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Oscillations in Chemical Systems. II. Thorough Analysis of Temporal Oscillation in the Bromate–Cerium–Malonic Acid System

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Abstract: In a stirred sulfuric acid solution containing initially potassium bromate, cerium sulfate, and malonic acid, the concentrations of bromide ion and of cerium(IV) undergo repeated oscillations of major proportions. The concentrations of these species have been followed potentiometrically, and the detailed mechanism of the reaction has been elucidated. When the solution contains sufficient bromide ion, BrO_3^- is reduced to Br_2 by successive oxygen atom transfers (two-equivalent redox processes), and the malonic acid is brominated by an enolization mechanism. When the concentration of bromide ion becomes too small to remove $HBrO_2$ sufficiently rapidly, the latter reacts with BrO_3^- to form $BrO_2\cdot$ radicals which oxidize cerium(III) by one-equivalent processes. As a result, $HBrO_2$ is produced autocatalytically in the net reaction $BrO_3^- + HBrO_2 + 2Ce^{3+} + 3H^+ \rightarrow 2HBrO_2 + 2Ce^{4+} + H_2O$. Indefinite buildup of $HBrO_2$ concentration is prevented by the second-order disproportionation of this species. The cerium(IV) oxidizes bromomalonic acid with liberation of bromide ion which ultimately terminates the autocatalytic production of $HBrO_2$ and initiates a repeat of the cycle. Rate of production of cerium(IV) is thereby related to the concentration of bromide ion much as the current in a thyratron tube is related to the grid potential. In the course of developing this mechanism, thermodynamic and kinetic characteristics have been estimated for most possible interactions of oxybromine species in acid solution, and the chemistry of positive oxidation states of bromine has been systematized. It appears feasible to construct a stirred continuous flow reactor in which certain bulk chemical properties would oscillate indefinitely at constant frequency; potential applications of such a chemical oscillator are still unexplored. The spatial oscillations that develop in unstirred solutions have not been explained quantitatively, but qualitative arguments demonstrate how horizontal oxidizing wave fronts are able to propagate more rapidly than individual molecules can diffuse.

In any homogeneous closed system at constant temperature and pressure, a spontaneous chemical change must indubitably be accompanied by a decrease in the Gibbs free energy of the system. Concentrations of individual chemical species in such a system usually vary monotonically with time or else pass through single maxima or minima. However, the restriction of monotonic change of free energy does not preclude repeated oscillation in the concentrations of specific constituents.

The theoretical analysis of such processes in open systems was apparently started by Lotka[1] using a scheme applicable to animal populations. Bak[2] and Higgins[3] have considered both open and closed systems and have generalized the theory of such reactions. Spangler and Snell[4] have analyzed a particularly nice model system. Considerable interest in oscillating reactions has been generated by the large number of such processes observed in biological systems, and recently these ideas have been extensively and elegantly developed by Prigogine and coworkers.[5,6] The oscillating reactions hypothesized by them generally involve two autocatalytic reactions that turn each other on and off in a manner somewhat analogous to the well-known "flip-flop" circuit in electronics. We shall show in this paper that it is possible to devise a mechanism of oscillation involving but a single autocatalytic process.

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(2) T. Bak, "Contributions to the Theory of Chemical Kinetics," W. A. Benjamin, New York, N. Y., 1963, p 31.

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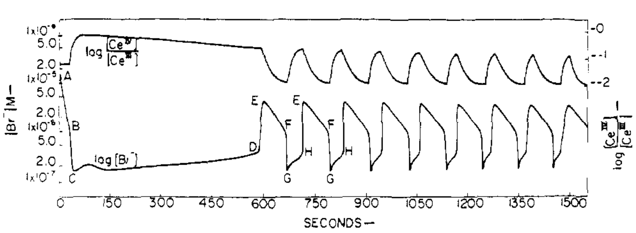

Figure 1. Potentiometric traces of log [Br^-] and log [Ce(IV)]/[Ce(III)] for a representative reaction exhibiting all six periods. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.032\ M$, $[KBrO_3]_0 = 0.063\ M$, $[KBr]_0 = 1.5 \times 10^{-5}\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.001\ M$, $[H_2SO_4]_0 = 0.8\ M$.

In addition to the requirement that at least one reaction be autocatalytic, repeated barely damped oscillations also require an effectively open system in the sense that reactants are taken in modest amounts from a large reservoir and products are dumped into a sink.

Apparently the first reaction believed to oscillate homogeneously was the iodine catalyzed decomposition of hydrogen peroxide.[7] This reaction is being reinvestigated by Liebhafsky.[8] It was Belousov[9] who first observed sustained barely damped oscillations in the ratio of [Ce(IV)]/[Ce(III)] during the cerium ion catalyzed oxidation of malonic acid by bromate in 1 M aqueous sulfuric acid. Zhabotinskii[10] has shown that similar oscillations are observed when the malonic acid is replaced by another organic material with an active methylenic hydrogen or when the cerium couple is replaced by the Mn(III)–Mn(II) couple or by the ferroin–ferriin one. Further work by Zhabotinskii[11,12] by Degn,[13] and by Kasperek and Bruice[14] have contributed to elucidating the mechanism. We[15] have proposed a detailed molecular mechanism for this reaction, and the present paper contains the justification for that proposal.

Prigogine's[5] theoretical work also showed that in the presence of a small initial concentration inhomogeneity the autocatalytic processes could couple with diffusion to form spatially organized inhomogeneities of readily observable proportions. Busse[16] and Zhabotinskii[17] have used a redox indicator to show just such inhomogeneities in an unstirred solution. These effects are very different from the supersaturation phenomena known as Liesegang rings[18] in that the inhomogeneities are not static but are propagated through the solution supported by the exothermicity of the reaction.

These spatial effects are of great interest in that they suggest mechanisms by which a chemical reaction could have induced primordial formation of a biological cell. However, we do not believe a detailed chemical mechanism of spatial inhomogeneities can be developed until the mechanism of temporal oscillation in a stirred homogeneous solution is understood. We have therefore confined ourselves in this paper to the stoichiometry and kinetics of the homogeneous reaction and believe that this mechanism is now understood.

Nature of the Problem

Figure 1 illustrates the potentiometric behavior of a stirred solution containing the indicated initial concentrations of potassium bromate, potassium bromide, malonic acid, and cerium(III) sulfate. The lower curve records the potential of an electrode specifically sensitive to bromide ion. Separate calibrations indicated that this potential varied linearly with log [Br^-] to concentrations as low as about 10^{-6} M. In static systems the electrode did not respond linearly to still lower bromide concentrations; however, it did appear to behave ideally during short periods of depleted bromide ion. Similar behavior and interpretation have been reported by Woodson and Liebhafsky[19] for iodide-sensitive electrodes.

The upper curve in Figure 1 records the simultaneous potential of a tungsten electrode. This electrode measured a mixed potential affected by concentrations of bromate as well as of cerium(IV). Although fluctuations at constant bromate concentration were directly related to changes in the [Ce(IV)]/[Ce(III)] ratio, the quantitative response differed from the theoretical ideal.

Figure 1 has been drawn far enough to illustrate the behavior of the electrodes, but the oscillations continued dozens of times more with only gradual damping. The trace of the bromide-sensitive electrode in Figure 1 can be cleanly resolved into six different periods, four of which are associated with the oscillation itself. The initial moderately rapid consumption of bromide, AB, is designated the "Bray period." The extended subsequent period of very low bromide concentration, CD, is designated the "induction period." The repeating periods, EF, during which bromide concentration is changing more slowly than during the Bray period are called "slow bromide consumption periods." The periods with much steeper slope, FG, are called "rapid bromide consumption periods;" the same mechanism evidently applies to period BC. The comparatively short GH periods are called "slow bromide production periods." Finally, the very steep HE periods are called "rapid bromide production periods;" the same mechanism almost certainly applies to the period DE.

Figure 1 was selected to illustrate the six period types cleanly. Some other behavioral characteristics of this versatile system are illustrated in Figures 2–6. Since these solutions did not contain initial added bromide ion, Bray periods are lacking from these plots.

Figure 2 contains a very low initial concentration of malonic acid. The induction period (broken in the graph) is very long, and the system oscillates only a few times. As reaction proceeds, the duration of the slow bromide consumption period increases, and the duration of the slow bromide production period gets less.

Figure 3 contains a very high initial concentration of malonic acid. Oscillations are much more frequent,

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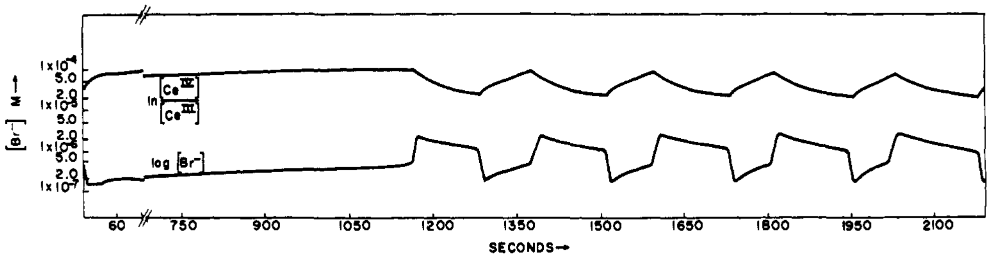

Figure 2. Potentiometric traces (without absolute calibration of cerium potentials) for a reaction with low malonic acid content. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.013\ M$, $[KBrO_3]_0 = 0.063\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.001\ M$, $[H_2SO_4]_0 = 0.8\ M$.

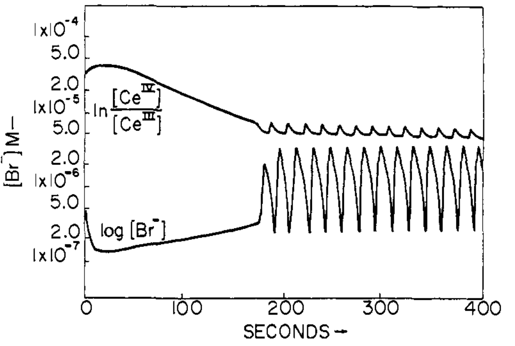

Figure 3. Potentiometric traces (without absolute calibration of cerium potentials) for a reaction with high malonic acid content. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.50\ M$, $[KBrO_3]_0 = 0.063\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.001\ M$, $[H_2SO_4]_0 = 0.8\ M$.

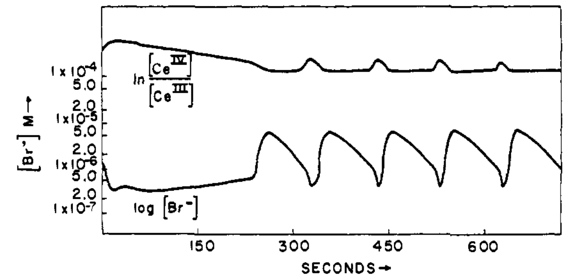

Figure 4. Potentiometric traces (without absolute calibration of cerium potentials) for a reaction with low bromate content. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.13\ M$, $[KBrO_3]_0 = 0.016\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.001\ M$, $[H_2SO_4]_0 = 0.8\ M$.

and the component periods are less well defined. The slow bromide production period seems to have disappeared entirely.

Figure 4 shows the comparatively small effects of reducing bromate ion concentration. Less cerium(IV) is produced in each oscillation, and this species essentially disappears before the end of the slow bromide consumption period. Effects of reducing sulfuric acid concentration are very similar to those of reducing bromate ion.

Figure 5 shows the effects of increased cerium concentration. The induction period is shorter with a higher concentration of cerium(IV) than during the subsequent oscillations, and the amplitude of the oscillation in cerium potential decreases perceptibly from one peak to the next. However, the amplitude of the variation in bromide potential does not differ significantly from that of a solution with only a fifth as much cerium.

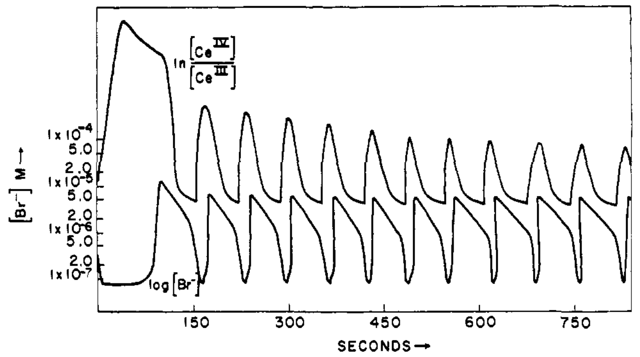

Figure 5. Potentiometric traces (without absolute calibration of cerium potentials) for a reaction with high cerium content. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.13\ M$, $[KBrO_3]_0 = 0.063\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.005\ M$, $[H_2SO_4]_0 = 0.8\ M$.

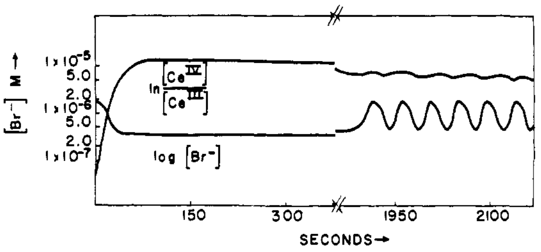

Figure 6. Potentiometric traces (without absolute calibration of cerium potentials) for a reaction with low cerium content. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.13\ M$, $[KBrO_3]_0 = 0.063\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.0001\ M$, $[H_2SO_4]_0 = 0.8\ M$. Because $KBrO_3$ was the last reactant added, the apparent initial surge in ln [Ce(IV)]/[Ce(III)] is really an increase in oxidizing power due to bromate.

Figure 6 shows the effects of very low cerium concentration. Variations in the cerium potential are a barely detectable ripple, and the variations in bromide potential have become more nearly sinusoidal with much less sharply defined periods.

An interpretation of the chemistry in this system could involve three overall reactions.[20]

$$BrO_3^- + 2Br^- + 3CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 3H_2O \qquad (A)$$

$$BrO_3^- + 4Ce^{3+} + CH_2(COOH)_2 + 5H^+ \longrightarrow BrCH(COOH)_2 + 4Ce^{4+} + 3H_2O \qquad (B)$$

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \qquad (R10)$$

Each one of these reactions is virtually irreversible.

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(20) In chemical equations, the cerium species are written simply as Ce^{3+} and Ce^{4+} even though complicated mixtures of complexes are present in this system. Inasmuch as virtually identical oscillatory behavior can be produced with other one-equivalent redox couples, the specific complications of cerium–sulfate chemistry are not germane to our argument.

Bromate ion and malonic acid are consumed and not regenerated. However, both oxidation states of cerium, bromide ion, and bromomalonic acid all appear as reactants in some reactions and as products in others. Therefore, concentrations of these four species might conceivably oscillate depending upon which net reaction was dominant at a particular time. Such oscillations need not and in general do not continue until the reactants are completely consumed.

In the following sections, we shall first demonstrate that the overall stoichiometry can be described in terms of the species present in these three reactions. We shall then categorize the various species in the system as *inorganic bromine, cerium, and organic* and shall consider what is known about reactions involving species in only two categories at a time. We shall finally combine our conclusions to present a detailed mechanism for the oscillating reaction and shall show that this mechanism is qualitatively and virtually quantitatively in agreement with what is known about the behavior of this system.

Stoichiometry of the Oscillating Reaction

Considerations of overall stoichiometry in an oscillating mixture should recognize that sulfuric acid is present in by far the largest molar concentration, that malonic acid and bromate ion are present at intermediate concentrations, and that cerium species are present in minor catalytic concentrations. Since cerium can exist in only two oxidation states, its final form can not significantly affect the stoichiometry of the overall reaction.

Since elementary bromine is the only other inorganic form in appreciable concentration in equilibrium with an excess of acid bromate, and since elementary bromine reacts rapidly and irreversibly with malonic acid, inorganic bromine species other than bromate can exist in appreciable concentrations only temporarily and in kinetically established steady states. Otherwise, bromine will be present in organic combination.

A solution with concentrations known to oscillate was kept for 2 days to ensure complete reaction and then extracted for 24 hr with ether. The total organic bromine in the extract was determined by hydrolysis. It accounted for over 90% of the bromate consumed, and 85% of it was found capable of oxidizing iodide ion and hence presumably was either monobromo- or dibromomalonic acid. Paper chromatography demonstrated the presence of monobromoacetic acid, $BrCH_2COOH$, but no detectable dibromo- or tribromoacetic acid.

Even the small amount of monobromoacetic acid we observed was very likely absent during the oscillations and was formed during the extensive period of standing and extraction. Muus[21] has shown that dibromomalonic acid would have almost quantitatively decarboxylated during two days at this acidity. Our complete failure to detect *any* dibromoacetic acid indicates either that dibromomalonic acid never formed in significant quantity or that it was destroyed before it could decarboxylate and produced only inorganic bromine species as products of that destruction.

The stoichiometry of reaction R10 was demonstrated by titration of the bromide ion produced and of the unreacted excess of cerium(IV) in a solution containing those reactants only. Degn[13] and others have remarked about production of carbon dioxide. Formic acid is the only other product consistent with the redox stoichiometry.

Of course an actual oscillating reaction does not have an excess of cerium(IV), and a significant concentration of an intermediate like mesoxalic acid, $O{=}C(COOH)_2$, may develop. Alternatively, the bromate or HOBr in the oscillating reaction may oxidize the formic acid to carbon dioxide even though cerium(IV) does not do so. In spite of these minor uncertainties, we see no reason to believe that any major species are produced other than those in the above three reactions. The major overall process in the system is therefore described by the stoichiometry of reaction C. It is the free energy change of this reaction that drives the oscillations.

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \longrightarrow 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad \text{(C)}$$

Thermodynamics of Oxybromine–Cerium Reactions

In an acid solution, the possible inorganic bromine species with odd oxidation number exist in singlet ground states as Br^-, HOBr, $HBrO_2$, BrO_3^-, and BrO_4^-. Equilibria involving proton transfer to and from such species are virtually instantaneously established. At least some of the free-radical species $Br\cdot$, $BrO\cdot$, and $BrO_2\cdot$ and the singlet dimers Br_2 and Br_2O_4 may also be mechanistically important.

Free energies of formation of all the singlet monobromine species except $HBrO_2$ and BrO_4^- are reported for aqueous solution by Latimer.[22] An argument claiming to give a value for BrO_2^- in strongly alkaline solution has recently been presented by Lee and Lister.[23] Arguments developed by Pauling[24] and analogies with other HXO_2 acids indicate it is probably an excellent approximation to assume the acid ionization constant of $HBrO_2$ is 10^{-2}. The combined values are presented in Table I.

Table I. Free Energies of Formation (kcal/mol at 25°) of Important Species with Singlet Ground States

Br^-	−24.57	BrO_2^-	6.5
Br_2	0.98	$HBrO_2$	3.8
BrO^-	−8.0	BrO_3^-	4.3
HOBr	−19.9	BrO_4^-	28.9
H_2O	−56.69		

The monobromine species with singlet ground states can be interconverted by oxygen transfer reactions listed according to the number of oxygen atoms in the transition state. The R designations indicate that these reactions are part of the mechanism proposed for the oscillating reaction. They are written in the direction important for that mechanism ($\Delta G°$'s in kcal/mol).

$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \qquad \Delta G°_1 = -11.2 \quad \text{(R1)}$$

$$HBrO_2 + Br^- + H^+ \longrightarrow 2HOBr \qquad \Delta G°_2 = -19.0 \quad \text{(R2)}$$

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(21) J. Muus, *J. Phys. Chem.*, **39**, 343 (1935).

(22) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, New York, N. Y., 1952.

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(24) L. Pauling, "General Chemistry," 3rd ed, W. H. Freeman, San Francisco, Calif., 1970, p 501.

$$BrO_3^- + Br^- + 2H^+ \longrightarrow HBrO_2 + HOBr \qquad \Delta G°_3 = 4.2 \qquad (R3)$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad \Delta G°_4 = -23.2 \qquad (R4)$$

The following discussion neglects all consideration of perbromate ion, BrO_4^-, because it is quite unstable with respect to oxygen transfer to other singlet monobromine species and should not form.

We can also write three equations, all of which probably have positive $\Delta G°$ values, for creation of the radical species. Thermodynamic data are not available for reaction D, but an estimate for (R5) is discussed below.

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2BrO_2\cdot + H_2O \qquad (R5)$$

$$HBrO_2 + HOBr \longrightarrow 2BrO\cdot + H_2O \qquad (D)$$

$$Br_2 \longrightarrow 2Br\cdot \qquad (E)$$

We can make an estimate for (E) by assuming K_c for bromine dissociation is the same in water as in the gas phase. Such an assumption is very good for iodine in hexane,[25] and any failure for bromine in water could hardly affect the conclusions by more than a few hundredths of a volt. Then $\Delta G°_E = 40.52$ kcal/mol.

All of the above data can be combined with cerium potentials from Latimer[22] to yield reduction potentials for a number of possible oxidation changes. In the following expressions, F is the Faraday in coulomb/mol, and $\Delta G°_5$ and $\Delta G°_D$ should be expressed in J/mol.

(a) $BrO_3^- + 6H^+ + 5e^- = {}^1/_2Br_2(aq) + 3H_2O \qquad E°_a = 1.51$ V

(b) $BrO_3^- + 5H^+ + 4e^- = HOBr + 2H_2O \qquad E°_b = 1.49$ V

(c) $BrO_3^- + 3H^+ + 2e^- = HBrO_2 + H_2O \qquad E°_c = 1.24$ V

(d) $HBrO_2 + 2H^+ + 2e^- = HOBr + H_2O \qquad E°_d = 1.74$ V

(e) $HOBr + H^+ + e^- = {}^1/_2Br_2(aq) + H_2O \qquad E°_e = 1.57$ V

(f) ${}^1/_2Br_2(aq) + e^- = Br^- \qquad E°_f = 1.09$ V

(g) $BrO_3^- + 2H^+ + e^- = BrO_2\cdot + H_2O \qquad E°_g = 1.24 - \Delta G°_5/2F$

(h) $BrO_2\cdot + H^+ + e^- = HBrO_2 \qquad E°_h = 1.24 + \Delta G°_5/2F$

(i) $HBrO_2 + H^+ + e^- = BrO\cdot + H_2O \qquad E°_i = 1.74 - \Delta G°_D/2F$

(j) $BrO\cdot + H^+ + e^- = HOBr \qquad E°_j = 1.74 + \Delta G°_D/2F$

(k) $HOBr + H^+ + e^- = Br\cdot + H_2O \qquad E°_k = 0.70$ V

(l) $Br\cdot + e^- = Br^- \qquad E°_l = 1.97$ V

(m) $Ce^{4+} + e^- = Ce^{3+}$ (in 1 m H_2SO_4) $\qquad E°_m = 1.44$ V

(n) $Ce^{4+} + e^- = Ce^{3+}$ (in 1 m $HClO_4$) $\qquad E°_n = 1.70$ V

From these potentials, the following mechanistic conclusions can be drawn.

(1) Acid bromate cannot oxidize cerium(III) significantly in perchloric acid. This conclusion is consistent with our complete failure to obtain oscillations in perchloric acid. Although sulfate and perchlorate ions are isoelectronic, the greater charge on sulfate evidently helps to stabilize the highly positive cerium(IV).[26]

(2) When cerium(III) is oxidized by bromate in sulfuric acid, the most stable final product is elementary bromine. If, as is observed, the reduction product is chiefly HOBr, then the reasons are kinetic rather than thermodynamic.

(3) In spite of the favorable potentials for four-electron and five-electron reductions, bromate will not oxidize cerium(III) significantly in a two-electron process. The potential is still more unfavorable for the one-electron process if bromate is to oxidize a single cerium ion directly.

(4) All radical species are stronger one-electron oxidants than are the singlet species having oxidation number one greater; all radical species are stronger one-electron reductants than are the singlet species having oxidation number one less.

(5) Although the singlet species $HBrO_2$ can oxidize cerium(III) in a two-electron process, it does not necessarily react directly with a single cerium ion.

(6) In spite of the large value of $E°_e$, the value of $E°_k$ demonstrates that HOBr will not oxidize cerium(III) at a significant rate by a one-electron process.

(7) The radical species $Br\cdot$ and $BrO\cdot$ can certainly oxidize cerium(III), and $BrO_2\cdot$ may also do so.

(8) The radical species $Br\cdot$ and $BrO_2\cdot$ can certainly reduce cerium(IV), and $BrO\cdot$ may also do so.

Kinetics of Oxybromine–Cerium Reactions

Assumptions about Activity Coefficients. All of the above thermodynamic data on oxybromine species are computed for a standard state of ideal 1 m solution; the oscillating reaction was studied kinetically in 1 M sulfuric acid where activity coefficients differed significantly from unity. In order to apply an approximate correction for activity effects, the following convention has been adopted for the rate constants reported below. A superscript zero (0) designates a value extrapolated to infinite dilution with standard states of ideal 1 m solution or a value involving only neutral species so that activity coefficient effects are presumably minimal. A prime (′) designates a rate constant for an ionic reaction measured directly in strongly acid medium. An asterisk (*) designates a value expected in acid medium and calculated from data for ideal standard states by assuming that neutral species have activity coefficients of unity and that singly charged ions have activity coefficients of 0.7. Fortunately no multiply charged ions need be considered as long as only oxybromine species are involved. No superscripts are used for expressions that do not depend upon specific numerical evaluations. The second ionization of H_2SO_4 was always neglected as of trivial significance.

Kinetics of (R1). The reaction of HOBr with bromide ion was studied by Eigen and Kustin[27] by

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(25) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

(26) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

(27) M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).

a relaxation technique. They report $k^0_1 = 1.6 \times 10^{10}\ M^{-2}\ \text{sec}^{-1}$ and $k^0_{-1} = 110\ \text{sec}^{-1}$. Then for our system

$$k^*_1 = 8 \times 10^9\ M^{-2}\ \text{sec}^{-1} \tag{1}$$

$$k^0_{-1} = 110\ \text{sec}^{-1} \tag{2}$$

Kinetics of (R3). The kinetics of reaction F were

$$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \longrightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \tag{F}$$

studied by Bray and Liebhafsky[28] and by Skrabal and Weberitsch.[29] The rate was proportional to $[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$ indicating that reaction R3 initiates the overall process and is rate determining.

When we added malonic acid to such a system, the stoichiometry was changed to that of reaction A. The slopes of traces like AB in Figure 1 obeyed the same kinetic form as that of Bray and Liebhafsky,[28] but the rate of bromide consumption was $^2/_5$ as great as they report, just as the relative stoichiometries of (A) and (F) require. Measurements between 5 and 44° indicated an activation energy of 11.8 kcal/mol in good agreement with the observations of Skrabal and Weberitsch.[29] Separate experiments confirmed that the rate of reaction A was independent of the concentrations of malonic acid and of Ce(III) just as expected. From this information, we conclude that in our solutions

$$k'_3 = 2.1\ M^{-3}\ \text{sec}^{-1} \tag{3}$$

$$k^0_{-3} = 1.0 \times 10^4\ M^{-1}\ \text{sec}^{-1} \tag{4}$$

Kinetics of (R2). Reactions A and F take place with clean kinetics and are initiated by rate-determining step R3 even though that step has a positive $\Delta G°$. These observations require that step R2 take place much more rapidly than the reverse of (R3) and that $k^*_2 \gg 2.1\ M^{-2}\ \text{sec}^{-1}$.

A more precise estimate is provided by the observation of Betts and MacKenzie[30] that the disproportionation of acid hypobromous acid is second order in HOBr. We have repeated and confirmed their results quantitatively. A plausible mechanism is

$$2\text{HOBr} \longrightarrow \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \tag{$-$R2}$$

$$\text{HOBr} + \text{Br}^- + \text{H}^+ \longrightarrow \text{Br}_2 + \text{H}_2\text{O} \tag{R1}$$

$$2\text{HBrO}_2 \longrightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+ \tag{R4}$$

If step $-$R2 is rate-determining, $-\text{d}[\text{HOBr}]/\text{d}t = 2.5k_{-2}\cdot[\text{HOBr}]^2$ and the data of Betts and MacKenzie can be combined with the thermodynamic data corrected for estimated activity coefficients to indicate that

$$k^*_2 = 2 \times 10^9\ M^{-2}\ \text{sec}^{-1} \tag{5}$$

$$k^0_{-2} = 5 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1} \tag{6}$$

When these values of k^*_1, k^*_2, and k^*_3 are applied to a hypothetical reacting system, they demonstrate that HBrO_2 and HOBr remain in very low steady-state concentrations and confirm the conclusion that step R3 is rate-determining for reaction F and therefore even more certainly for reaction A.

Kinetics of (R5). By analogy with reactions R1 and E, production of radicals by (R5) presumably involves a nucleophilic displacement followed by homolytic splitting of the resulting Br–Br bond by steps R5a and R5b.

$$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \longrightarrow \text{Br}_2\text{O}_4 + \text{H}_2\text{O} \tag{R5a}$$

$$\text{Br}_2\text{O}_4 \longrightarrow 2\text{BrO}_2\cdot \tag{R5b}$$

Buxton and Dainton[31] have studied these reactions by pulse radiolysis and have concluded that $k^0_{-5a} = 1.1 \times 10^6\ \text{sec}^{-1}$, $k^0_{5b} = 7 \times 10^7\ \text{sec}^{-1}$, $k^0_{-5b} = 1.4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, and $K_{5b} = 19\ M^{-1}$. These results indicate that, unlike the situation with Br_2, once Br_2O_4 is formed it is much more likely to dissociate than to disproportionate. Therefore, we may set $k_5 = k_{5a}$ and simplify our kinetic treatment by neglecting consideration of Br_2O_4.

Betts and MacKenzie[32] also studied the isotopic exchange of elementary bromine with bromate ion in 1.7 M perchloric acid. Satisfactory kinetics were obtained only if the intermediate oxidation states had become equilibrated before isotopic tracer was added. They observed empirically that the rate of exchange was proportional to $[\text{BrO}_3^-]^{1.7}[\text{Br}_2]^{0.3}[\text{H}^+]^{1.1}$ but did not draw mechanistic inferences. If exchange involves reaction of HBrO_2 with HBrO_3, the observed kinetics should be $[\text{BrO}_3^-]^{1.6}[\text{Br}_2]^{0.2}[\text{H}^+]^{1.6}$ and might be somewhat less dependent upon hydrogen ion if HBrO_3 were not completely dissociated in this strong acid. The exchange data indicate either that there is direct oxygen transfer between HBrO_2 and HBrO_3 or else that exchange results from step R5; we believe the latter interpretation is required by the kinetics of cerium(III) oxidation discussed below.

In a solution containing initially 0.082 M BrO_3^-, 0.0025 M Br_2, and 1.67 M HClO_4, Betts and MacKenzie[32] observed isotopic exchange at $2.6 \times 10^{-8}\ M\ \text{sec}^{-1}$. If the same activity coefficient corrections are assumed as for our solutions, the data from Table I indicate that during exchange $[\text{HBrO}_2] = 4 \times 10^{-11}\ M$. Since the rate of step R5 is twice the rate of exchange

$$k'_5 = 1.0 \times 10^4\ M^{-2}\ \text{sec}^{-1} \tag{7}$$

As discussed above, the data of Buxton and Dainton[31] indicate that

$$k^0_{-5} = 2 \times 10^7\ M^{-1}\ \text{sec}^{-1} \tag{8}$$

If the same activity coefficient estimate is applied, additional thermodynamic estimates are

$$\Delta G°_f(\text{BrO}_2\cdot) = 34.4\ \text{kcal/mol} \tag{9}$$

$$E°_g = 1.15\ \text{V} \tag{10}$$

$$E°_h = 1.33\ \text{V} \tag{11}$$

These results confirm the conclusion of the thermodynamics discussion that bromate ion will not oxidize cerium(III) by a one-electron process. The calculated value of $E°_h$ is distinctly less than the 1.44 V reduction potential of Ce(IV) in our medium, but $\text{BrO}_2\cdot$ could still oxidize Ce(III) because the reaction would be in competition with step $-$R5 which is second order in a species present at very low concentration.

Kinetics of (R4) and of Bromate Oxidation of Ce(III). Thompson[33] has reported that in the presence of a

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[28] W. C. Bray and H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **57**, 51 (1935).

[29] A. Skrabal and S. R. Weberitsch, *Monatsh. Chem.*, **36**, 211 (1915).

[30] R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, **29**, 666 (1951).

[31] G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc., Ser. A*, **304**, 427 (1968).

[32] R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, **29**, 655 (1951).

[33] R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971).

sufficiently great concentration of any of the weak one-electron reductants Ce(III), Mn(II), or Np(V) bromate is reduced at a rate second order in $[BrO_3^-]$ and independent of the concentration and chemical nature of the reductant. We have pointed out elsewhere[34] that this kinetic behavior is consistent with the mechanism

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2BrO_2\cdot + H_2O \qquad (R5)$$

$$BrO_2\cdot + Ce^{3+} + H^+ \longrightarrow HBrO_2 + Ce^{4+} \qquad (R6)$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad (R4)$$

A steady state is established such that $[HBrO_2] = (k_5/2k_4)[BrO_3^-][H^+]$ and the rate of reduction is then

$$-\frac{d[BrO_3^-]}{dt} = (k^2{}_5/4k_4)[BrO_3^-]^2[H^+]^2 \qquad (12)$$

If the Thompson[33] data in 3 M sulfuric acid are combined with eq 7 with the assumption that activity coefficients do not change rapidly at these high ionic strengths

$$k^0{}_4 = 4 \times 10^7\ M^{-1}\ sec^{-1} \qquad (13)$$

$$k^*{}_{-4} = 2 \times 10^{-10}\ M^{-2}\ sec^{-1} \qquad (14)$$

The large magnitude of k_4 and the irreversibility of the reaction make it clear that $HBrO_2$ will always be at very low concentration in acid solutions unless it is being produced at a very rapid rate.

Evidence Regarding Br(II) Species. The above discussion has evaluated rate constants in both directions for reactions R1 to R5. It is instructive to apply the results to an equilibrium mixture of species undergoing isotopic exchange. Betts and MacKenzie[32] specifically studied exchange in a solution containing the concentrations $[BrO_3^-] = 0.0815\ M$, $[Br_2] = 0.0013\ M$, $[HOBr] = 0.0024\ M$, $[H^+] = 1.67\ M$. For such a solution, we calculate that $[HBrO_2] = 4 \times 10^{-11}\ M$, $[Br^-] = 4 \times 10^{-9}\ M$. Let $v_{\pm1} = k^*{}_1[HOBr][Br^-]\cdot[H^+] = k^0{}_{-1}[Br_2]$ be the rate at which (R1) is taking place in each direction in the solution. Then the rate constants evaluated above predict for this solution

$$v_{\pm1} = 0.14\ M\ sec^{-1} \qquad (15)$$

$$v_{\pm2} = 3 \times 10^{-10}\ M\ sec^{-1} \qquad (16)$$

$$v_{\pm3} = 1.0 \times 10^{-9}\ M\ sec^{-1} \qquad (17)$$

$$v_{\pm4} = 6 \times 10^{-14}\ M\ sec^{-1} \qquad (18)$$

$$v_{\pm5} = 5 \times 10^{-8}\ M\ sec^{-1} \qquad (19)$$

The large value of $v_{\pm1}$ confirms that the species Br^-, Br_2, and HOBr will be isotopically equilibrated within any time of interest to us. The relative values of $v_{\pm3}$, $v_{\pm4}$, and $v_{\pm5}$ reinforce the assumptions above that (R5) is the step by which BrO_3^- becomes isotopically equilibrated with $HBrO_2$. However, the relative values of $v_{\pm2}$ and $v_{\pm3}$ to $v_{\pm5}$ indicate that on the basis of the reactions discussed above $HBrO_2$ and BrO_3^- should be so rapidly equilibrated that the rate-determining step for exchange of BrO_3^- with Br_2 is (R2); the kinetic data of Betts and MacKenzie[32] clearly demonstrate that $HBrO_2$ is isotopically equilibrated with Br_2 and that (R5) is rate determining.

Further evidence is provided by the time dependence of the apparent rate of exchange. If isotopic tracer is present when the solutions of Br_2 and BrO_3^- are mixed, the apparent rate of exchange is *faster* than the rate if tracer is added after the solution has become equilibrated. When the solutions are mixed, (R1) establishes a situation such that $[Br^-] = [HOBr] = 4 \times 10^{-6}\ M$. Within a second, reactions R3 and R2 establish a steady state such that $[HBrO_2] = (k_3/k_2)[BrO_3^-][H^+] = 1.4 \times 10^{-10}\ M$. As time goes on, the concentration of $HBrO_2$ decreases by a factor of about 3.5, and the concentrations of Br^- and HOBr decrease and increase, respectively, by two or three powers of 10. The apparent rate of exchange behaves very much as would be expected if $HBrO_2$ were always isotopically equilibrated with Br_2 and HOBr even though the initial rate of (−R2) is only about $10^{-15}\ M\ sec^{-1}$.

These observations require an additional reaction for isotopic equilibration of $HBrO_2$ with lower oxidation states. By analogy, the most plausible possibilities are (R3a) and (R3b), where the asterisk in (R3b) is used to label an oxygen atom.

$$HBrO_2 + HOBr \rightleftharpoons Br_2O_2 + H_2O \qquad (R3a)$$

$$HBrO_2 + HO^*Br \rightleftharpoons HBrOO^* + HOBr \qquad (R3b)$$

If the data of Betts and MacKenzie[32] are to be explained, either k_{3a} or k_{3b} must be at least $10^8\ M^{-1}\ sec^{-1}$. If the mechanism is (R3a), Br_2O_2 must be like Br_2 rather than Br_2O_4 in that it disproportionates much more easily than it dissociates; otherwise the very reactive $BrO\cdot$ radicals would certainly oxidize Ce(III), and the rate of oxidation of Ce(III) by bromate would increase as HOBr was formed instead of decreasing as reported by Thompson[33] and by Kasperek and Bruice.[14] If the mechanism is R3b, we must explain why a similar oxygen transfer does not take place between $HBrO_3$ and $HBrO_2$; otherwise the rate of $BrO_2\cdot$ formation would be less than the rate we have calculated on the basis of the Betts and MacKenzie[32] exchange, and the discrepancy in the critical bromide concentration for the oscillating reaction would be even worse than that discussed below. These problems are considered further in the Discussion.

Other Cerium Reactions with Oxybromine Species. The work of Thompson[33] indicates that $BrO_2\cdot$ is the species responsible for oxidizing cerium(III) in these systems. However, the relative values of $E°_m$ and $E°_h$ indicate that, in spite of the large magnitude of k_4, step R6 may become reversible as cerium(IV) accumulates.

The potentials make it clear that BrO_3^- does not oxidize cerium(III) directly in a one-electron process, but the reverse step R7 is probably important in the oscillating reaction.

$$BrO_2\cdot + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2H^+ \qquad (R7)$$

Although the value of $E°_i$ suggests that $HBrO_2$ might oxidize cerium(III) directly in a one-electron process, the Thompson[33] kinetics demonstrate that such a reaction cannot compete with step R4 even at cerium concentrations much greater than in our system.

The value of $E°_j$ demonstrates that $BrO\cdot$ could certainly oxidize cerium(III), and the failure of this step to contribute to the Thompson[33] kinetics demonstrates that $BrO\cdot$ is not formed at a significant rate in this system.

The values of $E°_k$ and $E°_l$ demonstrate that $Br\cdot$

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(34) R. M. Noyes, R. J. Field, and R. C. Thompson, *J. Amer. Chem. Soc.*, 93, 7315 (1971).

atoms are too unstable to be of importance in our system. Consistent with this conclusion, the rates of reduction of HOBr by Ce(III)[35] and of oxidation of Br^- by Ce(IV)[36] are both too slow to be significant in our system even though both should produce large amounts of bromine at equilibrium.

Reactions of Organic and Bromine Species

Bromination of Malonic Acid. In acid solution, bromine reacts rapidly and irreversibly with malonic acid according to process R8. As discussed in the

$$Br_2 + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + Br^- + H^+ \quad (R8)$$

section on Stoichiometry, we do not believe dibromination is significant in our system.

When even modest amounts of free bromine are present, the rate-determining step is clearly enolization of malonic acid.[37,38] The enolization is acid catalyzed, and the kinetics of the process are supposedly given by eq 20 where MA and BrMA indicate malonic and

$$\frac{d[\mathrm{BrMA}]}{dt} = k^{0}_{8}[\mathrm{H}^+][\mathrm{MA}] \quad (20)$$

bromomalonic acids, respectively. Although we have not studied this reaction in detail, very rough experiments indicate that

$$k^{0}_{8} = 1.3 \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1} \quad (21)$$

Hypobromous acid can also brominate malonic acid by process R8a. The rate is presumably determined by

$$HOBr + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + H_2O \quad (R8a)$$

the same enolization reaction as in (R8).

Process R8a is identically the sum of (R1) + (R8). If $[Br^-]$ is greater than about 10^{-8} M, any HOBr that is formed will be almost instantaneously converted to Br_2 unless it is intercepted by enol, but the detailed mechanism of bromination is usually unimportant kinetically.

We have examined the reaction of HOBr with malonic acid in a solution that also contained silver ion. Bromination proceeded cleanly in a clear solution until the HOBr was almost completely consumed, at which point a small precipitate of silver bromide suddenly appeared. The HOBr obviously maintains bromide ion at a very low concentration until it is almost consumed just as is predicted by the above discussion.

Reactions of Other Oxybromine Species with Malonic Acid. The section on stoichiometry pointed out that the oscillating reaction is driven by the free energy change of the reaction of acid bromate with malonic acid. However, the direct reaction is so slow that we have no evidence for its occurrence. All the complicated superstructure of this oscillating mechanism is significant precisely because of the slowness of the direct reaction!

We do not know whether the intermediate species $HBrO_2$ and $BrO_2\cdot$ will react directly with malonic or with bromomalonic acids. Many other facile reactions are available to both of these high energy species in our system, although we shall later present evidence that they may react somewhat with malonic acid or with species derived from it.

Cerium(IV) Oxidations of Organic Species

Oxidation of Malonic Acid. Sengupta and Aditya[39] established the stoichiometry of reaction R9 and found

$$CH_2(COOH)_2 + 6Ce^{4+} + 2H_2O \longrightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+ \quad (R9)$$

the rate was first order in oxidant. We have confirmed their stoichiometry. Kasperek and Bruice[14] studied the kinetics more thoroughly and reported the rate was given by eq 22 where $[Ce^{4+}]$ is the total concentration of Ce(IV) and K''_9 is an empirical constant. Values of the parameters were

$$v_9 = -\frac{d[\mathrm{MA}]}{dt} = \frac{k'_9[\mathrm{Ce}^{4+}][\mathrm{MA}]}{K''_9 + [\mathrm{MA}]} \quad (22)$$

$$k'_9 = 8.8 \times 10^{-2}\ \mathrm{sec}^{-1} \quad (23)$$

$$K''_9 = 0.53\ M \quad (24)$$

These observations indicate that reaction R9 is initiated by a rate-determining unimolecular reaction of a cerium(IV) complex of malonic acid. This process presumably produces a radical that reacts rapidly with more oxidant by one-electron processes. Hydroxy and keto derivatives of malonic and/or acetic acids are presumably formed as intermediates. Singlet organic molecules probably react with cerium(IV) by oxidative hydrogen abstraction, perhaps accompanied by decarboxylation. Radicals might react with Ce(IV) either by oxidative hydrogen abstraction or by hydroxylation by water. The details of these subsequent fast processes are not important to the kinetics of the oscillating reaction. As was indicated in the section on stoichiometry, we have not established that the low concentrations of cerium(IV) in our system pushed the oxidation clear to formic acid, but less complete oxidation would have rather little effect on our overall conclusions.

Oxidation of Bromomalonic Acid. As was mentioned in the section on stoichiometry, we have established that process R10 takes place with bromomalonic acid.

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \quad (R10)$$

Kasperek and Bruice[14] also studied the kinetics of this reaction and report

$$v_{10} = -\frac{d[\mathrm{BrMA}]}{dt} = \frac{k'_{10}[\mathrm{Ce}^{4+}][\mathrm{BrMA}]}{K''_{10} + [\mathrm{BrMA}]} \quad (25)$$

$$k'_{10} = 1.7 \times 10^{-2}\ \mathrm{sec}^{-1} \quad (26)$$

$$K''_{10} = 0.20\ M \quad (27)$$

It is the ability of the oxidizing species Ce(IV) to liberate the reducing species Br^- that makes this reaction important to the mechanism of the oscillating reaction.

Oxidation of Mixtures. Although reactions R9 and R10 proceed cleanly with the respective pure acids, the situation is more complicated when both are present

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[35] V. A. Vavilin and A. M. Zhabotinskii, *Kinet. Katal.*, **10**, 83 (1969).

[36] E. L. King and M. L. Pandow, *J. Amer. Chem. Soc.*, **75**, 3067 (1953).

[37] R. W. West, *J. Chem. Soc.*, **125**, 1277 (1924).

[38] S. L. Bafna, V. M. Bhale, and W. V. Bhagwat, *Agra Univ. J. Res., Sci.*, **4**, 341 (1955).

[39] K. K. Sengupta and S. Aditya, *Z. Phys. Chem.* (*Frankfurt am Main*), **38**, 25 (1963).

simultaneously. Figure 7 illustrates the peculiar behavior of a bromide sensitive electrode when cerium(IV) is added dropwise to a solution containing both acids. The trace is compared with the one obtained when the same concentration of bromomalonic acid is present alone.

This figure suggests either that the bromine in bromomalonic acid is not initially liberated as Br^- but rather as HOBr or some similar species capable of brominating unsubstituted malonic acid or else that partially oxidized organic intermediates can oxidize bromide ion to bromine. We have not yet resolved the complications associated with cerium oxidation of mixed acids, and the bromide ion produced by cerium(IV) oxidation during the oscillating reaction may be somewhat less than we predict on the basis of reaction R10.

Reactions Involving Species from All Three Categories

We have categorized the species in our system as inorganic bromine, cerium, and organic, and the preceding sections have examined the reactions of species in two categories at a time. We shall now try to develop a mechanism for the oscillating reaction on the basis of these observations of pairs of categories. However, we must recognize that our attempt may be incomplete and that some net processes involving species in all three categories may not be resolvable into processes involving pairs of categories only.

The most likely reason for concern arises from the radical and oxygenated intermediates formed during the oxidation of organic compounds by cerium(IV). We have shown that the direct reaction of bromate ion with malonic acid is too slow to be of importance, and we see little reason to believe that either $HBrO_2$ or $BrO_2\cdot$ is reacting directly with malonic acid. However, oxybromine species may compete with cerium(IV) for the organic intermediates produced during reactions R9 and R10. Such competition would affect our quantitative and perhaps even our qualitative description of the overall reaction. The possibilities of such complications are left open, and we present evidence below that some such reaction does indeed occur.

Mechanism of the Oscillating Reaction

Component Processes. As a result of the evidence discussed above, we propose that the mechanism of the oscillating reaction can be described by ten processes, each of which is elementary or at least has clearly defined kinetics. Unless a double arrow is included in an equation, the process may be regarded as virtually irreversible under our conditions.

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \qquad (R1)$$

$$HBrO_2 + Br^- + H^+ \longrightarrow 2HOBr \qquad (R2)$$

$$BrO_3^- + Br^- + 2H^+ \longrightarrow HBrO_2 + HOBr \qquad (R3)$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad (R4)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O \qquad (R5)$$

$$BrO_2\cdot + Ce^{3+} + H^+ \rightleftharpoons HBrO_2 + Ce^{4+} \qquad (R6)$$

$$BrO_2\cdot + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2H^+ \qquad (R7)$$

$$Br_2 + CH_2(COOH)_2 \longrightarrow BrCH(COOH)_2 + Br^- + H^+ \qquad (R8)$$

$$6Ce^{4+} + CH_2(COOH)_2 + 2H_2O \longrightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+ \qquad (R9)$$

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ \qquad (R10)$$

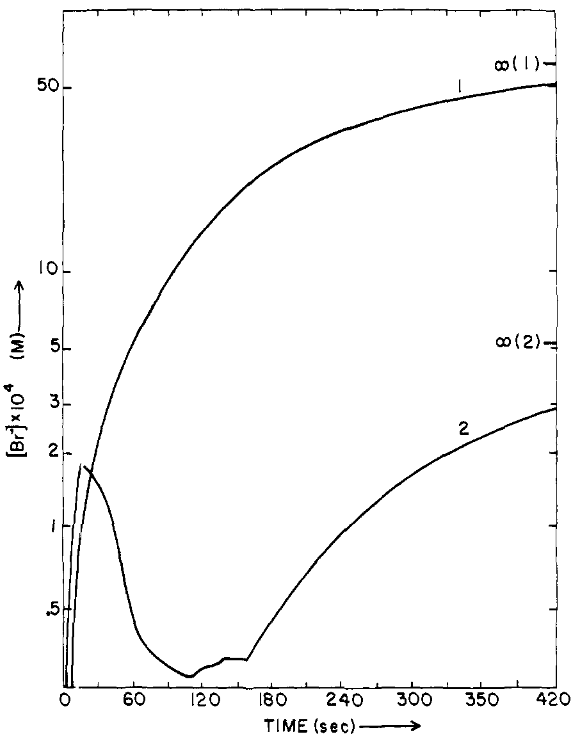

Figure 7. Time dependence of bromide ion concentration when 10 ml of 0.050 *M* cerium(IV) in 1 *M* H_2SO_4 was added dropwise to 40 ml of 0.0125 *M* bromomalonic acid. Curve 1 contained only these species; curve 2 had 0.025 *M* malonic acid in addition to the bromomalonic acid.

Rates of Component Processes. Let v_i be the net forward rate of process R_i. Thus $v_1 = k_1[HOBr]\cdot[Br^-][H^+] - k_{-1}[Br_2]$. The kinetics of the first five processes have been discussed above, and rate constants have been presented for calculating v_1 to v_5 in strongly acid medium.

Rate constants for (R6) and (R7) are not presently known. The thermodynamic and kinetic data presented above indicate that

$$k_6/k_{-6} = K_6 = 0.025\ M^{-1} \qquad (28)$$

The rate of bromination of malonic acid, v_8, is determined either by enolization of the acid or by formation of HOBr. Then

$$v_8 = k_8[H^+][MA] \quad \text{or} \quad v_8 = 2v_2 + v_3 + v_4 \qquad (29)$$

whichever is smaller.

The kinetic parameters for (R9) and (R10) have been determined by Kasperek and Bruice[14] and are presented above.

Classification of Reactants. The rates of the ten reactions postulated for the mechanism can be described in terms of the concentrations of eleven chemical species, and in principle this many quantities must be specified to define the state of the system well enough to predict its future kinetic behavior. In practice, rapid equilibria and steady-state restrictions on metastable intermediates will limit the number of parameters needed to define the state for kinetic purposes.

Four *major reactants*, BrO_3^-, $CH_2(COOH)_2$, $BrCH(COOH)_2$, and H^+, appear also in eq C describing the overall stoichiometry. The concentration of each may be varied independently, but these concentrations change by only small relative amounts during an individual oscillation.

The total concentration of catalytic cerium species may also be varied independently, and this total is chosen as the fifth member of the class of major reactants.

Concentrations of at least two and perhaps three additional *reference reactants* must be specified to define the state of the system for kinetic purposes. The choice may be somewhat arbitrary, and the analytical techniques we have used make it logical to select Br^- and Ce(IV) as two of the reference reactants. The chemistry of the mechanism is such that they are probably the best choice in any event. If a third reference parameter is needed, we have selected the sum of the concentrations of $HOBr + Br_2$.

By specifying the concentrations of the seven or eight major and reference reactants, the state of the system is uniquely defined for kinetic purposes. Such specification will fix the concentrations of the four or three other *derived reactants*. For our description, these are $HBrO_2$, $BrO_2\cdot$, and either one or both of HOBr and Br_2.

Concentration of Derived Reactants

Concentrations of HOBr and Br_2. The data of Eigen and Kustin[27] demonstrate that the species of (R1) become equilibrated within much less than a second, and the equilibrium can not be significantly perturbed by any processes on the time scale of interest here. Neither of the species HOBr or Br_2 ever becomes stoichiometrically significant when the concentration of malonic acid is high, but they may build up temporarily if there is little malonic acid. However, we may always assume

$$[Br_2] = \frac{K_1[H^+][Br^-]}{1 + K_1[H^+][Br^-]}\{[HOBr] + [Br_2]\} \quad (30)$$

$$[HOBr] = \frac{1}{1 + K_1[H^+][Br^-]}\{[HOBr] + [Br_2]\} \quad (31)$$

Because K_1 is almost $10^8\ M^{-2}$ and $[H^+][Br^-]$ is never less than about $10^{-7}\ M^2$, it will be a satisfactory approximation to assume that only Br_2 is present in our system.

Concentration of $BrO_2\cdot$. The steady-state approximation of eq 32 may certainly be applied to the transient intermediate $BrO_2\cdot$. The algebra of solving for its concentration is considerably simplified if we may neglect contributions from (−R5). Such neglect is permissible if $k_6[Ce^{3+}][H^+] \gg 2k_{-5}[BrO_2\cdot]$. The data of Thompson[33] demonstrate that this approximation is valid for $[Ce^{3+}] > 0.026\ M$; we can hope it is also valid for the lower concentrations in our system. Equation 32 then gives

$$\frac{d[BrO_2\cdot]}{dt} = 2v_5 - v_6 - v_7 = 0 \quad (32)$$

$$[BrO_2\cdot] = \frac{2k_5[BrO_3^-][H^+] + k_{-6}[Ce^{4+}]}{k_6[Ce^{3+}][H^+] + k_7[Ce^{4+}]}[HBrO_2] \quad (33)$$

Concentration of $HBrO_2$. Bromous acid is by far the most important derived reactant in this system. If the steady-state approximation of eq 33 is valid, then

$$\frac{d[HBrO_2]}{dt} = -v_2 + v_3 - 2v_4 - v_5 + v_6 = -\alpha[HBrO_2]^2 - \beta[HBrO_2] + \gamma \quad (34)$$

$$\alpha = 2k_4 \quad (35)$$

$$\beta = k_2[Br^-][H^+] - \frac{k_5[BrO_3^-][H^+]\{k_6[Ce^{3+}][H^+] - k_7[Ce^{4+}]\} - k_{-6}k_7[Ce^{4+}]^2}{k_6[Ce^{3+}][H^+] + k_7[Ce^{4+}]} \quad (36)$$

$$\gamma = k_3[BrO_3^-][Br^-][H^+]^2 \quad (37)$$

Although the concentration of $HBrO_2$ will change almost discontinuously whenever β approaches zero, a steady-state approximation may be applied to eq 34 at most times. Moreover, an examination of the magnitudes of the terms shows that $\beta^2 \gg 4\alpha\gamma$ is a good approximation for most of the anticipated finite values of β. If the subscript ss designates a steady-state approximation

$$\begin{aligned}[HBrO_2]_{ss} &= \frac{\beta}{2\alpha}(-1 + \sqrt{1 + 4\alpha\gamma/\beta^2}) \approx \gamma/\beta \qquad \beta > 0 \\ &= \frac{\beta}{2\alpha}(-1 - \sqrt{1 + 4\alpha\gamma/\beta^2}) \approx -\beta/\alpha \qquad \beta < 0\end{aligned} \quad (38)$$

When $\beta = 0$, the steady-state approximation predicts that $[HBrO_2]$ will have the geometric mean value of $\sqrt{\gamma/\alpha}$, but the concentration is then changing so rapidly that the steady-state approximation is inappropriate. Because k_4 and k_5 are more nearly comparable than k_2 and k_3 are, $HBrO_2$ will be present in much greater concentration when β is negative (very small amounts of bromide ion) than when it is positive (appreciable bromide ion).

Kinetic Behavior of Major Reactants

If we use the implications of steady-state applications to eq 32 and 34, we obtain eq 39–41. The major reactant H^+ is present in such high concentration that its kinetic behavior is of trivial significance. The total concentration of cerium species is constant during any single run.

$$\frac{d[BrO_3^-]}{dt} = -v_3 + v_4 - v_5 + v_7 = -v_2 - v_4 \quad (39)$$

$$\frac{d[MA]}{dt} = -v_8 - v_9 \quad (40)$$

$$\frac{d[BrMA]}{dt} = v_8 - v_{10} \quad (41)$$

These equations demonstrate that the species BrO_3^- and MA decrease monotonically as expected by the overall stoichiometry of eq C. Although eq 41 contains terms of opposite sign, the magnitudes are such that BrMA probably increases monotonically. The major reactants exhibit very normal kinetic behavior, and the oscillations of interest are confined to the reference reactants which are present in much lower concentration.

Kinetic Behavior of Reference Reactants

Behavior of HOBr + Br$_2$. Let τ designate a time (probably near the end of a slow bromide consumption period) at which the species HOBr and Br$_2$ are present at negligibly small concentration but are about to become significant. At some subsequent time t

$$[\mathrm{HOBr}] + [\mathrm{Br_2}] = \int_\tau^t (2v_2 + v_3 + v_4 - k_8[\mathrm{H^+}][\mathrm{MA}])\,\mathrm{d}t > 0 \quad (42)$$

The inequality is written to emphasize that the concentrations are always positive even though the integral will become negative for at least some times. The value of τ must correspond to the time at which the integrand changes from negative to positive sign. If the concentration of malonic acid is so low that the integral is positive at all times, the system probably will not oscillate. If the concentration of malonic acid is sufficiently high, the integral will be negative at all times and the species HOBr and Br$_2$ should be considered as derived rather than as reference reactants. However, Franck and Geiseler[40] have demonstrated spectrophotometrically that in some systems the concentration of Br$_2$ will fluctuate in synchronization with that of Ce(IV). As has been shown above, the concentration of HOBr is never more than a small fraction of that of Br$_2$.

Behavior of Ce(IV). Application of steady-state implications of eq 32 and 34 leads to

$$\frac{\mathrm{d}[\mathrm{Ce^{4+}}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{Ce^{3+}}]}{\mathrm{d}t} = v_6 - v_7 - 6v_9 - 4v_{10} = 2v_2 - 2v_3 + 4v_4 - 6v_9 - 4v_{10} \quad (43)$$

When concentrations of bromide ion are moderately high, v_2 and v_3 will be virtually equal and v_4 will be very small. Therefore, Ce(IV) will form only at very low concentrations of bromide ion. It will be appropriate during the induction period to use a steady-state approximation setting eq 43 equal to zero; such an approximation is not permissible at other times.

Behavior of Br$^-$. Bromide ion is the most important reference reactant to follow during oscillations in this system. The mechanism as developed here predicts that

$$\frac{\mathrm{d}[\mathrm{Br^-}]}{\mathrm{d}t} = -v_2 - v_3 + v_{10} \quad (44)$$

or

$$\frac{\mathrm{d}[\mathrm{Br^-}]}{\mathrm{d}t} = -3v_2 - 2v_3 - v_4 + k_8[\mathrm{H^+}][\mathrm{MA}] + v_{10} \quad (45)$$

Here, eq 44 applies if there is no significant concentration of Br$_2$, and eq 45 applies if this species is significant.

It is the magnitude of bromide concentration that determines the sign of β in eq 36. Let $[\mathrm{Br^-}]_{\mathrm{crit}}$ be the critical concentration at which β changes sign. At greater bromide concentrations, β will be positive, the concentration of HBrO$_2$ will be very small, and the rate of reaction B will be negligibly slow. At lesser bromide concentrations, β will be negative, the concentration of HBrO$_2$ will be greater, and the rate of reaction B will be significant. As we have pointed out before,[15] the concentration of HBrO$_2$ and the rates of its reactions depend upon the sign of β and hence upon whether the concentration of bromide ion is above or below a certain value much as the current in a thyratron tube depends upon whether the grid potential is above or below a particular value.

$$[\mathrm{Br^-}]_{\mathrm{crit}} = \frac{k_5[\mathrm{BrO_3^-}][\mathrm{H^+}]\{k_6[\mathrm{Ce^{3+}}][\mathrm{H^+}] - k_7[\mathrm{Ce^{4+}}]\} - k_{-6}k_7[\mathrm{Ce^{4+}}]^2}{k_2[\mathrm{H^+}]\{k_6[\mathrm{Ce^{3+}}][\mathrm{H^+}] + k_7[\mathrm{Ce^{4+}}]\}} \quad (46)$$

The concentration of bromide ion is so small that a steady-state approximation is permissible when Ce(IV) is present but Br$_2$ is not. Then eq 44 is valid and the approximation gives eq 47. Because concentrations of major reactants are so much greater than those of reference reactants, we may write eq 48. This equation is of importance because the potential of the bromide sensitive electrode varies logarithmically with bromide ion concentration.

$$[\mathrm{Br^-}]_{\mathrm{ss}} = \frac{k_{10}[\mathrm{BrMA}][\mathrm{Ce^{4+}}]}{\{K''_{10} + [\mathrm{BrMA}]\}\{k_2[\mathrm{HBrO_2}][\mathrm{H^+}] + k_3[\mathrm{BrO_3^-}][\mathrm{H^+}]^2\}} \quad (47)$$

$$\frac{\mathrm{d}\ln[\mathrm{Br^-}]_{\mathrm{ss}}}{\mathrm{d}t} = \frac{\mathrm{d}\ln[\mathrm{Ce^{4+}}]}{\mathrm{d}t} = -\frac{6k_9[\mathrm{MA}]}{K''_9 + [\mathrm{MA}]} - \frac{4k_{10}[\mathrm{BrMA}]}{K''_{10} + [\mathrm{BrMA}]} \quad (48)$$

Kinetic Behavior during Stages of Reaction

We shall now demonstrate that these expressions do indeed describe the complex behavior observed during different stages of this reaction. The bromide ion trace in Figure 1 will be emphasized, but the different behaviors in other figures will be pointed out.

Kinetics during the Bray Period. The Bray period, AB, occurs no more than once and then only at the very start of reaction in a system containing a finite initial concentration of bromide ion. Such a system contains no significant Ce(IV), but it of course contains bromate and malonic acid.

The principal overall process in such a system is (A),

$$\mathrm{BrO_3^-} + 2\mathrm{Br^-} + 3\mathrm{CH_2(COOH)_2} + 3\mathrm{H^+} \longrightarrow 3\mathrm{BrCH(COOH)_2} + 3\mathrm{H_2O} \quad (\mathrm{A})$$

resulting from the sequence (R3) + (R2) + 3(R1) + 3(R8).

The bromide ion concentration is great enough that β in eq 36 is positive. The concentration of bromous acid is given by eq 49, and the kinetics by eq 50. Bromide ion is consumed so rapidly that it has a half-life of only 8 sec under the conditions of Figure 1.

$$[\mathrm{HBrO_2}]_{\mathrm{ss}} = (k_3/k_2)[\mathrm{BrO_3^-}][\mathrm{H^+}] = 1.0 \times 10^{-9}[\mathrm{BrO_3^-}][\mathrm{H^+}] \quad (49)$$

$$\frac{\mathrm{d}[\mathrm{BrO_3^-}]}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}[\mathrm{Br^-}]}{\mathrm{d}t} = \frac{1}{3}\frac{\mathrm{d}[\mathrm{MA}]}{\mathrm{d}t} = -\frac{1}{3}\frac{\mathrm{d}[\mathrm{BrMA}]}{\mathrm{d}t} = -v_3 = -k_3[\mathrm{BrO_3^-}][\mathrm{Br^-}][\mathrm{H^+}]^2 \quad (50)$$

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(40) U. Franck and W. Geiseler, *Naturwissenschaften*, **58**, 52 (1970).

Under these conditions, cerium is being oxidized negligibly slowly. The $4v_4$ term in eq 43 is only 4×10^{-13} M/sec indicating it would take over 10^7 sec to oxidize 1% of the Ce(III) present! The steady-state concentration of Ce(IV) during this period is calculated to be about 10^{-11} M.

Our observations are in quantitative agreement with the above predictions. Separate experiments have confirmed the kinetics of eq 50, and we have shown that the rate during Bray periods is independent of the concentrations of malonic acid and of cerium(III) just as predicted.

Transition to Rapid Bromide Consumption. Rapid bromide consumption commences at points B and F when the concentration of bromide ion falls to a certain critical value in a solution containing negligible Ce(IV). As pointed out above, β (eq 36) becomes zero at this point and eq 46 reduces to eq 51.

$$[\mathrm{Br}^-]_{\mathrm{crit}} = (k_5/k_2)[\mathrm{BrO_3}^-] = 5 \times 10^{-6}[\mathrm{BrO_3}^-] \quad (51)$$

Our observations are in at least semiquantitative agreement with this prediction. When concentrations of other species were varied at a bromate concentration of 0.063 M, critical bromide concentrations at point B were 8–10 $\times 10^{-7}$ M independent of initial bromide ion between 2.5×10^{-5} and 2.5×10^{-4} M, independent of malonic acid between 0.05 and 0.5 M, independent of cerium(III) between 5×10^{-5} and 5×10^{-3} M, and independent of sulfuric acid between 0.8 and 1.6 M. When cerium(IV) was added initially, the transition of point B occurred at lower concentrations of bromide ion just as predicted by eq 46.

When the concentration of potassium bromate was varied between 0.05 and 0.15 M, the critical bromide concentration could be equated to 18×10^{-6} $[\mathrm{BrO_3}^-]$. When the concentration of bromate was lowered further to 0.006 M, the critical bromide concentration decreased less rapidly than predicted by eq 51.

Although critical bromide concentrations are about three times as great as predicted by eq 51, the discrepancy is acceptable in view of the large number of uncertainties in the argument including the very rough estimates of activity coefficients, the assumption about the ionization constant of bromous acid, and the 50° extrapolation of rate data measured by Lee and Lister[23] over a 20° range. We are unable to explain the apparent lack of proportionality between $[\mathrm{Br}^-]_{\mathrm{crit}}$ and $[\mathrm{BrO_3}^-]$ at the lowest bromate concentrations.

Kinetics during Rapid Bromide Consumption. The rapid bromide consumption periods, BC and FG, are initiated suddenly when the bromide concentration has fallen so low that step R2 is no longer able to prevent autocatalytic generation of bromous acid by process G.

$$\mathrm{BrO_3}^- + \mathrm{HBrO_2} + 2\mathrm{Ce}^{3+} + 3\mathrm{H}^+ \longrightarrow 2\mathrm{HBrO_2} + 2\mathrm{Ce}^{4+} + \mathrm{H_2O} \quad (\mathrm{G})$$

This process results from the sequence (R5) + 2(R6), and Thompson[33] has shown that step R5 is rate-determining unless significant Ce(IV) is present. The $\mathrm{HBrO_2}$ so formed is destroyed by step R4, and the resulting HOBr brominates malonic acid by the sequence (R1) + (R8) or directly by (R8a). The overall process is (B).

$$\mathrm{BrO_3}^- + 4\mathrm{Ce}^{3+} + \mathrm{CH_2(COOH)_2} + 5\mathrm{H}^+ \longrightarrow \mathrm{BrCH(COOH)_2} + 4\mathrm{Ce}^{4+} + 3\mathrm{H_2O} \quad (\mathrm{B})$$

As $\mathrm{HBrO_2}$ is formed, residual bromide is rapidly consumed by step R2, and β of eq 36 becomes strongly negative. The new steady-state concentration of bromous acid given by eq 52 is about 100,000 times the previous value given by eq 49 and explains the dramatic increase in the rate of cerium(IV) production at this time. The kinetics at the start of the period are then given by eq 53. Malonic acid is also brominated at the same rate provided it is present in sufficient concentration to form enol this rapidly.

$$[\mathrm{HBrO_2}]_{\mathrm{ss}} = (k_5/2k_4)[\mathrm{BrO_3}^+][\mathrm{H}^+] = 1.2 \times 10^{-4}[\mathrm{BrO_3}^-][\mathrm{H}^+] \quad (52)$$

$$\frac{\mathrm{d}[\mathrm{BrO_3}^-]}{\mathrm{d}t} = -\frac{1}{4}\frac{\mathrm{d}[\mathrm{Ce}^{4+}]}{\mathrm{d}t} = -v_4 = -(k_5{}^2/4k_4)[\mathrm{BrO_3}^-]^2[\mathrm{H}^+]^2 \quad (53)$$

As reaction proceeds, accumulation of cerium(IV) reduces the steady-state concentration of $\mathrm{HBrO_2}$ because of reactions −R6 and R7.

Although it is difficult to make quantitative measurements of this rapid reaction, our observations are in qualitative agreement with the above predictions. Slopes of bromide sensitive electrode traces become steeper with increasing concentrations of $\mathrm{BrO_3}^-$ and of Ce(III) just as predicted, and the rapid initial production of Ce(IV) slows very early in the period. We also observe that the slope of the trace by the bromide-sensitive electrode becomes less steep with increasing concentration of malonic acid; we are not presently able to offer an explanation but refer to this observation again during discussion of the induction period.

The concentration of bromide ion should continue to decrease until its rate of consumption by step R2 is balanced by its production by (R10). If the solution contains no bromomalonic acid initially, the concentration at point C should be much smaller than is indicated in Figure 1; however, the bromide-sensitive electrode will not give reliable readings at these very low concentrations.[19]

Kinetics during the Induction Period. The induction period, CD, occurs only once and is characterized by an appreciable concentration of cerium(IV), by an extremely small concentration of Br^-, and by a negligible initial concentration of bromomalonic acid. The induction period can be suppressed entirely if bromomalonic acid is deliberately added to the solution initially.

The principal overall process in such a system is (C).

$$3\mathrm{BrO_3}^- + 5\mathrm{CH_2(COOH)_2} + 3\mathrm{H}^+ \longrightarrow 3\mathrm{BrCH(COOH)_2} + 2\mathrm{HCOOH} + 4\mathrm{CO_2} + 5\mathrm{H_2O} \quad (\mathrm{C})$$

The net reaction is cerium catalyzed with Ce(III) being oxidized by process B and Ce(IV) being reduced by reactions R9 and R10. The bromide ion produced in (R10) is immediately destroyed by steps R2 and R8a.

Because of the low concentration of bromide, β of eq 36 is negative and the steady-state concentration of $\mathrm{HBrO_2}$ calculated by eq 38 is intermediate between the extremes of eq 49 and 52; a numerical value cannot be calculated until the values of k_6 and k_7 are known.

If a concentration of $\mathrm{HBrO_2}$ could be estimated, the kinetics of various reactions in the system would be calculable from the above equations. Thus the rate of consumption of BrO_3^- is $k_2[HBrO_2][Br^-][H^+] + k_4 \cdot [HBrO_2]^2$ from eq 39, and the concentration of Br^- attains a steady state determined by eq 47. The concentration of Ce(IV) also establishes a steady state given by eq 54.

$$[Ce^{4+}]_{ss} = \frac{2k_2[HBrO_2][Br^-] + 4k_4[HBrO_2]^2}{k_9[MA]/(K''_9 + [MA]) + k_{10}[BrMA]/(K''_{10} + [BrMA])} \tag{54}$$

We have not attempted to measure the absolute rate of process C during the induction period, but we have made a few observations of the duration of that period. Our observations are in only fair agreement with the above predictions. The length of the induction period decreases with increasing concentration of total cerium as would be expected. The length of the induction period is little dependent on bromate concentration but does become slightly longer as that concentration increases; dependence should be rather slight because added bromate increases both the rate of process C and the critical concentration of bromide ion needed to terminate the induction period. At low concentrations of malonic acid, the induction period is very long and varies inversely with the concentration of this species; these observations can be rationalized if significant concentrations of Br_2 accumulate because enolization of the acid is too slow to remove HOBr as it is formed. The inverse dependence of the duration of the period continues to high malonic acid concentrations even though eq 47 and 54 suggest that the duration should increase as high concentrations of malonic acid depress steady-state concentrations of Ce(IV) and Br^-; this discrepancy remains unresolved.

Increased concentrations of malonic acid both slow the rate of rapid bromide consumption and shorten the induction period even though these effects are not predicted by our mechanism as presented. These effects of malonic acid are only observed in solutions containing significant concentrations of Ce(IV) and of $HBrO_2$; they can be rationalized if malonic acid or one of the intermediates derived from it during oxidation can compete with bromide ion for reaction with $HBrO_2$. Any kinetic perturbation due to such a reaction is apparently minor.

Kinetics during Rapid Bromide Production. Rapid bromide production periods, DE and HE, are initiated in solutions containing both cerium(IV) and bromomalonic acid. As the concentration of bromide ion increases, it attains a value such that $HBrO_2$ is being removed more rapidly by step R2 than it is able to regenerate autocatalytically by process C. At this point, β in eq 36 becomes positive and the concentration of $HBrO_2$ decreases rapidly. Production of bromide ion by reaction R10 continues, and the concentration rises rapidly until the rate of production is balanced by the rate of process A initiated by step R3.

Our observations are in good qualitative agreement with the above predictions. The critical bromide concentrations at which rapid bromide production commences (points D and H) are less than those at which rapid bromide consumption commences (points B and F) because cerium(IV) is necessary for bromide ion production. A quantitative comparison with the predictions must await evaluation of rate constants for steps R6 and R7.

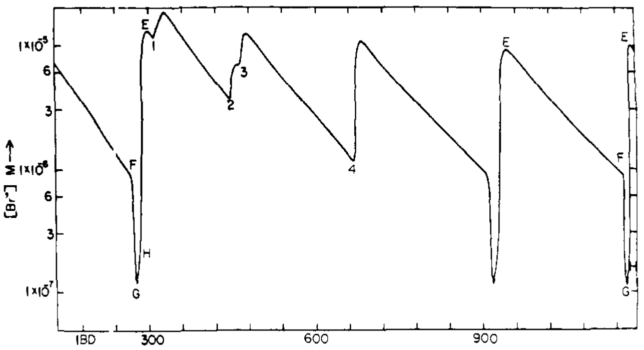

Figure 8. Potentiometric trace of the log $[Br^-]$ oscillations in a 40 ml solution having initial composition $[CH_2(COOH)_2]_0 = 0.25\ M$, $[KBrO_3]_0 = 0.0125\ M$, $[Ce(NH_4)_2(NO_3)_5]_0 = 0.001\ M$, $[H_2SO_4]_0 = 1.25\ M$. Letters follow the same system as in Figure 1. At point (1), 3 drops of 0.1 M $Ce(SO_4)_2$ were added. Further additions were 2 drops at point (2), 3 drops at point (3), and 8 drops at point (4).

Kinetics during Slow Bromide Consumption. A slow bromide consumption period, EF, differs from a Bray period in that both cerium(IV) and bromomalonic acid are also present. They react by process R10 to produce bromide ion which is consumed by process A just as during a Bray period. The concentration of bromide ion attains a steady state given by eq 47, and the potential of a bromide sensitive electrode decreases linearly with time according to eq 48. Just as is the case with a Bray period, the system will go into rapid bromide consumption when the concentration of bromide ion has fallen so low that β (eq 36) has become zero. If cerium(IV) is virtually depleted by that time, the bromide concentration at the transition is the same for both types of period; otherwise eq 46 indicates that it is lower when cerium(IV) is still present.

Our observations are in good semiquantitative agreement with the above predictions. Thus, the concentration of malonic acid initially present predicts a half-life of about 22 sec for bromide ion during the EF period of Figure 1. Because $6k_9$ is considerably greater than $4k_{10}$, and because some organic matter is being irreversibly oxidized, the slopes of successive EF traces decrease slowly. Because the rate of process B is approximately proportional to the square of bromate concentration,[33] less cerium(IV) is produced during an oscillation in Figure 4, and the steady-state approximation of eq 47 is not as applicable near the end of the slow bromide consumption; the trace is concave down as the system moves toward Bray period kinetics before the critical bromide concentration is reached. The trace is also concave down in Figure 3 with a high concentration of malonic acid because the period of an oscillation is so short that little cerium(IV) is produced during the time that β is negative. The trace is slightly concave up in Figure 2 at very low malonic acid concentration because enolization is so slow that some Br_2 has accumulated and is producing bromide ion by process R8 as the point of rapid bromide consumption is approached.

Figure 8 provides additional support for the claim of eq 47 that the steady-state concentration of bromide ion is directly related to that of cerium(IV). Addition of

Ce(IV) during a slow bromide consumption period caused a discontinuous increase in the concentration of bromide ion, but the slope of the subsequent trace of potential is little different from that before the cerium(IV) was added just as eq 48 would predict.

In spite of all this good semiquantitative agreement between observation and prediction, our attempts to synthesize fresh reaction mixtures corresponding to points like D or E in Figure 1 were not entirely successful. These mixtures did indeed oscillate, but the potentiometric behavior of the first oscillation was atypical even though subsequent oscillations were as expected. Apparently the behavior is significantly affected by small amounts of some unidentified reaction product or intermediate.

The argument as developed from eq 48 also predicts that the potentials related to cerium(IV) should be linear with the same slope as the potentials related to bromide ion. The traces of cerium potential in the figures are clearly nonlinear, but we ascribe the discrepancy to the obvious nonreversibility of the tungsten electrode and to the dependence of its potential on other couples besides Ce(IV)–Ce(III).

Kinetics during Slow Bromide Production. Slow bromide production periods, GH, are apparently observed only in solutions with quite low concentrations of malonic acid. In these solutions, the rate of enolization is unable to keep up with production of HOBr, and free Br_2 accumulates as was observed by Franck and Geiseler.[40] The kinetic behavior of bromide ion in such a solution is described by eq 45 rather than by eq 44, and production of HOBr that does not react immediately with malonic acid serves to prevent an immediate rapid increase in bromide ion concentration. The effect is somewhat analogous to an additional capacity in an electrical circuit, and the unreacted HOBr delays the appearance of bromide ion produced by reaction R10 yet it does not diminish the amount of bromide ultimately produced.

The above argument provides a satisfactory rationalization for our observations that slow bromide production occurs in Figures 1 and 2 but not in the other figures in which malonic acid concentrations are greater.

Additional Observations

In the course of our experiments we have observed a number of additional facts of potential mechanistic significance. It seems appropriate to mention some that might be relevant to further attempts to interpret this system.

The observation that oscillations will not occur in perchloric acid has been rationalized on the basis of the more positive reduction potential of cerium(IV) in this medium. We have thereby ignored the possibility that the well known sulfate radical anion, $SO_4\cdot^-$, is playing a direct role. Available data[22] make it appear the free energy of this species is too great to be of mechanistic significance in our system.

The oscillating reaction can be completely inhibited by traces of chloride ion. We discovered this effect, which has also been noted by Zhabotinskii,[11] when we tried to do potentiometric measurements with a potassium chloride salt bridge. No explanation has been developed.

Cerium(IV) does not attack aliphatic alcohols, but aldehydes are formed if malonic acid is also present.[41] The effect has been ascribed to hydrogen atom transfer from the alcohol to a radical derived from the acid. If small amounts of ethanol are added to an oscillating mixture, the oscillations are strongly damped and soon terminate altogether. An initial concentration of 0.07 *M* ethanol can completely inhibit oscillations.

We were unable to detect free radical esr spectra or to observe chemically induced dynamic nuclear polarization (CIDNP) in nmr spectra. The failure of these limited detection attempts in no way obviates the necessity that free radicals be involved in the processes being observed.

Shaw and Pritchard[42] have claimed that the periodicities in this reaction are associated with evolution of carbon dioxide and are presumably related to nucleation phenomena. Both Kasperek and Bruice[14] and we have independently noted that the oscillations continue unchanged when the solution is mixed by bubbling N_2, O_2, or CO_2 through it. The only change noted when an oscillating reaction was transferred from a glass container to one made of polypropylene is that point F occurs at a slightly higher bromide concentration. The mechanisms in the stirred solutions we studied were clearly homogeneous. Unstirred solutions develop the spatial inhomogeneities reported by Zhabotinskii[17] and Busse,[16] but these should not be confused with the effects observed when a reaction is heterogeneous in the conventional sense.

Discussion

Chemistry of Bromine. The literature survey involved in this study has made a major contribution to the mechanistic chemistry of positive oxidation states of bromine. A systematic discussion is now possible because Lee and Lister[23] have provided the first comprehensive thermodynamic tabulation for all singlet monobromine species. That tabulation confirms the prior qualitative knowledge that, as with other halogen(III) acids, $HBrO_2$ is quite unstable with respect to disproportionation. The explanation presumably involves some differences in hybridization of various oxidation states but is not understood.

The reactions for which we have correlated the kinetic data can be classified as oxygen transfers (nucleophilic displacements on oxygen), nucleophilic displacements on bromine, and homolytic Br–Br bond dissociations. The possible asymmetric oxygen transfers in acid solution are reactions R2, R3, and R4. We have estimated rate constants in both directions for all three, and Lee and Lister[23] have done the same for the three comparable reactions in alkaline solution.

In addition to these asymmetric oxygen transfer reactions, there may also be transfers that pass through symmetrical transition states and could only be detected by techniques like isotopic labeling. Because such reactions lead to no net chemical change, they probably have somewhat greater free energies of activation than do oxygen transfers leading to decreases in free energy. Nothing about our data suggests whether or not OH^+ is transformed rapidly between Br^- and

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(41) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 2456 (1954).

(42) D. H. Shaw and H. O. Pritchard, *J. Phys. Chem.*, 72, 2693 (1968).

HOBr. As we have discussed above, the observed rapid isotopic equilibration between $HBrO_2$ and HOBr could be explained by oxygen transfer reaction R3b, but such an explanation requires that k_{3b} be at least 10^4 times as great as k_{-3} although both reactions involve the same species and (−R3) involves a net decrease in free energy. As discussed above, the isotopic exchange data of Betts and MacKenzie[32] and the Thompson[33] data on oxidation of cerium(III) by bromate can be made consistent with our values of $[Br^-]_{crit}$ only if the symmetric oxygen transfer R5c is much slower than R5.

$$HBrO_3^* + HBrO_2 \longrightarrow HBrO_2O^* + HBrO_2^* \qquad (R5c)$$

This somewhat confusing set of observations can be rationalized by saying that oxygen transfers are particularly facile only when they are to Br^- or when they result in net destruction of $HBrO_2$.

Reactions R1 and R5a are both facile nucleophilic displacements on bromine in which a Br–Br bond is formed as a Br–O bond is broken. We therefore favor analogous reaction R3a to satisfy the requirements of the Betts and MacKenzie[32] data. Such an argument leads to a symmetric Br_2O_2 species, although Taube and Dodgen[43] felt required to postulate an asymmetric species like Cl–O–Cl–O or $Cl–ClO_2$ in order to explain their observations in the analogous oxychlorine system.

A species having a Br–Br bond could generate radicals by homolytic dissociation. Just such a reaction happens with Br_2O_4 and thereby initiates the one-electron processes associated with oxidation of cerium(III). The thermodynamic data are unequivocal that similar dissociation of Br_2 will not be sufficiently facile to affect our system. The oxidation kinetics of Thompson[33] seem to require that any Br_2O_2 that forms does not dissociate significantly to $BrO\cdot$ radicals.

Probable Validity of Mechanism. We have proposed a mechanism consisting of ten kinetically distinct reactions and have thereby accounted for such a large body of complex behavior we are convinced the reaction is understood. The peculiar effect in Figure 7 and the effects of increased malonic acid concentration on the induction and rapid bromide consumption periods suggest that when cerium(IV) is oxidizing organic species then the behavior of a complex mixture is not the sum of the behaviors of individual paired components. However, these discrepancies seem to be comparatively minor. We can fairly claim this is one of the most complicated chemical systems whose mechanistic behavior is understood in so much detail.

Implications for Other Oscillating Systems. Although Prigogine[5] and others have proposed various hypothetical mechanisms that could cause sustained oscillations, we believe they have all involved at least two autocatalytic processes. Reaction G is the only autocatalytic process in the mechanism we have developed here. Probably the most novel kinetic feature of our mechanism is the postulation of a species (bromous acid) that can be formed by alternative processes zero and first order in its concentration and can be destroyed by processes first and second order. Because the destruction reaction involves a higher order than the autocatalytic formation, there is no indefinite exponential increase in concentration such as is usually associated with autocatalytic reactions.

Another important feature of our mechanism is the separation into two-equivalent and one-equivalent reactions with the latter taking place during only part of the cycle. Process A takes place entirely by steps in which every species has an even number of electrons, and oxidation numbers change by two equivalents at a time. Process B is initiated by the formation of free radical species, and both it and process R10 are heavily dependent upon processes involving one-equivalent changes in oxidation number of cerium ions. Bromide ion, which is a key reference reactant, is consumed by a series of two-equivalent steps and is produced during an oxidation taking place by one-equivalent steps. If it were not for this clean separation of reaction types, it would certainly be more difficult to devise a mechanism by which oscillations in some species would accompany a monotonically decreasing free energy.

We anticipate that a similar separation of one-equivalent and two-equivalent processes will be involved in the oscillations during the iodate catalyzed decomposition of hydrogen peroxide,[7,8] and we also expect that many features of the oxyiodine chemistry in that reaction will parallel the oxybromine chemistry of this reaction. However, one-equivalent processes are not common in living systems, and some oscillatory biochemical processes probably take place entirely by means of singlet species. However, we suggest that a mechanistic feature of many of these reactions will be second-order destruction of species that have been generated autocatalytically.

Possible Applications of Stable Chemical Oscillators. The studies reported here involved systems that decayed irreversibly as process C proceeded. However, Vavilin, Zhabotinskii, and Zaikin[44] have confirmed that it is possible to maintain indefinite oscillations of constant frequency in a continuous flow stirred reactor to which bromate, malonic acid, and cerium catalyst are being added at a constant rate. The slow injection of concentrated hydrogen peroxide into a stirred iodate solution should make an even simpler chemical oscillator.[7,8] The reaction discussed here oscillates the oxidation potential for single electron transfer reactions in the solution; other bulk properties such as pH and temperature could probably also be made to oscillate over controlled ranges.

We are still unsure of the potential significance of these chemical oscillators as contrasted to electronic oscillators. Periods of chemical oscillators will probably be measured in seconds to days, while those for most electronic oscillators are in milli- and microseconds. The significance of a chemical oscillator is that bulk property can be made to alternate isotropically and simultaneously throughout the entire volume of a stirred system; such an effect is often difficult to accomplish by applying an external influence. Only the future can say whether such reactions will become more than a laboratory curiosity.

Implications for Spatial Oscillations. The work of the present paper was directed to elucidate the mechanism of temporal oscillations in a stirred homogeneous system. We believed that such an accomplishment was essential before any attempt was made to understand

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the still more complicated problem of moving spatial inhomogeneities[16,17,45] in unstirred solutions. We have subsequently developed a qualitative explanation of these effects also.[46] Spatial waves develop as an oxidizing region advances into a region of low but finite bromide ion concentration that falls to $[Br^-]_{crit}$ at the interface. Autocatalytic generation of bromous acid at the interface advances the wave more rapidly than any individual molecular species could diffuse. Because process R10 is undoubtedly much more exothermic than either A or B, oxidizing regions will be less dense than reducing regions and successive waves will tend to layer horizontally in a bulk solution subject to a gravitational field. A rigorous quantitative description is being developed.

Experimental Section

Materials. Except for HOBr and the brominated malonic acids, high purity samples of all the necessary chemicals were available commercially. They were generally used as received from the manufacturer after some tests showed that recrystallization did not affect behavior in the Belousov reaction. For some experiments, however, the $KBrO_3$ was recrystallized to remove bromide ion. The mono- and dibromomalonic acids were prepared from malonic acid by the bromination procedures of Conrad and Reinback.[47] Bromide-free HOBr was prepared from bromine and silver sulfate by the method of Chapin.[48]

Wet Methods of Analysis. The organic products of the Belousov reaction were analyzed by allowing a reaction mixture to stand for 2 days after oscillations had ceased and then extracting it with ether with a Heberlig-Furman[49] extractor. The extract was dried over sodium sulfate and evaporated, and the residue was stored over magnesium perchlorate. About 0.15 g of the residue was dissolved in 20 ml of 2 *N* HCl, and solid KI was added in the dark. The resulting iodine was titrated with thiosulfate and equated to the bromomalonic acids present; bromoacetic acids do not oxidize iodide under such conditions. The total organically bound bromine in another 0.25-g sample of the residue was determined by hydrolyzing for 20 min with boiling 0.1 *N* NaOH. The solution was then cooled, neutralized with 2 *N* $HClO_4$, diluted to a known volume, and analyzed with the bromide-sensitive electrode discussed below.

Organically bound bromine not present as bromomalonic acids was assumed to be in bromoacetic acids. The paper chromatography technique of Reid and Lederer[50] as extended to bromoacetic acids by Chittam, *et al.*,[51] was tested for use in the presence of malonic acid and found suitable. Under the conditions used, the R_f values for $BrCH_2COOH$, $Br_2CHCOOH$, and Br_3CCOOH were 0.02, 0.14, and 0.27, respectively.

Oxidizing power due to the total of Br_2, $BrCH(COOH)_2$, $Br_2C(COOH)_2$, and BrO_3^- was frequently determined by adding excess iodide ion and titrating with thiosulfate. Potential interference by any Ce(IV) present could be masked by complexation with an excess of EDTA. Bromine could be separated from the other oxidants by extraction into carbon tetrachloride. In some instances, Ce(IV) itself was determined by titration with standardized $Fe(NH_4)_2(SO_4)_2$ with use of ferroin as indicator.

Potentiometric Methods of Analysis. The [Ce(IV)]/[Ce(III)] ratio was monitored by recording the potential between a calomel cell and a tungsten electrode immersed in the reaction mixture. Because chloride ion from the calomel cell completely inhibited the Belousov reaction, a double junction reference electrode (Orion Research, Cambridge, Mass. 02139) was used with 10% KNO_3 as the electrolyte making contact with the reaction mixture.

The signal from this electrode combination was much too large for the 10 mV recorder available. Therefore, the signal was applied to the input of a VTVM (Heathkit Model IM-18), and a reduced signal proportional to the original was taken from the meter circuit of the VTVM. Relative measurement of [Ce(IV)]/[Ce(III)] could easily be made in this way, but absolute values were uncertain.

The instantaneous concentration of bromide ion was followed with a bromide sensitive electrode also obtained from Orion Research. Recent advances in such specific ion electrodes have been reviewed by Rechnitz.[52] The electrode was calibrated so that absolute bromide concentration could be read directly at any time. Experiments demonstrated that there were no interferences to normal operation of this electrode under the conditions of the Belousov reaction and that the response of the electrode was essentially instantaneous within the time scale of the oscillations being observed.

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