 4 and that the maximum sensitivity to oscillation will occur when n is very close to 2.

The net chemical change of the system as a whole will be a linear combination of processes A–D. That combination must recognize that the species Br(I), Br$^-$, and Ox are not stoichio-

metrically significant[21] to the total process. Therefore, for specified values of p and q the net stiochiometry over a complete cycle will be a unique function of n.

In classes i, ii, and iii, "inert Br" is an organic bromide in which the oxidation number of bromine is formally +1—equal to that of the hydrogen for which it is substituted. Then $p = 1$ and $q = 0$ in process D, and the net stoichiometry for reaction is 2(A) + n(B) + 4(C) + (2 + n)(D). When the system is most sensitive to oscillation, $n = 2$ and the stoichiometry becomes
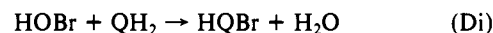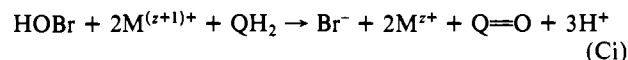
$$(A) + (B) + 2(C) + 2(D) \qquad (S1)$$
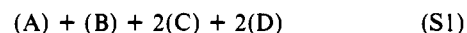
In class iv, "inert Br" is the free element and $p = q = 1$ in process D. Then the net stoichiometry for reaction is $(8 - n)$(A) + $5n$(B) + 20(C) + $(4 + 2n)$(D). When $n = 2$, maximum sensitivity to oscillation occurs for a stoichiometry of

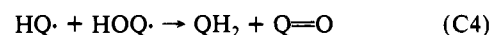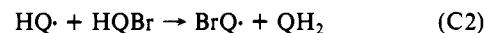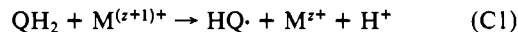$$3(A) + 5(B) + 10(C) + 4(D) \qquad (S2)$$
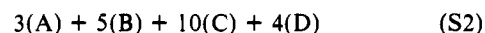
In class v, "inert Br" is silver bromide. Then $p = 0$ and $q = 1$ in process D and the net stoichiometry for reaction is $(4 - n)$(A) + $3n$(B) + 12(C) + $(4 + 2n)$(D). We have not carried out an analysis to determine the most sensitive stoichiometry for oscillators controlled by hypobromous acid.

Applications to Specific Reaction Classes

In the Belousov[2]–Zhabotinsky[3] systems of class i, the species Red and Ox are different forms of the metal ion catalyst and can be designated M^{z+} and M$^{(z+1)+}$, respectively. The organic substrate usually contains a methylene adjacent to a carboxyl or carbonyl and can be designated QH$_2$. For the $n = 2$ condition of maximum sensitivity to oscillation, processes C and D become
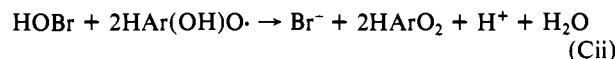
$$HOBr + 2M^{(z+1)+} + QH_2 \rightarrow Br^- + 2M^{z+} + Q{=\!=}O + 3H^+ \qquad (Ci)$$

$$HOBr + QH_2 \rightarrow HQBr + H_2O \qquad (Di)$$

An appropriate set of pseudoelementary processes is

$$QH_2 + M^{(z+1)+} \rightarrow HQ\cdot + M^{z+} + H^+ \qquad (C1)$$

$$HQ\cdot + HQBr \rightarrow BrQ\cdot + QH_2 \qquad (C2)$$

$$BrQ\cdot + H_2O \rightarrow Br^- + HOQ\cdot + H^+ \qquad (C3)$$

$$HQ\cdot + HOQ\cdot \rightarrow QH_2 + Q{=\!=}O \qquad (C4)$$

The stoichiometry of process Ci is generated by (Di) + 2(C1) + (C2) + (C3) + (C4). The overall stoichiometry obeys (S1).[22] Steps C1–C4 constitute a minimum set designed to generate optimum stoichiometry. Many other reaction steps are possible, and the carbonyl compound Q=O can be further oxidized. Modeling calculations by Edelson[7,8] demonstrate it is possible to assign rate constants so that this sequence and more complex ones derived from it can certainly generate oscillations. The discussion below indicates that all previous modeling attempts have neglected still other processes that may be occurring.

In the uncatalyzed Körös–Orbán[9,10] systems of class ii, the organic substrate is often a polyphenol that can be designated HAr(OH)$_2$, and this species is also Red. The designation for Ox is the quinhydrone HAr(OH)O·, and HArO$_2$ is the corresponding quinone. For the $n = 2$ condition of maximum sensitivity to oscillation, processes C and D become

$$HOBr + 2HAr(OH)O\cdot \rightarrow Br^- + 2HArO_2 + H^+ + H_2O \qquad (Cii)$$

$$HOBr + HAr(OH)_2 \rightarrow BrAr(OH)_2 + H_2O \qquad (Dii)$$

An appropriate set of pseudoelementary processes is

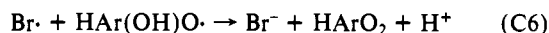(17) Field, R. J.; Noyes, R. M. *Acc. Chem. Res.* **1977**, *10*, 214.

(18) Clarke, B. L. *Adv. Chem. Phys.* **1980**, *43*, 1.

(19) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.

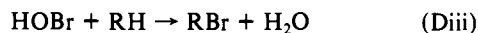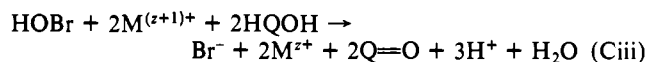(20) Field, R. J.; Noyes, R. M. *Faraday Symp. Chem.* **1974**, *9*, 21.

(21) Noyes, R. M. "Techniques of Chemistry", Part 1; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. 6, p 498.

(22) It need not cause any difficulty that process Di is a component of (Ci) because the (A) + (B) portion of (S1) produces four Br(I) and the 2(C) portion consumes only two of them. The other two BrQH are "inert" to further reaction.
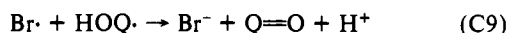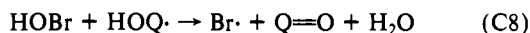
$$HOBr + HAr(OH)O\cdot \rightarrow Br\cdot + HArO_2 + H_2O \quad (C5)$$

$$Br\cdot + HAr(OH)O\cdot \rightarrow Br^- + HArO_2 + H^+ \quad (C6)$$

The stoichiometry of (Cii) is generated by (C5) + (C6). The overall stoichiometry obeys (S1). OKN[11] have indicated other processes that might displace n from its optimum value of 2.

In the Rastogi et al.[13] system of class iii, the mixed substrates of acetone and tartaric acid can be designated RH and HQOH, respectively. For the condition $n = 2$, processes C and D become
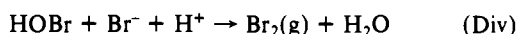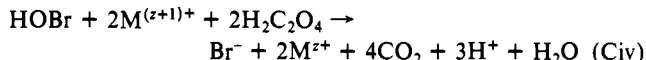
$$HOBr + 2M^{(z+1)+} + 2HQOH \rightarrow$$
$$Br^- + 2M^{z+} + 2Q{=}O + 3H^+ + H_2O \quad (Ciii)$$

$$HOBr + RH \rightarrow RBr + H_2O \quad (Diii)$$

An appropriate set of pseudoelementary processes is

$$HQOH + M^{(z+1)+} \rightarrow HOQ\cdot + M^{z+} + H^+ \quad (C7)$$

$$HOBr + HOQ\cdot \rightarrow Br\cdot + Q{=}O + H_2O \quad (C8)$$

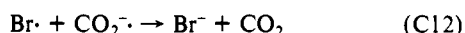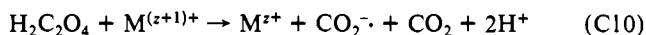$$Br\cdot + HOQ\cdot \rightarrow Br^- + Q{=}O + H^+ \quad (C9)$$

The stoichiometry of (Ciii) is generated by 2(C7) + (C8) + (C9). The overall stoichiometry obeys (S1). An oxidation mechanism with identical stoichiometry may be obtained if oxalic acid is substituted for tartaric.[14] No modeling computations have been attempted for this system, but processes C8 and C9 resemble (C5) and (C6). There is no obvious reason similar reactions involving bromine atoms might not occur with oxygenated derivatives of malonic acid in the BZ[2,3] systems of class i even though such a possibility has not been included in previous attempts to model such systems. The steps presented here are only a few of the many that are possible. However, a full mechanistic description must lead to an overall stoichiometry not greatly different from that generated by the representative steps we have selected.

In the Noszticzius–Bódiss[15] system of class iv, the oxalic acid substrate is $H_2C_2O_4$. For the condition $n = 2$, processes C and D become

$$HOBr + 2M^{(z+1)+} + 2H_2C_2O_4 \rightarrow$$
$$Br^- + 2M^{z+} + 4CO_2 + 3H^+ + H_2O \quad (Civ)$$

$$HOBr + Br^- + H^+ \rightarrow Br_2(g) + H_2O \quad (Div)$$

An appropriate set of pseudoelementary processes is

$$H_2C_2O_4 + M^{(z+1)+} \rightarrow M^{z+} + CO_2^- + CO_2 + 2H^+ \quad (C10)$$

$$HOBr + CO_2^- + H^+ \rightarrow Br\cdot + CO_2 + H_2O \quad (C11)$$

$$Br\cdot + CO_2^- \rightarrow Br^- + CO_2 \quad (C12)$$

Other reaction steps are also possible. The stoichiometry of (Civ) is generated by 2(C10) + (C11) + (C12). The overall stoichiometry obeys (S2). No modeling computations have been attempted, but oscillations are clearly possible.

In the Noszticzius[15] system of class v, the (Cv) process is identical with (Ci), but process D becomes

$$Ag^+ + Br^- \rightarrow AgBr(s) \quad (Dv)$$
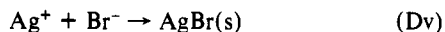
This reaction class will be considered further in a subsequent publication.

Thermodynamic Constraints on the Mechanism

The reduction potentials can be estimated for the various species associated with reactions of classes i–iv. The bases of these estimates and their approximate reliability are discussed in the Appendix. Those potentials have been used to prepare Figures 1, 2, and 3 which illustrate the driving forces for processes of types A, B, and C, respectively.

The potentials in the Appendix can be combined to generate eq P1. Figure 1 is calculated at pH 0 and shows deviations of

$$BrO_3^- + 6H^+ + 6e^- = Br^- + 3H_2O \qquad E^\circ = 1.44 \text{ V} \quad (P1)$$

individual species (in volt equivalents) from the free energies they would have if each of the six one-equivalent steps had the same
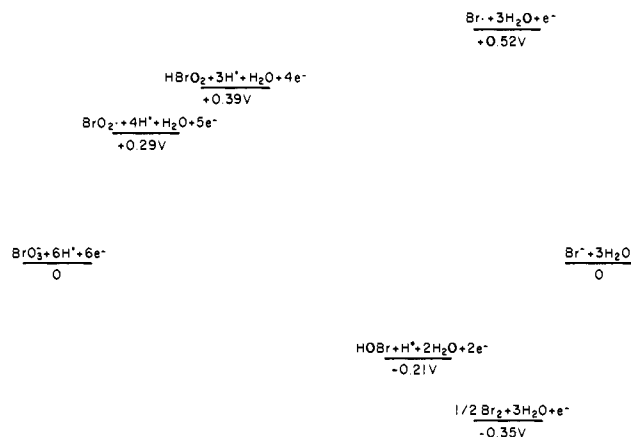

Figure 1. Relative free energies of different oxidation states of bromine at pH 0. Bromate and bromide are arbitrarily assigned free energies of zero, and free energies of other species are deviations in volt equivalents from the values they would have if reduction potentials were the same for each step.
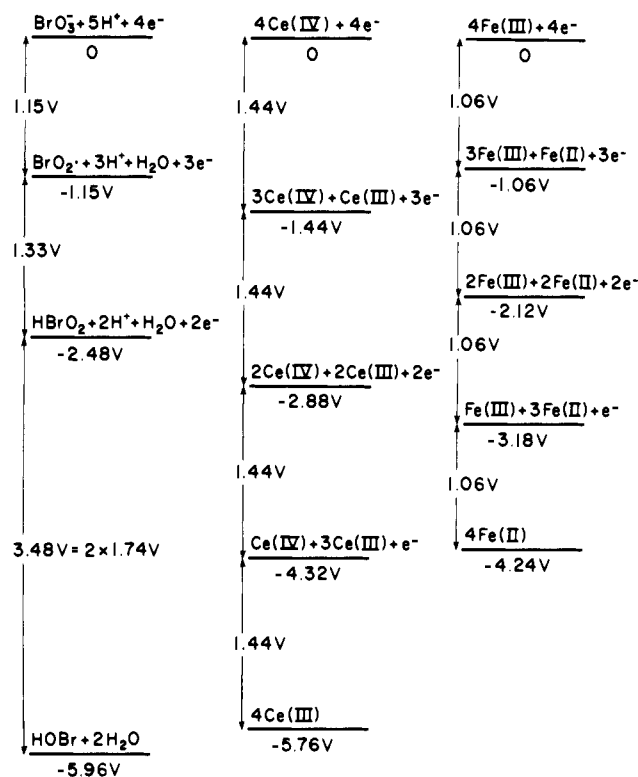

Figure 2. Free-energy changes in volt equivalents at pH 0 for half-reactions associated with process B. The reduction potential of Ce(IV) is that reported[24] in 1 M H_2SO_4. The species designated Fe(III) and Fe(II) are $Fe(phen)_3^{3+}$ and $Fe(phen)_3^{2+}$, respectively.

reduction potential. The figure illustrates the well-known facts that Br_2 is the most stable species in an acidic mixture of oxybromine species, that the other most prevalent species in an equilibrium mixture will be either BrO_3^- or Br^-, depending upon which is in excess, that process A is thermodynamically favored, and that the equilibrium constant for step B1 is only modestly unfavorable under these conditions.

Figure 2 shows free-energy changes in volt equivalents for the stepwise reduction of bromate by metal ions in 1 M sulfuric acid. It illustrates that net process B is only modestly favored when M^{z+} is Ce(III) but is strongly favored when it is $Fe(phen)_3^{2+}$. The entries for cerium show why process B can not be initiated effectively by the superficially attractive step $Br(V) + Ce(III) \rightarrow Br(IV) + Ce(IV)$ and why the more cumbersome sequence of (B1)–(B3) is necessary. However, no such objection applies to the direct reaction of bromate with ferroin. Kinetic rather than
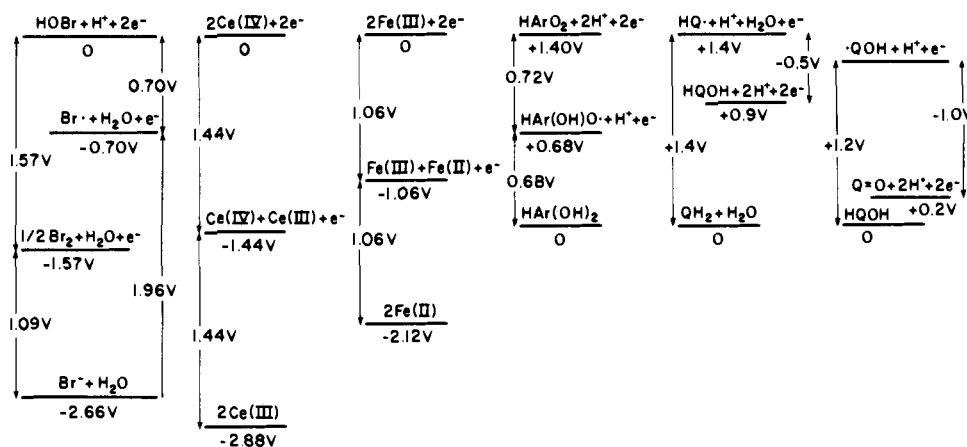
(figure diagram with free-energy level labels: HOBr+H$^+$+2e$^-$, 0.70V, Br$\cdot$+H$_2$O+e$^-$, −0.70V, 1.57V, 1/2 Br$_2$+H$_2$O+e$^-$, −1.57V, 1.96V, 1.09V, Br$^-$+H$_2$O, −2.66V; 2Ce(IV)+2e$^-$, 0, 1.44V, Ce(IV)+Ce(III)+e$^-$, −1.44V, 1.44V, 2Ce(III), −2.88V; 2Fe(III)+2e$^-$, 0, 1.06V, Fe(III)+Fe(II)+e$^-$, −1.06V, 1.06V, 2Fe(II), −2.12V; HArO$_2$+2H$^+$+2e$^-$, +1.40V, 0.72V, HAr(OH)O$\cdot$+H$^+$+e$^-$, +0.68V, 0.68V, HAr(OH)$_2$, 0; HQ$\cdot$+H$^+$+H$_2$O+e$^-$, +1.4V, −0.5V, HQOH+2H$^+$+2e$^-$, +0.9V, +1.4V, QH$_2$+H$_2$O, 0; ·QOH+H$^+$+e$^-$, −1.0V, +1.2V, Q=O+2H$^+$+2e$^-$, HQOH, +0.2V, 0)

Figure 3. Free-energy changes in volt equivalents for half-reactions associated with process C in several of the possible classes. The potential oxidants HOBr, Ce^{4+}, and Fe(phen)$_3^{3+}$ are all placed at the same initial level, and the potential reductants HAr(OH)$_2$, QH$_2$, and HQOH are all placed at another.

thermodynamic considerations must be invoked to explain why this ion also reacts by the sequence (B1)–(B3).

Figure 3 shows successive potential changes for a number of two-equivalent half-reactions that could contribute to net process C. Hypobromous acid, HOBr, is a strong enough two-equivalent oxidant to consume any reductant in the figure except cerium(III). However, it is a relatively weak one-equivalent oxidant, although it can oxidize the aromatic substrates of class ii systems. It can also oxidize all of the organic radicals formed in the other reaction classes. One-equivalent reduction of HOBr produces a bromine atom which can easily oxidize any of the reductants in Figure 3. Therefore, HOBr can behave both as an oxidant and as a brominating agent when in the presence of various organic compounds.

Kinetic Constraints on the Mechanism

Thermodynamic peculiarities certainly contribute to the unusual behavior in these systems. Thus, the relative stability of Br$_2$ and instability of HBrO$_2$ facilitate events that would not occur if reduction of bromate involved steps of nearly equal potential. It is also important that most organic free radicals are very unstable to oxidation. However, the rich phenomenology would still be impossible if there were not gross differences in the rates of thermodynamically allowed processes. We shall attempt here to systematize what is known about rates of possible processes in these systems in order to provide justification for the detailed mechanisms we have assumed:

Oxygen atom transfers between odd oxidation states of bromine are always rapid in the thermodynamically allowed directions. The only possible examples are steps A1, A2, and B3.

Nucleophilic attack on bromine is also rapid. Examples are (B1) and the homogeneous analogue of (Div). Step B1 initiates radical reactions[23] because of the weak Br–Br bond in Br$_2$O$_4$.

Both BrO$_3^-$ and HBrO$_2$ are very sluggish one-equivalent oxidants. The reasons are often thermodynamic but are kinetic in some cases.

Bromine dioxide, BrO$_2$·, is a facile one-equivalent oxidant of species that can transfer an electron to it. For thermodynamic and perhaps also for kinetic reasons, it is sluggish at abstracting a hydrogen atom from carbon.

Hypobromous acid, HOBr, can be rapid as a one-equivalent oxidant, presumably by electron transfer to H$_2$OBr$^+$. It does not abstract hydrogen atoms from organic compounds.

Bromine atoms are very rapid oxidants, abstracting either electrons or hydrogen atoms.

Substitution-inert ions like Fe(phen)$_3^{2+}$ react only by electron transfer.

Substitution-labile ions like Ce(III) and Mn(II) are oxidized by electron transfer. The resulting ions oxidize organic compounds

by forming bidentate complexes and then abstracting an electron simultaneously with rupture of a C–H or C–C bond.

In these oxybromine systems, single-step two-equivalent oxidations of organic compounds are negligibly slow. There does not seem to be any elementary process that can rapidly insert an oxygen atom into a C–H bond no matter how favorable the energetics of such insertion may be. All of the organic substrates in these systems are therefore oxidized by odd-electron processes.

The oxyaromatic compounds of system ii undergo facile oxidation by electron transfer.

Oxalic and malonic acids are attacked by the oxidized form of a substitution-labile ion. The methylene group of malonic acid can also be attacked by a hydrogen atom abstractor.

Oxyaliphatic compounds such as those from partial oxidation of malonic acid can also be oxidized by electron transfer as from HOBr.

Organic free radicals react rapidly with oxidizing metal ions, with hypobromous acid, and with any odd-electron species they encounter.

Although these kinetic constraints have not been spelled out in detail, they indicate a pattern that can only be justified by consistency in behavior as more systems are studied.

Loose Ends

The preceding sections attempt to systematize what has become a large body of often unusual chemical information. It is probably inevitable that a few components of the mechanism are not yet entirely clear. We shall mention three that seem particularly to deserve attention:

Stability of Bromous Acid. Figures 1 and 2 show that HBrO$_2$ is quite unstable to disproportionation to other paired-electron bromine species. Our assignments generate an equilibrium constant of 8×10^{16} for reaction B3. In the oxychlorine system, the corresponding constant is[24] 5×10^{14}. Further studies of iodate-peroxide driven oscillators[25] indicate that in the oxyiodine system the corresponding equilibrium constant is several orders of magnitude smaller than either of these values. If the three halogen systems are to show a consistent trend, the free energy of formation of HBrO$_2$(aq) should be somewhat less than the 3.8 kcal/mol presently[6] assigned. More information is needed before any changes are justified.

Mechanistic Significance of Bromine Atoms. Free bromine atoms are so unstable that they were ignored when the original FKN[6] mechanism was developed for reactions of class i. However, they had to be invoked for the OKN[11] mechanism of class ii and also for classes iii and iv discussed above. Figure 3 makes it clear that any of the organic radicals could easily reduce HOBr to Br·. Such processes were not invoked during the modeling computations

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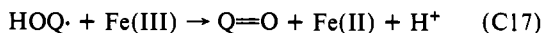
(25) Furrow, S. J., private communication.

of class i by Edelson.[7,8] If rate constants were empirically selected and the atom processes were added to the mechanism, experimental observations could certainly be modeled at least as faithfully as they were when bromine atoms were neglected as intermediates.

Catalysis by Substitution-Inert Ions. Historical accident directed the first detailed mechanistic studies to the cerium-catalyzed oxidation of malonic acid. Cerium(IV) is substitution labile with a reduction potential of 1.44 V. The detailed studies by Jwo[26] indicate that an organic substrate is not oxidized by Ce(IV) at a significant rate unless it is at least a bidentate ligand. Substrates forming five-membered rings are oxidized much more rapidly than if the rings are six-membered.

Ferroin, $Fe(phen)_3^{2+}$, also catalyzes oscillatory oxidation of malonic acid. The oxidized form of this ion has a reduction potential of only 1.06 V, and both reduced and oxidized forms are inert to substitution by other ligands. Therefore, both thermodynamic and kinetic arguments indicate that ferroin should not oxidize malonic acid (QH_2) by the same mechanism appropriate to cerium(IV).

Not only do the two oxidants react differently with organic substrates, but both Körös et al.[4] and Smoes[27] have noted that ferroin-catalyzed systems oscillate without an induction period while cerous-catalyzed systems do not. The induction period in the cerous system arises because sufficient malonic acid must be brominated by process Di before bromide ion can be liberated by the sequence of (C1)–(C3). If ferroin-catalyzed systems start to oscillate immediately, the bromide ion product in process C must come directly from HOBr without the intermediacy of bromomalonic acid.

Because of differences in the two catalyst systems, Smoes[27] has recently questioned the previous implicit assumption that reaction mechanisms were the same with both catalysts. The question is justified, and the following sequence illustrates how ferroin might accomplish process C by a sequence different from that proposed above for cerium.

$$HOBr + Fe(II) + H^+ \rightleftarrows Br\cdot + Fe(III) + H_2O \quad (C13)$$

$$Br\cdot + QH_2 \rightarrow Br^- + \cdot QH + H^+ \quad (C14)$$

$$\cdot QH + Fe(III) + H_2O \rightarrow HOQH + Fe(II) + H^+ \quad (C15)$$

$$HOQH + Fe(III) \rightarrow HOQ\cdot + Fe(II) + H^+ \quad (C16)$$

$$HOQ\cdot + Fe(III) \rightarrow Q=O + Fe(II) + H^+ \quad (C17)$$

The stoichiometry of process Ci is generated by (C13) + (C14) + (C15) + (C16) + (C17). Step C13 is rather unfavorable thermodynamically, but the reverse activation barrier is undoubtedly small, and we do not see any other way process C could be initiated by a substitution-inert catalyst. The mechanism in this form requires that HOQH can be oxidized by electron transfer to ferriin even though QH_2 can not.

This sequence generates the precise stoichiometry of $n = 2$ corresponding to maximum sensitivity to oscillation. One of the remarkable characteristics of ferroin-catalyzed systems is the formation of excitable stationary states through which trigger waves[28] can propagate.[29,30] These excitable stationary states involve the reduced Fe(II) form of the catalyst with $n < 2$ and could occur if radical reactions like (C18) competed with (C15) and (C17).

$$\cdot QH + HOBr \rightarrow HOQH + Br\cdot \quad (C18)$$

Smoes[27] has also reported interesting excitable stationary states in which the oxidized Fe(III) form of the catalyst predominates. These states are observed only at low concentrations of malonic acid and could occur if the sequence (C19) + (C20) competed with (C14) to reduce the amount of bromide resulting from (C13).

$$Br\cdot + Br\cdot \rightarrow Br_2 \quad (C19)$$

$$QH_2 + Br_2 \rightarrow BrQH + Br^- + H^+ \quad (C20)$$
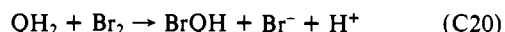
After the manuscript to this paper had been completed, Professor Richard J. Field of the University of Montana pointed out that step C13 predicts that ferroin will reduce bromate all the way to Br_2 even though cerous ion reduces it only to HOBr. Simple qualitative tests confirmed this prediction. Careful quantitative kinetic and stoichiometric studies will be needed before it is possible to establish the detailed mechanisms of catalysis by substitution-labile and substitution-inert ions. The mechanisms may differ enough to justify splitting class i.

Conclusions

In systems as complicated as these, it is inevitable that mechanistic understanding will develop by successive approximations. Chemical oscillations were well established as a phenomenon before any detailed chemical explanations were attempted. The original FKN[6] mechanism was proposed before the authors even knew how to calculate the stability of the steady state so generated, and Clarke[31] immediately pointed out that its stoichiometry could not be correct because it was equivalent to $n > 4$ in process C above. Even the first efforts at quantitative modeling[7] included a stoichiometric error that was later corrected.[8]

A considerable increase in experimental information has now made it clear that in at least some systems free bromine atoms play a more important role than was originally realized. However, the necessary mechanistic modifications are minor refinements rather than major changes. It is perhaps surprising that the original FKN mechanism has stood up as well as it has.

By now there are five distinct classes of bromate-driven oscillators, four of which are treated consistently in the present paper. That treatment suggests many possibilities for further test and refinement of the mechanism. Thus, the mixed substrates of class iii permit oxidation and bromination characteristics to be separated and studied independently by appropriate changes of reactants. Bromate-driven oscillators are now ready to join the many other types of organic reactions whose basic mechanisms are clearly understood and whose further study involves quantitative analysis of rate effects resulting from changes in structure of substrates.

Appendix

Assignment of Potentials. Bromine Species. The free energies of formation of $Br_2(aq)$, $BrO_3^-(aq)$, $HOBr(aq)$, and $Br^-(aq)$ are well established[24] and generate the entries in the figures; they are almost certainly valid to the indicated 0.01 V.

The entry for $Br\cdot(aq)$ is based on the assumption the equilibrium constant (in concentration units) for dissociation of Br_2 is the same in solution as in gas phase. That approximation is excellent for iodine in nonpolar solvents;[32,33] it probably introduces an uncertainty of no more than a few hundredths of a volt equivalent.

The other two entries require potentials for the half-reactions a and b.

$$BrO_3^- + 2H^+ + e^- = \cdot BrO_2 + H_2O \quad (a)$$

$$BrO_3^- + 3H^+ + 2e^- = HBrO_2 + H_2O \quad (b)$$

We have used estimates adopted previously.[6] The value of E_b° was based on a kinetic study by Lee and Lister[34] of the reversible

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reactions $BrO_3^- + BrO^- \rightleftarrows 2BrO_2^-$ in strongly alkaline solution and on an estimate[35] of 0.01 for the acid ionization constant of $HBrO_2$. Such constants for $HClO_2$ and HNO_2 are[24] 1.1×10^{-2} and 4.5×10^{-4}, respectively. If the estimate for $HBrO_2$ were reduced to 0.001, E_b° would decrease 0.03 V.

The value for E_a° is derived from observations[23,36] that permitted an estimate[6] of the equilibrium constant for $BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2BrO_2 \cdot + H_2O$. Any change in E_b° would change E_a° in the same direction but by only half as much.

Metal-Ion Catalysts. Reduction potentials are not well-defined for the strongly oxidizing substitution-labile ions. Latimer[24] quotes about 1.5 V for Mn(III) and 1.44 V for Ce(IV) in 1 M sulfuric acid. The substitution-inert catalysts are not as strong oxidants. Reported reduction potentials are 1.06 V[24] for $Fe(phen)_3^{3+}$ and 1.29 V[37] for $Ru(bpy)_3^{3+}$.

Aromatic Compounds. The potentials in Figure 3 for $HArO_2$, $HAr(OH)O\cdot$, and $HAr(OH)_2$ are those for the *p*-benzoquinone system. Those potentials are known to four significant figures;[38] potentials for other quinones in class ii are probably sufficiently similar for the purposes of this paper.

Oxalic Acid. Treatment of the oxalic acid examples of classes iii and iv requires potentials for half-reactions c and d. Data from

$$2CO_2 + 2H^+ + 2e^- = H_2C_2O_4 \tag{c}$$

$$CO_2 + \cdot CO_2^- + 2H^+ + e^- = H_2C_2O_4 \tag{d}$$
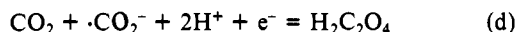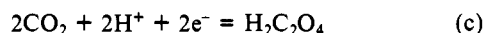
Latimer[24] indicate $E_c^\circ = -0.39$ V. The facile oxidation of oxalate by manganese(III)[38] demonstrates that E_d° is certainly less than 1.5 V, but no firm estimate is possible without information on the free energy of formation of $\cdot CO_2^-$. No effort has been made to illustrate this system in Figure 3.

Other Aliphatic Paired-Electron Compounds. Reduction potentials involving Q=O, HQOH, and QH_2 were calculated by use of the group additivities of Benson.[39] Such calculations should be valid to about 0.1 V in the gas phase. Differences in solvation will make the uncertainty greater in Figure 3 but will not alter the mechanistic conclusions.

Other Organic Radicals. Reactions of classes i, iii, and v involve one-equivalent oxidations of the species QH_2 and HQOH. If these are designated SH, entries in Figure 3 are derived from considering half-reactions e–g. If D's are bond dissociation enthalpies in

$$S\cdot(aq) + H^+(aq) + e^- = SH(aq) \tag{e}$$

$$H\cdot(g) + H^+(aq) + e^- = H_2(g) \tag{f}$$

$$S\cdot(g) + H_2(g) = SH(g) + H\cdot(g) \tag{g}$$

kcal/mol, the free-energy change in (g) can be approximated by (E1). If SH and S· have almost equal free energies of solvation,

$$\Delta G_g^\circ \approx \Delta H_g^\circ = D(H-H) - D(S-H) \tag{E1}$$

we obtain (E2). Data from Latimer[24] give $E_f^\circ = 2.11$ V. Tabulations

$$E_e^\circ = E_f^\circ - \frac{D(H-H) - D(S-H)}{23.0} \tag{E2}$$

by Benson and O'Neal[40] suggest that for malonic acid (QH_2) $D(S-H)$ should be about 88 kcal/mol and then $E_e^\circ = 1.4$ V. For HQOH, $D(S-H)$ should be about 84 kcal/mol and then $E_e^\circ = 1.2$ V. These estimates are shown in Figure 3; they are more uncertain than the other values in the figure but probably no more than a few tenths of a volt. The qualitative mechanistic conclusions remain valid.

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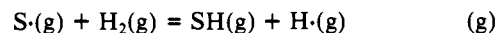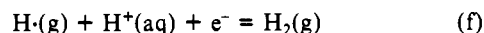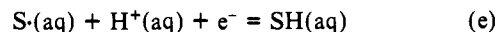(36) Betts, R. H.; MacKenzie, A. N. *Can. J. Chem.* **1951**, *29*, 655.

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Diffusional Charge Transport through Ultrathin Films of Radiofrequency Plasma Polymerized Vinylferrocene at Low Temperature

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Abstract: In room-temperature butyronitrile, films of plasma polymerized vinylferrocene on Pt electrodes, which contain $7-10 \times 10^{-9}$ mol/cm^2 of ferrocene sites, undergo rapid exchange of electrons with the Pt electrode. At low temperature (−50 to −85 °C), the transport of electrochemical charge through the polymer film is controlled by diffusion according to Fick's law under infinite and finite boundary conditions depending on time and temperature. Activation energies and entropies for the charge-diffusion process are approximately 3.7 kcal/mol and −32 cal/(mol deg), respectively. Charge diffusion is interpreted as controlled by the cooperative motions of polymer chains required for site–site collisions and counterion transport. The electron self-exchange rate between ferrocene and ferricenium sites is diffusion controlled and approximately 10^2 L/(mol s).

Considerable attention has been given recently to the preparation and properties of thin films of polymeric materials bonded to or coated on metal and semiconductor electrodes.[1–9] In many cases the polymer films contain, or are later modified to contain, electrochemically reactive groupings. These groupings can be

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