A, therefore it does not react in this case. On the contrary, it reacts with DA to give an adduct which subsequently dissociates to yield a product very similar to the starting dye.

The $(CH_3)_2\dot{C}OH$ radical can give both addition and reduction. With A the addition, as observed also in the case of the $\dot{C}H_2OH$ radical, is unfavored, so that only reduction of the azo bond takes place. With DA the addition reaction occurs at first, but formation of the hydrazyl radical is observed with the dissociation of the adduct.

Complete reduction of the azo bond occurs by second-order disproportionation of the semireduced radical intermediate, leading to the hydrazo derivative and to the original azo compound in a 1:1 ratio.[9] The rate constants for this process have been found to be of the order of 10^9 M^{-1} s^{-1}, similar to that found for the disproportionation of hydrazyl radicals in aqueous media, but 2-3 orders of magnitude higher than that attributed to this reaction in alcoholic solvents.[9] In competition with this second-order process, hydrazyl radicals have been found to undergo a pseudo-first-order reaction with the parent compound (rate constants 10^7-10^8 M^{-1} s^{-1}), leading to a radical dimer with spectroscopic characteristics quite similar to the hydrazyl itself. These radical dimers undergo a second-order reaction themselves with a much slower rate compared to that of the hydrazyl radicals. Rates of 10^6-10^7 M^{-1} s^{-1} can be calculated for the disproportionation of radical dimer, assuming ϵ similar to that of the hydrazyl. This order of magnitude matches with that of the rate constants attributed to hydrazyl dismutation in alcohols.[9] Since the solvent dependence of the disproportionation rate constants of hydrazyl radicals has not been reasonably explained so far, we propose that association phenomena with negligible spectral consequences similar to those observed by us can be at the origin of the observed rate constant lowering in alcohols.[9]

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Registry No. A, 17082-12-1; DA, 6860-63-5; MeOH, 67-56-1; *i*-PrOH, 67-63-0; $(CH_3)_2\dot{C}OH$, 5131-95-3; $\dot{C}H_2OH$, 2597-43-5.

Bromine-Hydrolysis Control in the Cerium Ion-Bromate Ion-Oxalic Acid-Acetone Belousov-Zhabotinskii Oscillator

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Chemical oscillations in reacting systems containing BrO_3^- have been interpreted as a switching phenomenon in which control of the overall reaction is passed back and forth between a set of radical reactions and a set of nonradical reactions. Switching is assumed to be controlled by $[Br^-]$. When $[Br^-]$ is high, control is by the nonradical reactions, whose major effect is the removal of Br^-. Control switches to the radical reactions when $[Br^-]$ is driven low enough. Oscillation occurs because Br^- is an indirect product of the radical reactions, causing control to be returned to the nonradical reactions. Bromide ion control of BrO_3^--driven oscillations has been challenged on the basis that in some systems the usual source of Br^- from the radical reactions is absent. It has been suggested that the oscillations are in fact Br_2 controlled. It is shown here that one of these puzzling oscillators can be simulated as Br^- controlled. By implication the others also can be. Bromine is an important intermediate in these systems as the controlling Br^- comes from Br_2 hydrolysis and is in equilibrium with Br_2 and HOBr. We call such an oscillator Br_2-hydrolysis controlled. The simulation is based on 31 elementary reactions of which 9 are reversible. It was constructed on the basis of a large number of experiments on simpler, nonoscillatory reactions involving the same reactants and is much simpler than the mechanisms of other BrO_3^--driven oscillators because of the relative simplicity in it of the reactions of oxalic acid and acetone. The rate constants thus determined were used without modification to obtain an essentially quantitative simulation of the oscillatory system. It is thus the most complete and quantitatively accurate simulation of a BrO_3^--driven oscillator with an organic substrate yet carried out. The complete mechanism can be reduced to a simple five-variable Oregonator-like model that contains no expendable stoichiometric factor and whose rate parameters all can be related directly to the concentration of a principal reactant.

Introduction

In its classic form the Belousov-Zhabotinskii (BZ) reaction is the metal-ion-catalyzed oxidation of an easily brominated organic substrate by BrO_3^- in a strongly acid medium.[1,2] Oscillations may be readily measured in the ratio of the concentration of the oxidized form to the concentration of the reduced form of the metal-ion catalyst and in $[Br^-]$. In 1972 Field, Körös, and Noyes (FKN)[1] proposed a detailed mechanism for the BZ reaction with malonic acid as the organic substrate. The FKN mechanism is fundamentally dependent upon control of the oscillations by $[Br^-]$ and has been successful in rationalizing[2] essentially all observed behaviors of the BZ reaction and various bromate-ion-driven[3,15] oscillators derived from it. The FKN mechanism can be reduced to a much simpler model,[4] called the Oregonator, which has proved to be very useful for connecting the observed behavior of the BZ reaction to basic ideas from nonlinear dynamics.[5-7]

However, several modifications of the BZ reaction have been reported by Noszticzius[8-10] and others[11,12] that do not fit easily

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into the FKN framework. These discoveries have led to the proposal of a BZ mechanism fundamentally different from the FKN mechanism in that it relies upon Br_2 control rather than Br^- control of the oscillations. We report here detailed simulations which demonstrate that the FKN framework with Br^- control is able to rationalize in detail one of these puzzling experiments, and thus by implication the others. In doing so the importance of the Br_2-hydrolysis equilibrium (reaction 3, Table I) and oxidative reactions of HOBr with organic compounds is emphasized.

The system considered is oscillatory and composed of cerium ion, BrO_3^-, H_2SO_4, oxalic acid, and acetone (see Figure 9). Its simulation is based on a mechanism composed of 31 elementary reactions, 9 of which are reversible. Experiments have been carried out on subsystems of the overall reaction, and these are used to construct the oscillatory mechanism. The result is substantially simpler than the FKN mechanism with malonic acid as the interaction of Ce(IV) with a mixture of oxalic acid, acetone, and bromoacetone is much simpler than its interaction with a mixture of malonic and bromomalonic acids. The only intermediate species present in the former case is $HCO_2\cdot$, and the simulation presented here is more complete than any previous simulation[13,14] of the BZ reaction with an organic substrate present. The mechanism can be reduced to an Oregonator-like model that, as predicted by Noyes,[15] does not contain an expendable stoichiometric factor.

The FKN Mechanism

The FKN mechanism is based on three component processes labeled A, B, and C. Process A is the sequence of oxygen-atom transfers given by reactions 1–3. In the case of easily brominated organic substrates such as malonic acid, Br_2 rapidly reacts to yield products such as bromomalonic acid (BrMA). The overall stoichiometry of process A is given by

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

Process A is dominant at higher $[Br^-]$, and its most important net effect is the removal of Br^-.

Process B is composed of reactions 4–8, excluding reaction 6, and becomes dominant when $[Br^-]$ falls to where reaction 4 rather than reaction 2 becomes the dominant fate of $HBrO_2$. Its overall stoichiometry is given by

$$5H^+ + 4Ce(III) + BrO_3^- \rightarrow 4Ce(IV) + 3H_2O + HOBr \quad (B)$$

Because of chain branching in reactions 4 and 5, process B takes control suddenly when $[Br^-]$ drops below a critical value. Cerium(III) then is rapidly oxidized to Ce(IV) while $[Br^-]$ is driven very low. The form of processes A and B seems well understood.[2]

A third set of reactions, process C, must be added for oscillation to occur, and this is where difficulties have arisen.[16] Process C has two functions. The first is that some product(s) of process B must react in process C to yield a species which inhibits process B by competing with reaction 4 for $HBrO_2$. This is a negative feedback on process B, and for oscillation to occur it must be delayed in process C. The second is to reinitialize the system by reducing Ce(IV) to Ce(III) after process B has stopped. In a flow reactor these functions may be carried out by the flow, leading to the so-called minimal BrO_3^- oscillator.[17] With malonic acid as the organic substrate they were originally[1] assumed to be carried out by

$$4Ce(IV) + BrCH(COOH)_2 + 2H_2O \rightarrow 4Ce(III) + HCOOH + 2CO_2 + 5H^+ + Br^- \quad (C1)$$

that both produces Br^- to inhibit process B (reaction 2) and reduces Ce(IV) to Ce(III). This form of process C implies that Br^- is the critical species which controls the BZ oscillations.

There is substantial evidence for reaction C1 in the malonic acid system. An induction period before the appearance of oscillations can be interpreted as the time required for sufficient BrMA to accumulate to yield enough Br^- to inhibit process B. It can be suppressed by the initial addition of BrMA. Burger and Rácz[18] as well as Burger and Körös[19] have carefully investigated the effect of added BrMA and have shown that a critical amount of BrMA must accumulate before the induction period ends.

There are also problems with reaction C1. The first involves its stoichiometry. Process C is represented in the Oregonator reduction[4] of the FKN mechanism[2] by the stoichiometry

$$2Ce(IV) \rightarrow 2Ce(III) + f Br \quad (O)$$

where f is an expendable stoichiometric factor. Oscillation occurs only for $0.5 < f < 1 + 2^{1/2}$. The value of f in reaction C1 is 0.5, exactly at the limit of oscillation. The stoichiometry of reaction C1 seems accurate, though, as only very small quantities of partially oxidized malonic acid derivatives (e.g., tartronic, ketomalonic, or oxalic acids) are detected among the BZ products.[18] There is also the problem that some Ce(IV) must react with MA rather than BrMA. Even considering the addition by Noyes and Jwo (see in ref 2) of the reactions

$$Ce(IV) + CH_2(COOH)_2 \rightarrow Ce(III) + \dot{C}H(COOH)_2 + H^+ \quad (C2)$$

$$\dot{C}H(COOH)_2 + BrCH(COOH)_2 \rightarrow CH_2(COOH)_2 + Br\dot{C}(COOH)_2 \quad (C3)$$

$$Ce(IV) + Br\dot{C}(COOH)_2 + H_2O \rightarrow O{=}C(COOH)_2 + Br^- + 2H^+ + Ce(III) \quad (C4)$$

the value of f for the entire process cannot exceed 0.5, and is likely to be somewhat less than this value. Another source of Br^- is necessary if oscillation is to occur. In the MA case it is assumed[2] to be

$$HOBr + HCOOH \rightarrow Br^- + H^+ + CO_2 + H_2O \quad (C5)$$

which added to reaction C1 yields $f = 1$ if no Ce(IV) is lost in non-bromide-ion-producing side reactions. Thus oxidation of MA derivatives by HOBr is apparently an important source of added Br^-. The BZ reaction, including the induction period, can be simulated[13,14,20] on the basis of reactions C1–C5.

There is direct evidence for the production of Br^- in process C from sources other than BrMA. Körös et al.[21] have used an isotope tracer experiment to demonstrate that a large fraction of the Br^- produced in process C comes from reduction products of BrO_3^-, e.g. HOBr, and not from BrMA. Thus it is not surprising that little formic, tartronic, ketomalonic, or oxalic acids are found among the BZ reaction products. They are presumably removed by reactions with both HOBr and Ce(IV). We have determined experimentally that the rate constant for the reaction of HOBr with tartronic acid is near 10^5 M^{-1} s^{-1}. Of course, the reaction of malonic acid derivatives with HOBr rather than Ce(IV) also decreases the average amount of Ce(IV) required to oxidize a malonic acid molecule to CO_2 and thus increases f. One HOBr is produced in reaction B for each four Ce(IV). If all of this HOBr reacts with bromomalonic derivatives to produce Br^-, and reactions C2–C5 are assumed, a maximum value of $f = 1$ may be ap-

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proached. The possibility of analogous reactions of $HBrO_2$ with organic materials has not yet been assessed but seems real.

The necessity of a source of Br^- in addition to reaction C1 becomes even more apparent in several modifications of the BZ reaction. Noszticzius and Bődiss[8] reported oscillations in a heterogeneous system consisting only of cerium ion, BrO_3^-, H_2SO_4, and oxalic acid when N_2 is bubbled through the reaction mixture to remove Br_2. Noszticzius[9] found oscillations in the system that is the subject of this report, and Rastogi et al.[12] found oscillations in a similar system. These experiments are impossible to interpret in terms analogous to reaction C1; there is no brominated organic material equivalent to BrMA present. Oxalic acid does not yield a brominated derivative. Bromine is removed from these systems either by the bubbling gas or by acetone. However, bromoacetone has only a single carbonyl group and does not react readily with Ce(IV). Thus if the oscillations in these systems are to be Br^- controlled there must be a source of Br^- other than reactions analogous to reaction C1. We suggest the source of this Br^- to be the oxidation of oxalic acid by HOBr.

An even greater problem for the FKN mechanism is the apparently non-bromide-ion controlled oscillations discovered by Noszticzius.[10] In this experiment Ag(I) is added to a BZ reaction with malonic acid that is monitored by both a platinum electrode and a bromide-ion-selective electrode. The Ag(I) forces $[Br^-]$ to a very low value, and the bromide-ion-selective electrode shows a flat nonoscillatory response. The remarkable observation is that the platinum electrode continues to show an oscillatory potential. A similar result was obtained by Körös et al.[22] upon the addition of Tl(III), which removes Br^- from the system through the formation of Tl(III)–Br^- complexes. These observations are even more difficult to fit into the FKN Br^--control framework than are the problems with reaction C1.

Bromine Control and the Explodator. In an attempt to explain the above observations, Noszticzius et al.[16] suggested that the BZ oscillations are not Br^- controlled but are Br_2 controlled. They proposed reaction N to implement Br_2 control. There is only very indirect experimental evidence for reaction N.[23] We are unable to imagine a reasonable transition state by which it could occur as an elementary reaction. However, oscillations do appear[16,24] in a skeleton model, called the Explodator, based upon reaction N. The dynamical structure of the Explodator relies on the interaction of two autocatalytic reactions to generate oscillations and is profoundly different from the Oregonator, which relies on the bistability implicit in processes A and B and switching between them for the generation of oscillations.[7] The Explodator resembles the Lotka–Volterra model[25] more closely than it does the Oregonator. It is unable to reproduce some fundamental features of the BZ reaction including excitability[26,27] and bistability.[7,28,29]

$$H_2O + Br_2 + HBrO_2 \rightarrow 3HOBr \qquad (N)$$

Bromine-Hydrolysis Control in the FKN Mechanism. We suggest that Noszticzius et al.[16] are correct in proposing that Br_2 is a critical intermediate in systems where reactions C cannot be responsible for the inhibition of process B and that reaction N is the net stoichiometry by which process B is inhibited. However, we find that the modified systems without added Ag(I) or Tl(III) can be rationalized as Br^- controlled with the Br^- coming from the hydrolysis of Br_2,[30] reaction 3. The same conclusion now has been reached independently by Noszticzius et al.[31] Stoichiometry N is the sum of reactions 2 and –3. We have previously shown[2] that the heterogeneous oxalic acid system[8] can be simulated as a Br_2-hydrolysis-controlled oscillator.

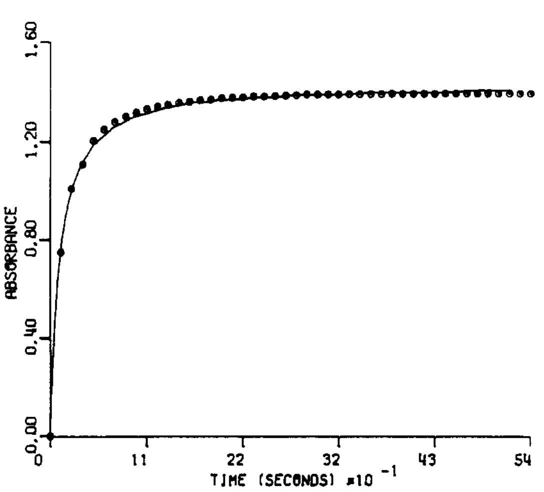

Figure 1. Experimental (O) and calculated (—) absorbances due to Br_2, Br_3^-, and HOBr at 397 nm. Absorbances calculated by assuming ϵ_{Br_2} = 165.7 M^{-1} cm^{-1}, $\epsilon_{Br_3^-}$ = 593 M^{-1} cm^{-1}, and ϵ_{HOBr} = 4 M^{-1} cm^{-1}. Initial concentrations: $[KBrO_3]$ = 0.0025 M, [NaBr] = 0.01375 M, and $[H_2SO_4]$ = 1.0 M.

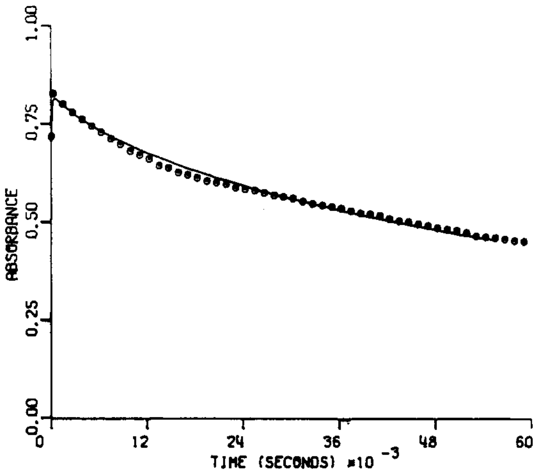

Figure 2. Experimental (O) and calculated (—) absorbances due to Br_2, Br_3^-, and HOBr at 397 nm. Absorbances calculated as in Figure 1. Initial concentrations: $[KBrO_3]$ = 0.001612 M, [NaBr] = 0.009646 M, [oxalic acid] = 0.100 M, and $[H_2SO_4]$ = 1.0 M.

Ruoff has shown[32,33] that the Ag(I) addition experiments can be rationalized by the Oregonator without recourse to stoichiometry N. Körös et al.[22] have shown that their experiments with Tl(III) also can be rationalized in terms of the Oregonator. Thus there is no reason to consider Br_2 control or the Explodator as a viable model of the BZ reaction.

Simulation of the Cerium Ion–H_2SO_4–Oxalic Acid–Acetone Oscillator

Simulation of this reaction is based on the mechanism and rate constant values shown in Table I. We have carried out a large number of experiments on systems involving only a subset of the reactants present in the oscillatory system. These experiments were simulated by using the complete mechanism with appropriate reactant concentrations set to zero. Unknown rate constants were adjusted to simulate these simpler reactions. In this way only one or a small number of rate constants were dealt with at each stage of construction of the complete mechanism. Rate constant values so obtained were used unchanged for simulation of the oscillatory system. A variation of ±25% was allowed in rate constant values during the simulation of component reaction experiments to obtain polished fits.

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TABLE I: Reactions and Rate Constants

no.	reaction	rate constant	ref
1	$Br^- + BrO_3^- + 2H^+ \rightleftharpoons HOBr + HBrO_2$	$k_1 = 5\ M^{-3}\ s^{-1}$ $k_{-1} = 1 \times 10^4\ M^{-1}\ s^{-1}$	34 modified here
2	$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr$	$k_2 = 2.0 \times 10^9\ M^{-2}\ s^{-1}$ $k_{-2} = 5.0 \times 10^{-5}\ M^{-1}\ s^{-1}$	34
3	$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O$	$k_3 = 8.0 \times 10^9\ M^{-2}\ s^{-1}$ $k_{-3} = 110\ s^{-1}$	34
4	$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O$	$k_4 = 1 \times 10^4\ M^{-2}\ s^{-1}$ $k_{-4} = 2 \times 10^7\ M^{-1}\ s^{-1}$	34
5	$BrO_2\cdot + Ce(III) + H^+ \rightleftharpoons Ce(IV) + HBrO_2$	$k_5 = 7.0 \times 10^4\ M^{-2}\ s^{-1}$ $k_{-5} = 8.0 \times 10^5\ M^{-1}\ s^{-1}$	34, 40 modified here
6	$BrO_2\cdot + (COOH)_2 \rightarrow HBrO_2 + CO_2 + HCO_2\cdot$	$k_6 < 150\ M^{-1}\ s^{-1}$	this work
7	$HBrO_2 + HBrO_2 \rightleftarrows HOBr + BrO_3^- + H^+$	$k_7 = 4 \times 10^7\ M^{-1}\ s^{-1}$ $k_{-7} = 2.1 \times 10^{-10}\ M^{-2}\ s^{-1}$	34
8	$Ce(IV) + BrO_2\cdot + H_2O \rightleftarrows Ce(III) + BrO_3^- + 2H^+$	$k_8 = 9.6\ M^{-1}\ s^{-1}$ $k_{-8} = 1.3 \times 10^{-4}\ M^{-3}\ s^{-1}$	34
9	$HOBr + (COOH)_2 \rightarrow H_2O + H^+ + CO_2 + HCO_2\cdot + Br\cdot$	$k_9 = 25\ M^{-1}\ s^{-1}$	35
10	$Br\cdot + Br\cdot \rightarrow Br_2$	$k_{10} = 1 \times 10^8\ M^{-1}\ s^{-1}$	this work
11	$Br\cdot + HCO_2\cdot \rightarrow Br^- + H^+ + CO_2$	k_{11} does not contribute	this work
12	$HCO_2\cdot + HCO_2\cdot \rightarrow (COOH)_2$	$k_{12} = 1.2 \times 10^9\ M^{-1}\ s^{-1}$	43
13	$HCO_2\cdot + HCO_2\cdot \rightarrow HCOOH + CO_2$	k_{13} cannot be separated from reaction 12	43
14	$Ce(IV) + (COOH)_2 \rightarrow Ce(III) + CO_2 + HCO_2\cdot + H^+$	$k_{14} = 27.5\ M^{-1}\ s^{-1}$	42 modified here
15	$Ce(IV) + HCO_2\cdot \rightarrow Ce(III) + CO_2 + H^+$	$k_{15} = 1.0 \times 10^6\ M^{-1}\ s^{-1}$	43
16	$Br\cdot + (COOH)_2 \rightarrow Br^- + H^+ + HCO_2\cdot + CO_2$	$k_{16} = 2000\ M^{-1}\ s^{-1}$	this work
17	$Br\cdot + CH_3COCH_3 \rightarrow Br^- + CH_3COCH_2\cdot + H^+$	k_{17} does not contribute	this work
18	$CH_3COCH_2\cdot + Br_2 \rightarrow BrCH_2COCH_3 + Br\cdot$	k_{18} does not contribute	this work
19	$CH_3COCH_2\cdot + CH_3COCH_2\cdot \rightarrow CH_3COCH_2CH_2COCH_3$	$k_{19} = 1 \times 10^8\ M^{-1}\ s^{-1}$	this work
20	$CH_3COCH_3 + H^+ \rightleftarrows CH_2{=}CHOHCH_3 + H^+$	$k_{20} = 8.3 \times 10^{-5}\ M^{-1}\ s^{-1}$ $k_{-20} = 21.3\ M^{-1}\ s^{-1}$	36 modified here
21	$CH_2{=}CHOHCH_3 + Br_2 \rightarrow BrCH_2COCH_3 + Br^- + H^+$	$k_{21} = 1.03 \times 10^7\ M^{-1}\ s^{-1}$	36
22–25	deleted		
26	$BrO_3^- + (COOH)_2 \rightarrow BrO_2\cdot + H_2O + CO_2 + HCO_2\cdot$	$k_{26} = 5 \times 10^{-6}\ M^{-1}\ s^{-1}$	this work
27	$BrO_2\cdot + CH_3COCH_3 \rightarrow CH_3COCH_2\cdot + HBrO_2$	k_{27} does not contribute	this work
28	$HOBr + HCO_2\cdot \rightarrow H_2O + Br\cdot + CO_2$	$k_{28} = 2.0 \times 10^7\ M^{-1}\ s^{-1}$	this work
29	$Br^- + Br_2 \rightleftarrows Br_3^-$	$k_{29} = 1 \times 10^8\ M^{-1}\ s^{-1}$ $k_{-29} = 7.5 \times 10^6\ s^{-1}$	36
30	$HCO_2\cdot + BrO_2\cdot \rightarrow HBrO_2 + CO_2$	k_{30} does not contribute	this work
31	$HCO_2\cdot + H^+ + BrO_3^- \rightarrow BrO_2\cdot + CO_2 + H_2O$	$k_{31} = 2.7 \times 10^3\ M^{-2}\ s^{-1}$	this work
32	$Br_3^- + CH_2{=}CHOHCH_3 \rightarrow BrCH_2COCH_3 + 2Br^- + H^+$	$k_{32} = 2.8 \times 10^6\ M^{-1}\ s^{-1}$	36
33	$Br^- + Br^- + BrO_3^- \rightarrow 3HOBr$	k_{33} does not contribute	this work
34	$Br_2 + BrCH_2COCH_3 \rightarrow BrCH_2COCH_2Br + Br^- + H^+$	$k_{34} = 5 \times 10^{-3}\ M^{-1}\ s^{-1}$	this work
35	$Br_3^- + BrCH_2COCH_3 \rightarrow BrCH_2COCH_2Br + 2Br^- + H^+$	$k_{35} = 5 \times 10^{-3}\ M^{-1}\ s^{-1}$	this work
36	$HCO_2\cdot + Br_2 \rightarrow H^+ + CO_2 + Br^- + Br\cdot$	k_{36} cannot be separated from reaction 28	this work

$Br^- + BrO_3^- + H^+$. Figure 1 shows the experimental and simulated absorbances due to Br_2 in this reaction. Reaction 1 is rate determining, and the difference between our value of k_1 and that of earlier simulations[17,34] results from the higher (29 °C vs. 24 °C) temperature here.

$Br^- + BrO_3^- + H^+$ + Oxalic Acid. Figure 2 shows experimental and simulated absorbances due to Br_2 in this reaction. Bromine initially is produced rapidly and then reacts slowly with oxalic acid at a rate determined by reaction 9. Initial concentrations were adjusted so that very little BrO_3^- was present after the generation of Br_2. The value of k_9 resulting from our experiments is somewhat higher than previously reported[35] because of a temperature difference. In some experiments the calculated absorbances were higher than observed. We attribute this to a side reaction in which $HBrO_2$ oxidizes oxalic acid rather than Br^- and are investigating this effect quantitatively to polish the simulation.

$Br^- + BrO_3^- + H^+$ + Acetone. Figure 3 shows the experimental and simulated absorbances due to Br_2 in this reaction. Removal of Br_2 by reaction with acetone is competitive with its formation. Very little BrO_3^- was present after the formation of Br_2. The enolization of acetone (reaction 20) is rate determining for its bromination.[36] There does not seem to be any interference by acetone to the production of Br_2. Our value of k_{20} is somewhat higher than reported by Bell and Davis,[36] again because of a temperature difference. The tribromide equilibrium (reaction 29) and the reactions of Br_3^- were considered. Symmetrical dibromination of acetone was assumed to proceed at the same rate as monobromination. We have not treated the kinetics of the second bromination in detail.

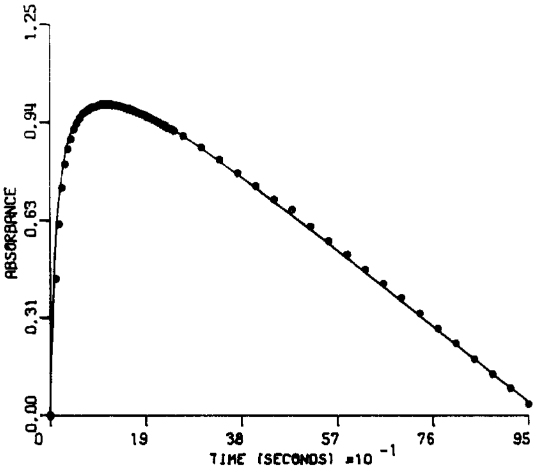

Figure 3. Experimental (○) and calculated (—) absorbances due to Br_2, Br_3^-, and HOBr at 397 nm. Absorbances calculated as in Figure 1. Initial concentrations: $[KBrO_3] = 0.0200$ M, $[NaBr] = 0.0120$ M, [acetone] = 0.070 M, and $[H_2SO_4] = 1.0$ M.

$BrO_3^- + H^+$ + Oxalic Acid. Figure 4 shows the experimental and calculated absorbances due to Br_2 in this reaction, which is slow and does not seem to have been investigated in water.[37] The

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(34) Barkin, S.; Bixon, M.; Noyes, R. M.; Bar-Eli, K. *Int. J. Chem. Kinet.* **1977**, *9*, 841.

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(36) Bell, R. P.; Davis, G. G. *J. Chem. Soc.* **1964**, 902.

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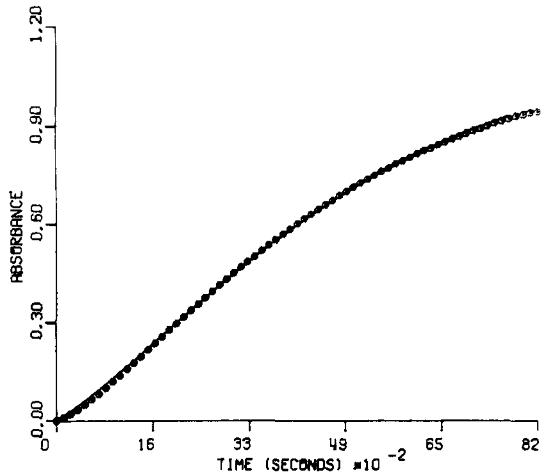

Figure 4. Experimental (O) and calculated (—) absorbances due to Br_2, Br_3^-, and HOBr at 397 nm. Absorbances calculated as in Figure 1. Initial concentrations: $[KBrO_3] = 0.0133$ M, [oxalic acid] = 0.0702 M, and $[H_2SO_4] = 1.0$ M.

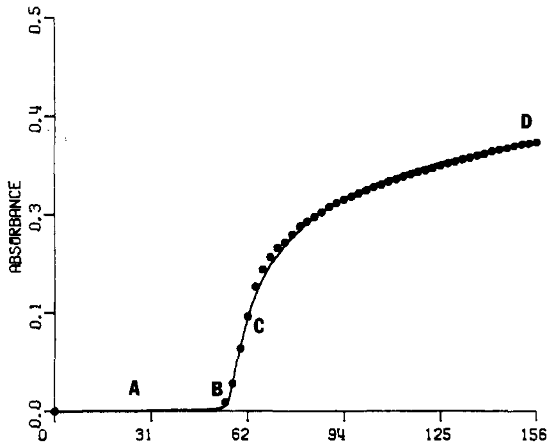

Figure 5. Experimental (O) and calculated (—) absorbances due to Ce(IV), Br_2, and HOBr at 318 nm. Absorbance calculated by assuming $\epsilon_{Ce(IV)} = 5500$ M^{-1} cm^{-1}, ϵ_{Br_2} 15 M^{-1} cm^{-1}, and $\epsilon_{HOBr} = 33$ M^{-1} cm^{-1}. Initial concentrations: $[Ce_2(SO_4)_3] = 0.000120$ M, $[KBrO_3] = 0.00800$ M, and $[H_2SO_4] = 1.0$ M.

direct reaction of BrO_3^- and oxalic acid (reaction 26) is slow, and the following reactions are complex. The reaction is autocatalytic which we ascribe to the reactions of $HCO_2\cdot$ with HOBr and/or Br_2 (reactions 28 and 36), but we are unable presently to separate these two reactions. The autocatalysis cannot be simulated on the basis of the reaction of $BrO_2\cdot$ with oxalic acid (reaction 6), and we conclude that $k_6 < 150$ M^{-1} s^{-1}. Uncertainty also exists concerning the rate of the reactions of Br· with oxalic acid (reaction 16) and $HCO_2\cdot$ with BrO_3^- (reaction 31). Independent values of the rate constants for one or both of these reactions are required for further progress to be made, and we are undertaking this problem. Even with these uncertainties we are able to simulate the overall reaction adequately.

Ce(III) + BrO_3^- *+* H^+. Figure 5 shows experimental and calculated absorbances due to Ce(IV) and HOBr in this reaction, which is essentially process B of the FKN mechanism. While the form of process B is well established,[2,5,13,17,34] there has been some question concerning rate constant values.[5] The problem is that, while values of k_2/k_4 and k_4/k_7 are experimentally accessible,[1,5] direct determination of absolute values is difficult. The commonly used[13-15,17,34] set of rate constants was originally inferred by FKN[1] and later refined by Barkin et al.,[34] but another set has been suggested by Tyson[5] on the basis of a recently determined[23] value of k_7 and other considerations.

The disproportionation of $HBrO_2$, reaction 7, has been studied directly (although in a difficult experiment) by both Noszticzius et al.[23] and by Försterling et al.[38] The resulting values of k_7 are quite different. The Försterling et al. value agrees with that used by Barkin et al.[34] while that determined by Noszticzius et al.[23] is much smaller. Tyson's[5] "low" rate constants are based upon the latter value of k_7 and are much smaller than the Barkin et al. "high" set. Both sets maintain the experimental ratios and are internally consistent thermodynamically.

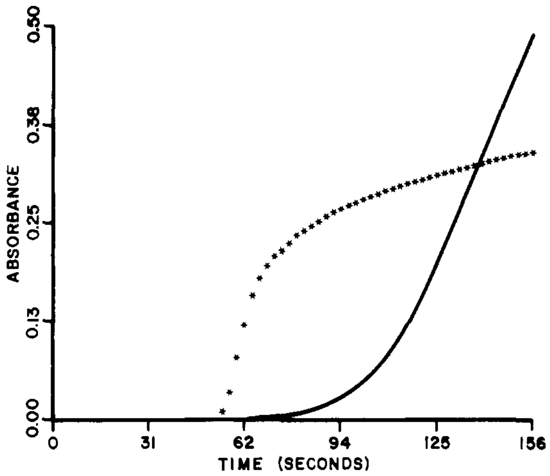

Figure 6. Simulation (—) of the experimental data (*) in Figure 5 using the "low" process B rate constants.

We started out with the Barkin et al. values and attempted to reproduce the following features of our data: (1) the induction period before the onset of process B (region A, Figure 5), which we assume results from Br^- remaining as an impurity in BrO_3^- (the reaction is under the control of process A during the induction period, whose length is determined mainly by the value of k_2/k_4); (2) the sharpness with which process B takes control from process A (point B, Figure 5), which depends strongly on the value of k_4; (3) the rate of steady-state oxidation (region C, Figure 5) of Ce(III) to Ce(IV), which depends strongly on k_4/k_7; (4) the fraction of Ce(III) oxidized to Ce(IV) at equilibrium (region D, Figure 5), which depends mainly on k_5/k_{-5}.

Only the sharpness of the transition from process A to process B depends mainly upon the absolute value of a single rate constant. Figure 6 shows a simulation of the transition from process A to process B in Figure 5 using the "low" rate constants. The induction period length and the steady-state rate of Ce(IV) production are reproduced quite well as they depend upon k_2/k_4 and k_4/k_7, respectively. However, the transition from process A to process B is too slow, even when all rate constants but the "low" value of k_4 are adjusted to maximize its sharpness. We thus conclude that the "low" rate constants are too small. A similar conclusion has been reached by Bar-Eli and Ronkin.[39] It also can be argued that if the rates of reaction of $HBrO_2$ with organic materials approach those of the analogous reactions of HOBr, then process B could not compete with them for $HBrO_2$ on the basis of the "low" rate constants.

The value of k_{-5} has considerable effect on several features. As its value is increased the sharpness of the transition from process A to process B softens somewhat, the steady-state rate of Ce(IV) production decreases, and the total Ce(IV) present at equilibrium decreases. The simulation of Barkin et al.[34] was not quantitative; their calculated rate of Ce(IV) production was much too fast, and process B took control too sharply. Increasing k_{-5} in our simulations by a factor of ten to about 2×10^8 M^{-1} s^{-1} substantially improved agreement, but large discrepancies still remained. Furthermore, this value of k_{-5} is much higher than a value obtained directly by Sullivan and Thompson.[40] Thus we decreased both k_5 and k_{-5} below the Barkin et al. values to gain good quantitative agreement between experiment and simulation

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(38) Försterling, H.-D.; Lamberz, H.; Schreiber, H. *Z. Naturforsch. A*, **1980**, *35A*, 1354.

(39) Bar-Eli, K.; Ronkin, J. *J. Phys. Chem.* **1984**, *88*, 2844.

(40) Sullivan, J. C.; Thompson, R. C. *Inorg. Chem.* **1979**, *18*, 2375.

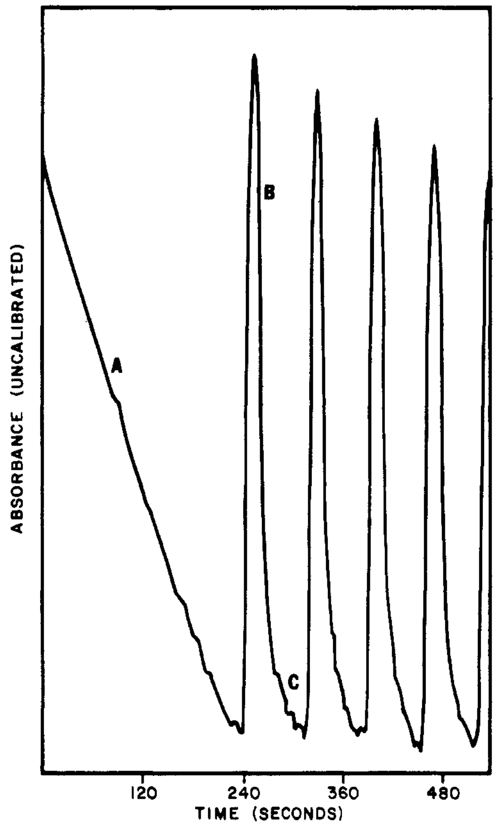

Figure 7. Oscillations monitored spectrophotometrically at 400 nm. The absorbance is mainly due to Ce(IV), but the shoulders (region C) are due to Br_2. Initial concentrations: $[KBrO_3] = 0.0200$ M, $[Ce(SO_4)_2] = 0.0005$ M, $[H_2SO_4] = 1.0$ M, [oxalic acid] = 0.0300 M, and [acetone] = 0.0700 M.

(Figure 5). While some features of our data could be reproduced slightly better by a set of rate constants generally somewhat lower than the Barkin et al. set, this advantage was finally determined not to be great enough to justify a general modification of the Barkin et al. set, which simulated other experiments (including the oscillations) somewhat better than this lower set.

There is a general problem with the values of rate constants for reactions of Ce(IV) in a medium containing SO_4^{2-}. They are substantially affected by the SO_4^{2-} coordination state of Ce(IV), which reaches equilibrium relatively slowly after Ce(IV) is produced by oxidation of Ce(III). This was pointed out by Ganapathisubramanian and Noyes[41] and the effect of $[SO_4^{2-}]$ on reaction −5 was studied in detail by Sullivan and Thompson.[40] Apparently relaxation to the equilibrium coordination state is rapid when Ce(IV) is reduced to Ce(III). Thus it is not clear whether the value of k_{-5} determined by Sullivan and Thompson under equilibrium conditions is applicable to freshly generated Ce(IV) as is present during process B. A graphic example of a difference in rate resulting from Ce(IV) coordination state is shown in Figure 7, which displays the absorbance due to Ce(IV) and Br_2 during oscillations in the system under consideration here. Section A corresponds to the reduction by oxalic acid of Ce(IV) initially present in its equilibrium coordination state. This rate is about that found by Kansal et al.[42] in an equilibrium experiment. Section B corresponds to the reduction of freshly generated Ce(IV) in the same system, which is about 1000 times faster than the rate in section A. We ascribe this difference in rates to a difference in Ce(IV) coordination states. For the same reason the value of E^0 for the Ce(IV)/Ce(III) reduction potential required for the value of $K_5 = k_5/k_{-5}$ determined here to be thermodynamically consistent with the Barkin et al. rate constants is about 0.1 V higher than the equilibrium E^0 in 1 M H_2SO_4. This again suggests that Ce(IV) freshly oxidized in process B does not have the equilibrium SO_4^{2-} coordination state.

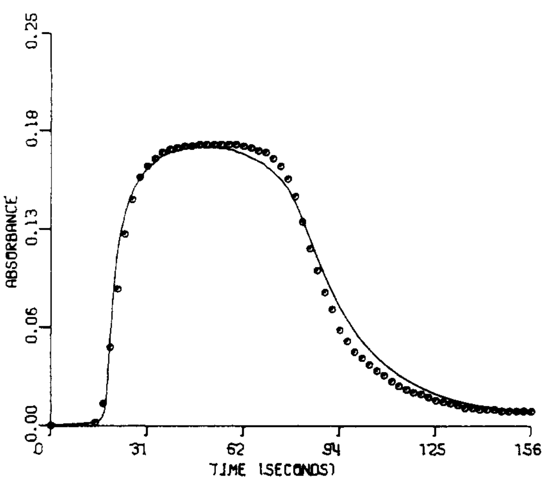

Figure 8. Experimental (○) and simulated (—) absorbances due to Ce(IV), Br_2, and HOBr at 318 nm. Absorbances calculated as in Figure 5. Initial concentrations: $[KBrO_3] = 0.0160$ M, $[Ce_2(SO_4)_3] = 0.000240$ M, [oxalic acid] = 0.009 M, and $[H_2SO_4] = 1.0$ M.

Ce(III) + BrO_3^- + H^+ + Oxalic Acid. This reaction mixture gives one cycle of the oscillations that appear when acetone is also present. Process A gives away to process B when the initial Br^- is consumed, and Ce(III) is oxidized to Ce(IV) as HOBr is produced. A steady state is then entered during which process B oxidizes Ce(III) to Ce(IV) as Ce(IV) is reduced to Ce(III) by oxalic acid. Eventually, the HOBr is reduced to Br_2 by oxalic acid, and process B is inhibited by the Br^- in equilibrium with Br_2 and HOBr. The remaining Ce(IV) is then rapidly reduced by oxalic acid. The rate constant for the reduction of freshly generated Ce(IV) (reaction 14) was assigned to simulate the decay of Ce(IV) in this region as well as the steady-state [Ce(IV)]. The species $HCO_2\cdot$ is important here. Its major fates seem to be reaction with either HOBr or Ce(IV), reactions 28 and 15. The value of k_{15} has been measured directly[43] in the case of Ti(III), and the same value is used here for reaction 15. The value of k_{28} was adjusted to give the proper length steady-state period. Figure 8 shows a typical experiment and simulation. If acetone were present it would eventually remove sufficient Br_2 for $[Br^-]$ to decrease to the point where process B would begin again, and this is the mechanism by which oscillation occurs. We have directly verified that freshly oxidized Ce(IV) does not react with acetone or bromoacetone fast enough to be important here.

The sharpness with which the steady-state period in Figure 8 ends suggests that Br^- is autocatalytically produced at this point, in keeping with the Explodator.[23]

Simulation of Oscillations. The entire system cerium ion + BrO_3^- + H^+ + oxalic acid + acetone was simulated by using without change the rate constant values developed in the preliminary experiments. The simulation program, which shows the exact rate expressions and rate constants used, is available as supplementary material. (See paragraph at end of text regarding supplementary material.) The results of a typical experiment and simulation are shown in Figure 9. Agreement is quite satisfying. As expected of a Br_2-hydrolysis-controlled oscillator,[2] no induction period appears as there is no need to wait for the accumulation of brominated and partially oxidized organic materials before oscillation begins. The experimental and simulated periods agree well, and both show a gradual shortening as reactants are consumed. There is good agreement between the number of oscillations appearing in experiment and simulation.

Figure 9 shows the results of potentiometric measurement of the oscillations. The simulated waveform was originally calculated by assuming that the observed potential resulted only from the

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[41] Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 5158.

[42] Kansal, B. D.; Singh, N.; Singh, H. *J. Indian Chem. Soc.* **1978**, *55*, 304.

[43] Ellis, J. D.; Green, M.; Sykes, G.; Buxton, G. V.; Sellers, R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1724.

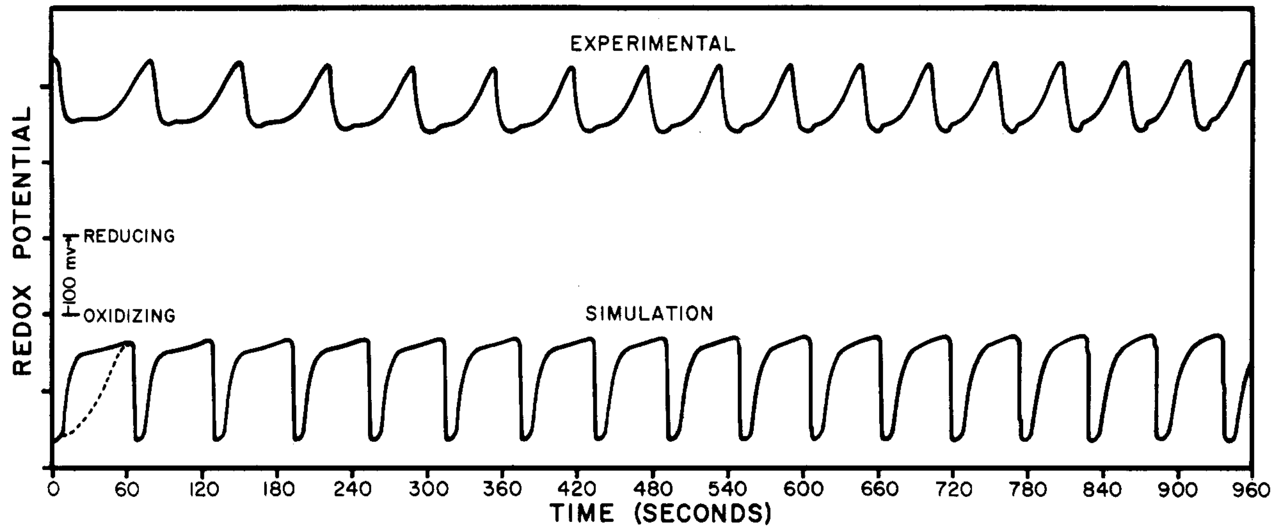

Figure 9. Experimental (top) and simulated (bottom) redox potentials due to Ce(IV)/Ce(III) and Br_2/Br^- in an oscillatory system. Initial concentrations are the same as in Figure 7. The simulated curve is the redox potential calculated on the basis of the Ce(IV)/Ce(III) couple. The dashed line in the first cycle of the simulation is calculated from the Ce(IV)/Ce(III) or the Br_2/Br^- couple, whichever is the higher. The Br_2/Br^- couple cannot be ignored when significant Br_2 accumulates.

Ce(IV)/Ce(III) couple. Agreement between experimental and simulated waveforms was not good under this assumption. The dashed line in the first cycle of the simulation in Figure 9 shows the waveform calculated by assuming that the observed potential is the larger of the Ce(IV)/Ce(III) or the Br_2/Br^- couples. Agreement of experimental and calculated waveforms is excellent with this assumption. This procedure is necessary as relatively large concentrations of Br_2 must accumulate periodically in a Br_2-hydrolysis-controlled oscillator. The absorbance due to accumulated Br_2 can be seen as a shoulder at point C in Figure 7.

Modified Oregonator

Bromine-hydrolysis control can be introduced into the Oregonator by replacing process C (reaction O) by appropriate reactions involving HOBr and Br_2. This increases the number of concentration variables from three to five but also eliminates the undefined stoichiometric factor in reaction O. In the case of the system considered here the model has the added feature that each parameter in it is directly related to the concentration of a single reactant. The model is given as follows:

$$A + Y \rightarrow X + P \quad \text{(M1)}$$

$$X + Y \rightarrow 2P \quad \text{(M2)}$$

$$A + X \rightarrow 2X + Z \quad \text{(M3)}$$

$$X + X \rightarrow P + A \quad \text{(M4)}$$

$$Z \rightarrow \text{inert products} \quad \text{(M5)}$$

$$P \rightarrow Y \quad \text{(M6)}$$

$$P + Y \rightleftharpoons W \quad \text{(M7)}$$

$$W \rightarrow Y \quad \text{(M8)}$$

Variable identifications are $X \equiv HBrO_2$, $Y \equiv Br^-$, $Z \equiv 2Ce(IV)$, $P \equiv HOBr$, $W \equiv Br_2$, and $A \equiv BrO_3^-$. The rate parameters are given in Table II as functions of the concentrations of cerium ion, BrO_3^-, H_2SO_4, oxalic acid, and acetone, and rate constant values from the complete mechanism. This model is similar to one proposed by Noyes[15] and analyzed by Tyson.[44]

TABLE II: Rate Parameters for the Br_2-Hydrolysis-Controlled Oregonator

step	defining equation	value[a]
1	$5.0[H^+]^2$	$5.0\ M^{-1}\ s^{-1}$
2	$2.0 \times 10^9[H^+]$	$2.0 \times 10^9\ M^{-1}\ s^{-1}$
3	$1.0 \times 10^4[H^+]$	$1.0 \times 10^4\ M^{-1}\ s^{-1}$
4	4.0×10^7	$4.0 \times 10^7\ M^{-1}\ s^{-1}$
5	27.5[oxalic acid]/$[H^+]$	$0.825\ s^{-1}$
6	150[oxalic acid][b]	$4.5\ s^{-1}$
7	$8.0 \times 10^9[H^+]$	$8.0 \times 10^9\ M^{-1}\ s^{-1}$
−7	110	$110\ s^{-1}$
8	8.3×10^{-6}[acetone]$[H^+]$	$5.8 \times 10^{-5}\ s^{-1}$

[a] For this calculation: $[BrO_3^-] = 0.02$ M, $[H^+] = 1.0$ M, [oxalic acid] = 0.03 M, [acetone] = 0.07 M, and total cerium = 0.0005 M. [b] Note that k_6 is six times greater than indicated in Table I. This change is made to make the calculated period agree with the experimental period. Reversibility can be taken into account (Showalter, K.; Noyes, R. M.; Bar-Eli, K. **1978**, *69*, 2514) and should give better quantitative results without this modification.

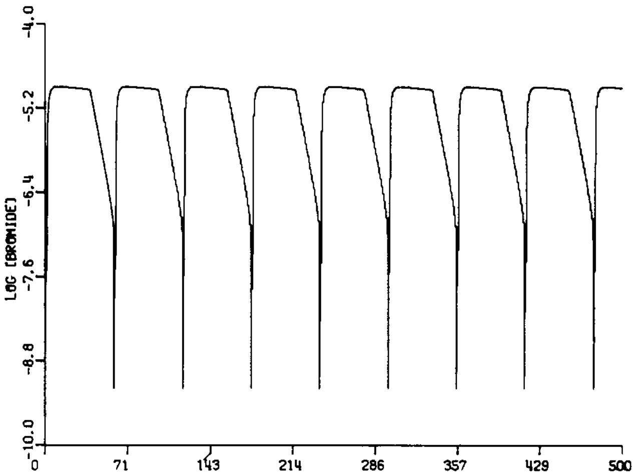

Figure 10. Calculated log $[Br^-]$ vs. time resulting from numerical integration of the Br_2-hydrolysis Oregonator (eq M1–M8) rate expressions. The rate constants used are given in Table II.

Figure 10 shows oscillations in log $[Br^-]$ obtained by numerical integration of the rate equations resulting from reactions M1–M8. Equivalent plots for the other four variables are in the supplementary material. Agreement between the calculated oscillations in Figure 10 and the experimental oscillations shown in Figure 9 is quite good. The calculation shown in Figure 10 was done, requiring conservation of cerium ion.[45] The enolization mechanism of the bromination of acetone[36] also was taken explicitly into account. These refinements have only quantitative effects on the basic behavior of the model. The program used to calculate

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[44] Tyson, J. J. *J. Chem. Phys.* **1984**, *80*, 6079.

[45] Tyson, J. J. *J. Phys. Chem.* **1982**, *86*, 3006.

Figure 10, which includes the detailed rate equations, is in the supplementary material.

The rate constants used here for reactions M1–M4 are derived from Table I. Because reversibility is ignored, they are effectively too large. The Tyson[5] "low" rate constants are expected to give better agreement with experiment for such things as the amplitude of the oscillations and the fraction of Ce(III) oxidized to Ce(IV) in each cycle. The shift from process A to process B will be too slow using the "low" rate constants.

Experimental Section

Oxalic acid, acetone, and sulfuric acid were Baker Analyzed Reagent grade. The NaBr, $KBrO_3$, and $Ce(SO_4)_2$ used were MCB Reagent grade and $Ce_2(SO_4)_3$ was Aldrich Reagent grade. All chemicals were used without further purification except $KBrO_3$ which to remove Br^- was slurried several times in methanol and dried at 150 °C before use.[46] The water used was singly distilled from a Corning AG-3 still. Most experiments were carried out with solutions deoxygenated by purging with N_2 for at least 15 min, although spot checks showed no detectable kinetic effects of dissolved oxygen.

Reactions were run in a 10-mm, teflon-stoppered quartz cuvette located in the sample compartment of a Beckman Model 24 UV–visible spectrophotometer. Reagents were brought to 29 °C by a Braun 1420 thermostatted water circulator before introduction to the cuvette, which was maintained at 29 ± 0.1 °C. For rapid reactions the cuvette was placed in the closed spectrophotometer and the reactants were introduced through tubes by means of a pair of syringes. Mixing occurred in a chamber placed before the cuvette. The resulting digital data were entered into the University of Montana DEC-2060 computer.

Experiments on the complete oscillatory system were carried out with stirring and monitored potentiometrically with a Photovolt platinum electrode, an Altex double-junction reference electrode with KNO_3 in the outer jacket, and an Orion Model 701A digital meter. Output was to a Bausch and Lomb potentiometric recorder.

Simulations were carried out using the DEC-2060 computer with a Tektronix Model 4001 graphics terminal and the Gear numerical integration package.[47] Experimental data and the corresponding simulation were displayed on the same axis, and appropriate rate constants were adjusted to give the best agreement between experimental data and simulation. Hard copies were obtained from a Houston Instruments DP-11 digital plotter. A general discussion of methods of simulating oscillating reactions has been given by Edelson and Rabitz.[48]

Acknowledgment. This work was partially supported by the National Science Foundation under Grant CHE80-23755 and benefited from discussions with Professors Maria Burger and Endre Körös of the L. Eötvös University, Budapest and Professor John J. Tyson of the Virginia Polytechnic Institute and State University. We thank the University of Montana Computer Center for computing facilities and Mr. Robert Yokelson for programming help.

Registry No. BrO_3^-, 15541-45-4; Br^-, 24959-67-9; Br_2, 7726-95-6; Ce, 7440-45-1; oxalic acid, 144-62-7; acetone, 67-64-1.

Supplementary Material Available: Programs to integrate the full model and the Br_2-hydrolysis-controlled Oregonator and plots of log $[HBrO_2]$, log [Ce(IV)], log $[Br_2]$, log [HOBr], and [Ce(IV)] vs. time for the Br_2-hydrolysis-controlled Oregonator (18 pages). Ordering information is available on any current masthead page.

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[46] Field, R. J.; Raghavan, N. V.; Brummer, J. G. *J. Phys. Chem.* **1982**, *86*, 2443.

[47] Hindmarsh, A. C. "Gear: Ordinary Differential Equation Solver", Technical Report No. UCID-3001, Rev. 2, Lawrence Livermore Laboratory, 1972; Based upon Gear, C. W. *Commun. ACM* **1971**, *14*, 185.

[48] Edelson, D.; Rabitz, H. In "Oscillations and Traveling Waves in Chemical Systems", Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985; Chapter 6.

High-Temperature Stabilities of Hydrocarbons

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A chemical thermodynamic analysis of hydrocarbon molecules from 1500 to 3000 K is presented for species $C_{2n}H_{2m}$, $n = 1$–21, $m = 1$–8. With group additivity as the primary estimation method, the nature and chemical thermodynamic properties of the most stable molecules ("stabilomers") are found. Concentrations of these molecules are then examined in equilibrium with acetylene and molecular hydrogen after taking into account numbers of isomers. Thermodynamically favored pathways leading to large, condensed polyaromatic species are examined in detail. Two general types of paths are found. At higher H_2/C_2H_2 ratios ($\gtrsim 1$), most species on these paths are polycyclic aromatic molecules and, depending on partial pressures of C_2H_2 and H_2, a free energy barrier appears in the range 1400–1800 K which increases sharply with increasing temperature. At lower H_2/C_2H_2 ratios, many smaller species are acyclic, and as this ratio becomes smaller the barrier declines and becomes less sensitive to temperature. A brief discussion of the connection between these results and the kinetics of carbon polymerization is then presented.

Introduction

At sufficiently high temperatures, hydrocarbons "polymerize" to form complex mixtures of polyaromatic molecules, polyacetylenes, and solid carbon. Because of the practical importance and ubiquity of these processes, they have long been the subject of study. Chemical complexities and analysis problems have, however, prevented the development of widely accepted chemical mechanisms for these reactions, even in relatively well-controlled reaction environments such as those generated in shock-heated gases.

In this work we present a chemical thermodynamic analysis of hydrocarbons intended to aid the development of such mechanisms. A global equilibrium analysis is presented here which can both place constraints on reaction paths and provide a logical framework on which mechanisms may be built. In addition, the

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