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Oscillations in Chemical Systems. X.[1] Implications of Cerium Oxidation Mechanisms for the Belousov–Zhabotinskii Reaction

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Abstract: Although oxidations of malonic acid derivatives by cerium(IV) involve very complicated mechanisms, the mixture of unoxidized and partially oxidized species in an oscillating solution will react by kinetics first order in Ce(IV). The apparent rate constant will be such that oscillations may occur only if between 0.25 and 0.75 bromide ions are produced per cerium(IV) ion consumed. The stoichiometry originally proposed does not quite fall in this range, but addition of hypobromous acid oxidation of formic acid generates exactly the stoichiometry of maximum sensitivity to oscillation. Explanation of oscillations also requires that malonyl radicals preferentially attack bromomalonic acid to liberate bromide ions. We have not been able to resolve complications involving possible independent oxidation of malonic acid, possible accumulation of tartronic acid, and possible oxidation of organic molecules by oxybromine intermediates, but we do not believe these complications are serious.

Chemical oscillators must be considered among the most complicated of chemical systems. Probably the best characterized homogeneous oscillator is the Belousov–Zhabotinskii reaction[2,3] involving the cerium ion catalyzed oxidation of malonic acid by acidic bromate. The principal features of the mechanism are now well established.[4,5]

An important component of this mechanism is the oxidation of a mixture of malonic (MA) and bromomalonic (BrMA) acids with liberation of bromide ion. The previous paper[1] has elucidated many features of the sequence of events by which this oxidation occurs. The reaction is unexpectedly complex, and the observations include sudden virtually discontinuous changes in rate. It is the object of the present paper to show that these mechanistic complications of the oxidation reaction are probably of very little significance to the understanding of the oscillating Belousov–Zhabotinskii reaction!

Pertinent Experimental Facts

The Belousov–Zhabotinskii reaction involves repeated oscillation in the oxidation state of the system. These oscillations can be followed by observing the [Ce(IV)]/[Ce(III)] ratio directly or by using a redox indicator such as ferrous phenanthroline. The concentration of bromide ion undergoes synchronous oscillations that can be followed potentiometrically with an ion specific electrode. Relative concentrations of reactants can greatly affect the period, amplitude, and shape of these oscillations. We restrict comment here to three chemical observations of significance to the subsequent discussion.

1. Thermodynamic data demonstrate that in an acidic bromate, BrO_3^-, solution elementary bromine, Br_2, is the only other inorganic bromide species that can be present in stoichiometrically significant concentration (ref 4, pp 8652 and 8653). Elementary bromine reacts rapidly and irreversibly with malonic acid. Therefore, virtually all of the bromine in a Belousov–Zhabotinskii system is present either as bromate or in organic combination.

2. Studies by Hess et al.[6,7] indicated that about 75% of the organically bound bromine is present as monobromomalonic acid (BrMA), and the remainder as dibromoacetic acid, $Br_2CHCOOH$. No other bromine-containing compounds were detected. Somewhat similar studies in this laboratory (ref 4, p 8652) indicated 85–95% of organic bromine as BrMA and the remainder as monobromoacetic acid. The apparent discrepancies undoubtedly reflect different extents of bromination of malonic acid and different times before analysis of the two test solutions; the two studies agree that the major part of the organically bound bromine is present as BrMA.

3. Stoichiometry of the Ce(IV) oxidation of malonic acid (MA) indicates 1 mol of formic acid (FA) product for each mole of reductant (ref 1, Results section A). However, Hess et al.[8] were unable to detect any formic acid in a solution that had undergone repeated oscillations. Failure to detect this material indicates that reactions with cerium(IV) alone are not enough to explain all behavior of organic species in the Belousov–Zhabotinskii reaction.

Basic Chemical Mechanism

The essential features of the chemical mechanism[4] are summarized in steps C1 to C5. Steps C1 and C2 lead to reduction of bromate by bromide ion; the reactant species retain paired electrons at all times. Steps C3 and C4 lead to reduction of bromate by cerium(III). The mechanism assumes step C3a is rate determining for the autocatalytic generation of bromous acid, but this species does not attain massive concentrations because of the second-order destruction by step C4. Steps C1 to C4 have nothing to do with the organic species in solution.

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \qquad (C1)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \qquad (C2)$$

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O \qquad (C3a)$$

$$Ce(III) + BrO_2\cdot + H^+ \rightarrow Ce(IV) + HBrO_2 \qquad (C3b)$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \qquad (C4)$$

$$HOBr + \text{organic matter} \rightarrow \text{bromoorganic compounds} \qquad (C5a)$$

$$n\text{Ce(IV)} + \text{brominated and unbrominated organic compounds} \rightarrow n\text{Ce(III)} + Br^- + \text{oxidized products} \qquad (C5b)$$

In step C5a, the hypobromous acid, HOBr, formed by reduction of bromate then brominates organic matter (fact 1 above) with bromomalonic acid (BrMA) a major product (fact 2). The final products are probably the same whether or not elementary bromine is an intermediate during this bromination reaction. The ostensibly simple step C5b includes all of the complexities we have observed in cerium(IV) oxidations.[1] We wish to show that the effects of all these complexities on the Belousov-Zhabotinskii reaction can be handled by a simple model that regards step C5b as a single unimolecular process!

Mechanistic Requirements of the Oregonator Model

The chemical mechanism presented above can be approximated by the "Oregonator" model[9] of steps M1 to M5. This computational model assumes the chemical identities $A \equiv B \equiv BrO_3^-$, $X \equiv HBrO_2$, $Y \equiv Br^-$, $Z \equiv 2Ce(IV)$. It can be solved numerically[9] and exhibits limit cycle type oscillations for certain values of the rate constants. The rate constants for steps C1 to C4 can be estimated with some confidence, and calculations have used the experimentally appropriate conditions of $[BrO_3^-] = 0.06\ M$ and $[H^+] = 0.8\ M$.

$$A + Y \rightarrow X \qquad (M1)$$

$$X + Y \rightarrow P \qquad (M2)$$

$$B + X \rightarrow 2X + Z \qquad (M3)$$

$$2X \rightarrow Q \qquad (M4)$$

$$Z \rightarrow fY \qquad (M5)$$

The tendency of the system to oscillate is then determined solely by the two parameters k_{M5} and f. A previous treatment[9] based on sufficient conditions is modified only very slightly when both necessary and sufficient conditions are substituted.[10] The system cannot exhibit oscillations for any positive value of k_{M5} unless the stoichiometric factor f is between about 0.5 and 2.4. Even within this range, oscillations are impossible unless k_{M5} is less than a calculable value. The system is most unstable when f is about unity, and k_{M5} may be as great as 440 sec^{-1} in this region. If k_{M5} is only 1 sec^{-1}, the region of oscillations is approximately $0.5 < f < 1.5$.

Kinetic Consistency of the Model

In spite of all the complexities exhibited by cerium(IV) oxidations,[1] our data are almost always consistent with the assumption that reaction in any medium is first order in the oxidant. The only exception involves the dramatic "break points" during bromomalonic acid (BrMA) oxidation (ref 1, Results section F). Even these break points involve a discontinuous transition between two different first-order rate constants for Ce(IV) consumption.

The break points occur only during oxidation of an initially pure sample of bromomalonic acid. Even small additions of presumed oxidation intermediates such as glyoxylic acid (GOA) cause a more rapid initial rate and eliminate the break point. During chemical oscillation, the solution presumably contains species like tartronic (TTA) and glyoxylic (GOA) acids left over from previous cycles. When a sudden pulse of cerium(IV) is generated by step C3b, its subsequent reduction probably obeys first-order kinetics without a break point.

It is perhaps significant that we were unable to synthesize a typical "instantaneous" oscillator with malonic and bromomalonic acids as the only organic species present (ref 4, p 8662). The behavior of systems started from pure malonic acid was observed, and we attempted to synthesize mixtures at various stages during oscillation. The first cycle was always atypical, but subsequent cycles were typical of what was expected. The failure apparently arose because the first cycle did not have the oxidation intermediates that must form before the Ce(IV) + BrMA system attains the break point.

If concentrations of malonic and bromomalonic acids are less than about 1 M (which was always true in our experiments), first-order rate constants for cerium(IV) consumption are always less than 1 sec^{-1}.

We conclude that step M5 of the Oregonator will satisfactorily model the Belousov-Zhabotinskii reaction if the stoichiometric factor, f, is indeed between about 0.5 and 1.5.

Stoichiometric Consistency of the Model

The stoichiometric factor f is the number of bromide ions produced during reduction of two cerium(IV) ions. In terms of the nomenclature of the previous paper[1] we get eq 1. Then the Oregonator model indicates that $[Ce(IV)]_r/[Br^-]_p$ must be between 4 and 1.3 if oscillations are to occur.

$$\frac{[Ce(IV)]_r}{[Br^-]_p} = -\frac{d[Ce(IV)]}{d[Br^-]} = \frac{2}{f} \qquad (1)$$

Most of the organically bound bromine is present as monobromomalonic acid (BrMA), but some bromoacetic acids are also present (fact 2 above). The bromoacetic acids are probably oxidized only very slowly if at all. It will be a good approximation to assume BrMA is the only source of bromide ion that was previously organically bound.

We have previously[4] proposed that Ce(IV) and BrMA react by eq 2. This stoichiometry is equivalent to $f = 0.5$, and the Oregonator stability analysis indicates such a system would be just outside the range of possible oscillations. Moreover, if any cerium(IV) were reduced by malonic acid or by the bromide catalyzed oxidation of formic acid, the value of f would be decreased!

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \rightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \qquad (2)$$

This difficulty can be overcome by adding the reaction (ref 1, Discussion section D) of eq 3. Then the overall stoichiometry becomes that of eq 4 which gives $f = 1$ corresponding to the maximum sensitivity to oscillation. Of course this stoichiometry also explains the failure of Hess et al.[8] to detect formic acid in the reaction products.

$$HOBr + HCOOH \rightarrow Br^- + CO_2 + H_2O + H^+ \qquad (3)$$

$$4Ce^{4+} + BrCH(COOH)_2 + HOBr + H_2O \rightarrow 2Br^- + 4Ce^{3+} + 3CO_2 + 6H^+ \qquad (4)$$

Although eq 4 can generate the proper stoichiometry to produce oscillations, there are several potential complications. Thus, the reacting system contains considerable amounts of both malonic and bromomalonic acids, and malonic acid is actually the more reactive species (ref 1, Table II). If the two organic acids reacted independently with cerium(IV), f would be much smaller and would certainly go below the value corresponding to oscillation. We can resolve this dilemma by postulating considerable efficiency for the reaction of eq 5 (ref 1, Discussion section K). The brominated radical is then hydrolyzed with production of bromide ion (ref 1, Discussion section F). To the extent that eq 5 is the preferred fate of malonyl radicals in this system, malonic acid increases the rate of cerium(IV) reduction without affecting the stoichiometry by which bromide ion is liberated from bromomalonic acid. To the extent that malonyl radicals react with each other or with cerium(IV) (ref 1, Discussion section H), f will be decreased.

$$\mathrm{CH(COOH)_2 + BrCH(COOH)_2 \rightarrow CH_2(COOH)_2 + BrC(COOH)_2} \quad (5)$$

The stoichiometry of eq 4 assumes that bromomalonic acid is completely oxidized. We have proposed a tartronyl-type radical, $\cdot\mathrm{OCH(COOH)_2}$, as an intermediate. It can produce tartronic acid, TTA, both by disproportionation (ref 1, Discussion section I, eq 11) and by radical attack on BrMA (ref 1, Discussion section L, eq 24). Tartronic acid evidently does accumulate in the Ce(IV) + BrMA system. Thus, even when 60% of the initial Ce(IV) has been reduced by a stoichiometric excess of BrMA, the ratio $-d[\mathrm{Ce(IV)}]/d[\mathrm{Br^-}]$ is less than 2 and far below the 4 predicted by eq 2 (Jwo thesis[11] Table 10). To the extent that tartronic acid accumulates during Belousov-Zhabotinskii oscillations, f will be increased.

Finally, we have generally neglected the direct oxidation of organic compounds by oxybromine species. It is clear that bromate ion itself does not attack malonic or bromomalonic acid at a significant rate even though the reaction is thermodynamically favored. In fact, it is the slowness of this reaction that permits the oscillations associated with cerium catalysis. We have not directly examined the reaction of bromate with tartronic (TTA), glyoxylic (GOA), or formic (FA) acids which are intermediates during reaction. Moreover, we do not know anything about how the oxybromine species $\mathrm{BrO_2}$, $\mathrm{HBrO_2}$, or HOBr react with any of the organic species except for the proposed formic acid (FA) reaction of eq 3. To the extent that oxybromine species do attack organic matter, f will be increased.

In summary, the stoichiometry of eq 4 is exactly that for maximum sensitivity to oscillation. The stoichiometry in an oscillating system might also be affected by independent oxidation of malonic acid, by accumulation of unoxidized tartronic acid, and by reaction of oxybromine and organic species with each other. These potential complications occur to presently undetermined extents and can modify the stoichiometric factor f in both directions. Further careful experimental work could certainly refine the understanding of the system. However, enough has been done to narrow greatly the mechanistic possibilities. Moreover, facile and sustained oscillations are observed over a great variety of concentration ranges. We therefore believe that the net stoichiometry does not differ greatly from $f = 1$ and that eq 4 is probably a pretty good description of the net process leading to oxidation of organic matter in this system.

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