

## Mechanistic Details of the Oscillatory Belousov-Zhabotinskii Reaction

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The reactions constituting the mechanism of the oscillatory Belousov-Zhabotinskii (BZ) reaction may be divided into an inorganic and an organic subset. The former is well established and generally accepted, but the latter remains under development. There has been considerable work on component reactions of the organic subset over the past few years, but little effort has been made to incorporate the results of this work into an improved BZ mechanism. We do so and present a BZ mechanism containing 80 elementary reactions and 26 variable species concentrations and which implements recent experimental results and suggestions concerning the complicated organic chemistry involved. The possible role of organic radicals as a second control intermediate is explored. The rate constants of the inorganic subset also are adjusted for acidity effects. The performance of the model in simulating either quantitatively or semiquantitatively a number of recent BZ experiments is substantially better than that of previous models. Several areas in need of further work are identified.

### Introduction

The cerium ion catalyzed oxidation of malonic acid (MA) by  $\text{BrO}_3^-$ , the classic Belousov-Zhabotinskii<sup>1</sup> (BZ) reaction, is the most thoroughly studied oscillating chemical reaction<sup>2</sup> in both batch and continuous-flow, stirred tank reactor (CSTR) modes. Its basic mechanism was elucidated in 1972 by Field, Körös, and Noyes<sup>3</sup> (FKN). Although its details have been debated, the FKN mechanism supplies the framework for understanding and modeling the temporal and spatial<sup>2</sup> phenomena observed in various BZ reagents.

Despite its success, the FKN mechanism needs to be refined continuously as more information becomes available. It now seems useful to incorporate some recent experimental results into the FKN framework to test the validity and mechanistic effect of some new reactions and to identify areas that need further experimental work. We present a model of the BZ reaction based on a critical evaluation of currently available experimental data and containing 80 elementary reactions and 26 concentration variables. The model simulates semiquantitatively both the normal BZ oscillations and several  $\text{O}_2$ -free experiments that cannot be understood on the basis of previous mechanistic models.

**Mechanism of the Belousov-Zhabotinskii Reaction.** The FKN mechanism is a subset of the model in Table I, to which all reaction numbers refer. The basis of the oscillations is that there are two states (referred to as reduced and oxidized) available to the BZ reaction depending on  $[\text{Br}^-]$ . The reduced state is dominant at high  $[\text{Br}^-]$  where the Ce ion catalyst is in or approaches its reduced state, Ce(III), and the overall chemistry is the bromination of MA with simultaneous removal of  $\text{Br}^-$ . The system switches to the oxidized state when  $[\text{Br}^-]$  becomes sufficiently low. This state is characterized by high values of  $[\text{HBrO}_2]$ ,  $[\text{Ce}^{4+}]$ , and organic radical concentrations and by the simultaneous oxidation and bromination of MA. Relaxation oscillations occur via switches between these states. Bromide ion is slowly consumed by  $\text{BrO}_3^-$ , and the reduced state becomes unstable when  $[\text{Br}^-]$  falls below a critical value, allowing the autocatalytic  $\text{BrO}_3^-$ - $\text{HBrO}_2$  reaction (reactions 9-14) to take over and oxidize Ce(III) to Ce(IV). Reaction 3 between  $\text{Br}^-$  and  $\text{HBrO}_2$  inhibits this process in the presence of sufficient  $\text{Br}^-$  by suppressing reaction 9.

The reverse switch from the oxidized to the reduced state was suggested by FKN to be due to regeneration of  $\text{Br}^-$  by Ce(IV) oxidation of brominated organics, mainly bromomalonic acid (BrMA). The FKN mechanism is thus referred to as  $\text{Br}^-$  controlled. Cerium(IV) and the organic radicals are products of the oxidized state, so this reverse transition results from a delayed negative feedback loop. The relaxation oscillations are preceded under most experimental conditions by a few minutes long to more

than 20-min long, oxidized, nonoscillatory induction period that is apparently<sup>4</sup> necessary for the synthesis of bromine-containing derivatives of MA used in  $\text{Br}^-$  regeneration. However, the simple application of this idea does not produce sufficient  $\text{Br}^-$  per Ce(IV) consumed<sup>5</sup> for oscillation to occur, and <sup>82</sup>Br-tracer experiments<sup>6</sup> suggest that a significant amount of  $\text{Br}^-$  may also be produced by the reduction of oxybromine compounds, perhaps by organic radicals.

**Non-Bromide Control.** There has been some controversy concerning the identity of the control intermediate in the BZ reaction. Noszticzius<sup>7</sup> added  $\text{Ag}^+$  to an oscillating BZ reagent and found that small-amplitude, high-frequency oscillations persist even under conditions when  $[\text{Br}^-]$ , as calculated from the solubility product of  $\text{AgBr}$ , is too low to control the oscillations. He referred to these oscillations as "non- $\text{Br}^-$ -controlled". This began a controversy concerning the existence of another control intermediate, which is not yet fully resolved.<sup>8-10</sup> Molecular bromine,<sup>5</sup>  $\text{Br}^*$ ,<sup>11</sup> and the malonyl radical,  $\text{MA}^*$ , have been suggested as alternate control intermediates, but  $\text{Br}_2$  was quickly eliminated.<sup>12</sup>

The malonyl radical is expected to be an important intermediate in the FKN mechanism. Brusa et al.<sup>13</sup> pointed out that  $\text{MA}^*$  could replace  $\text{Br}^-$  in the negative feedback loop. This suggestion resulted from an ESR study of the formation and self-decay of  $\text{MA}^*$  generated by the reaction of Ce(IV) with MA in 2 M  $\text{HClO}_4$ . They also investigated the reaction of  $\text{MA}^*$  with  $\text{BrO}_3^-$ . Försterling and Noszticzius<sup>14</sup> carried out a detailed investigation of the reactions of  $\text{MA}^*$  with several BZ oxybromine intermediates in 1 M  $\text{H}_2\text{SO}_4$  (the usual BZ medium) and found that  $\text{MA}^*$  reacts with  $\text{BrO}_2^*$  at a diffusion-controlled rate. They thus claim that  $\text{MA}^*$  is indeed a second control intermediate as  $\text{BrO}_2^*$  is involved in the autocatalytic  $\text{BrO}_3^-$ - $\text{HBrO}_2$  reaction. They also point out

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that this claim is not tenable if the products of the reaction are  $\text{HBrO}_2$  and  $\text{CHOH}(\text{COOH})_2$  as this is analogous to reaction 13 between  $\text{Ce}(\text{III})$  and  $\text{BrO}_2^*$ .

Other support for  $\text{MA}^*$  control comes from Försterling et al.,<sup>15</sup> who found that in 3 M  $\text{H}_2\text{SO}_4$ <sup>16</sup> and at very high  $[\text{MA}]_0/[\text{BrO}_3^-]_0$  the potential of a  $\text{Br}^-$ -selective electrode oscillates in a range characteristic of  $\text{HOBr}$  rather than of  $\text{Br}^-$ . They also found that dissolved  $\text{O}_2$  may inhibit the oscillations, presumably because  $\text{MA}^*$  is removed by  $\text{O}_2$  rather than by  $\text{BrO}_2^*$ . They concluded that the oscillations are not  $\text{Br}^-$  controlled and suggested a model (the "Radicalator") in which  $\text{MA}^*$  is the control intermediate. They later modified<sup>17</sup> the model, allowing the  $\text{MABrO}_2$  formed from  $\text{MA}^*$  and  $\text{BrO}_2^*$  to decompose by two different routes, one leading to  $\text{HBrO}_2$  and  $\text{CHOH}(\text{COOH})_2$  and the other leading to  $\text{HOBr}$ ,  $\text{HCOCOOH}$ , and  $\text{CO}_2$ . The probabilities of these two routes were inferred to be equal on the basis of fitting experimental data. This modified Radicalator nicely simulates some phenomena found during the induction period in 1 M  $\text{H}_2\text{SO}_4$  medium but completely fails to simulate anything after the induction period, indicating that  $\text{Br}^-$  control cannot be completely replaced by  $\text{MA}^*$  control. They conclude that the Radicalator describes a second negative feedback loop that is always present but not always important.

### The Bases of an Expanded FKN Mechanism

*Parts of the FKN Mechanism.* The FKN mechanism may be regarded as containing an inorganic part mainly involving reactions of oxybromine species among themselves and with the metal ion catalyst, and an organic part involving the reactions of malonic acid and its derivatives with  $\text{Ce}(\text{IV})$  and oxybromine species. Field and Noyes<sup>18</sup> reduced the FKN mechanism to a skeleton model, the Oregonator,<sup>18</sup> that treats the oxybromine chemistry in some detail but lumps the organic part together into a single overall reaction. Showalter et al.<sup>19</sup> included reverse reactions and some subtleties of the oxybromine chemistry, allowing Oregonator to simulate the complex wave forms found in some experiments. Experimental work of Noszticzius et al.<sup>20a</sup> and calculations of Tyson<sup>20b</sup> indicated that some of the original FKN oxybromine rate constants must be in error. The experiments of Ariese and Ungvárai-Nagy<sup>21</sup> and of Field and Försterling<sup>22</sup> have confirmed this. A revised set of rate constants for the FKN oxybromine chemistry is available.<sup>22</sup> Kshirsagar and Field<sup>23</sup> found while studying the equilibrium involving  $\text{Br}_2$ ,  $\text{HOBr}$ , and  $\text{Br}^-$  that the usual value<sup>22</sup> of the  $\text{Br}_2$ -hydrolysis equilibrium constant may need modification. Försterling et al.<sup>24</sup> have disputed this suggestion on the basis of titrations of solutions of  $\text{Br}_2$  and  $\text{HOBr}$  with  $\text{Ag}^+$  with spectrophotometric endpoint detection. While there may still be some quantitative problems with the  $\text{Br}_2$ -hydrolysis process, the oxybromine part of the FKN mechanism is regarded as well established.

The only previous mechanistic model of the BZ reaction dealing in any detail with the elementary reactions of the BZ organic chemistry was constructed by Edelson et al.<sup>25</sup> This model successfully simulated oscillatory behavior but used the original FKN rate constant values for the inorganic reaction subset. Its organic

subset (meaning all the reactions having at least one organic reactant) reflects the lack of detailed information available when it was created.

There are a number of potential intermediates in the mechanism of the oxidation of  $\text{CH}_2(\text{COOH})_2$  to  $\text{CO}_2$ . Hansen, Ruoff, and co-workers identified the more important stable intermediates by proton NMR spectroscopy. They found<sup>26</sup> that no formic acid is formed (or consumed) during the normal oscillations. Ruoff et al.<sup>27</sup> later added glyoxylic acid and observed the production of formic acid, suggesting that glyoxylic acid also cannot be a major intermediate.

Also related to the mechanism of oxidation of organics in the BZ medium is the observation of Noszticzius<sup>28</sup> that there is periodic carbon monoxide evolution during the course of the oscillations. Bódiss et al.<sup>29</sup> studied the reactions of several possible organic intermediates with different one-electron-oxidizing agents and found that  $\text{CO}$  is formed only when bromomalonic acid is present. Our preliminary experiments with  $^{13}\text{C}$ -labeled  $\text{BrMA}$  show that it is the central carbon atom in  $\text{BrMA}$  which is oxidized to carbon monoxide, but the route to  $\text{CO}$  is still unknown.

Field and Boyd<sup>30</sup> studied a modified BZ system, the  $\text{Ce}(\text{IV})/\text{Ce}(\text{III})\text{-BrO}_3\text{-oxalic acid (OA)-acetone}$  oscillating reaction. They performed kinetic studies on different subsets of this complicated system, out of which the  $\text{Ce}(\text{III})\text{-BrO}_3\text{-OA}$  subset is clearly a part of the classic BZ reaction. Following Field and Boyd,<sup>30</sup> we assume that the oxidation of organic matter in the BZ reaction mixture proceeds by a series of one-electron-transfer steps. The only exception to this is the oxidation of  $\text{MA}^*$  by  $\text{BrO}_2^*$ , for which the interpretation of Försterling et al.<sup>17</sup> was used.

It is normally assumed that organic radicals disproportionate rather than recombine, although in the case of  $\text{MA}^*$  the rate constant reported<sup>13</sup> for its self-destruction seems high for a disproportionation. We reluctantly continue this assumption. However, because  $\text{HCOOH}$  is not found among the BZ reaction products, we assume that the formyl radical (hydroxyoxomethyl radical,  $^*\text{COOH}$ ) must either recombine<sup>30</sup> or react with another species.

The abstraction of H atoms by various radicals has not been extensively investigated in aqueous solution. Several reactions of this type are incorporated in the mechanism without attempting to determine which are the most important. Most information concerning the chemistry of free radicals in aqueous solution results from systems amenable to investigation by radiation chemistry,<sup>31</sup> and little systematic knowledge has accumulated. However, on the basis of experimentally determined rate constant values<sup>31</sup> and general laws of free-radical chemistry,<sup>32</sup> it is possible to formulate some guidelines.

i. When H atom abstraction is endothermic (as it is with less reactive abstracting radical, e.g.,  $\text{Br}^*$ ), the structure of the transition state is closer to that of the products than the reactants. Thus the stability of the product radical determines the rate. In contrast, the rates of exothermic H atom abstractions are rapid and not very sensitive to either the strength of the bond broken or the stability of the product radical.

ii. The relative rates of hydrogen abstraction reactions in water decrease in the following order:<sup>33</sup> a C-H bond, the O-H bond in alcohols, the O-H bond in carboxylic acids.

iii. The reactivity of carbon radicals is increased by an electron-withdrawing group (such as  $\text{HO-}$ ) attached to the same

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TABLE I: Mechanistic Model of the Belousov-Zhabotinskii Reaction ( $[H_2O] = 55 \text{ M}$  Included in the Rate Constants)<sup>f</sup>

		rate constant <sup>f</sup>	reference
1. Inorganic Subset			
1	$\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	$2.3\text{E}+9 \text{ M}^{-2} \text{ s}^{-1}$	23
2	$\text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{Br}^- + \text{H}^+$	$2.0 \text{ s}^{-1}$	23
3	$\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightarrow 2\text{HOBr}$	$2.0\text{E}+6 \text{ M}^{-2} \text{ s}^{-1}$	22 <sup>c</sup>
4	$2\text{HOBr} \rightarrow \text{Br}^- + \text{HBrO}_2 + \text{H}^+$	$2.0\text{E}-5 \text{ M}^{-1} \text{ s}^{-1}$	22, 23
5	$\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightarrow \text{HOBr} + \text{HBrO}_2$	$2.0 \text{ M}^{-3} \text{ s}^{-1}$	22 <sup>c</sup>
6	$\text{HOBr} + \text{HBrO}_2 \rightarrow \text{Br}^- + \text{BrO}_3^- + 2\text{H}^+$	$3.3 \text{ M}^{-1} \text{ s}^{-1}$	22 <sup>c</sup>
7	$2\text{HBrO}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$	$3.0\text{E}+3 \text{ M}^{-1} \text{ s}^{-1}$	22
8	$\text{BrO}_3^- + \text{HOBr} + \text{H}^+ \rightarrow 2\text{HBrO}_2$	$7.5\text{E}-9 \text{ M}^{-2} \text{ s}^{-1}$	22 <sup>c</sup>
9	$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow \text{Br}_2\text{O}_4 + \text{H}_2\text{O}$	$33.0 \text{ M}^{-2} \text{ s}^{-1}$	22 <sup>c</sup>
10	$\text{Br}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+$	$2200 \text{ s}^{-1}$	22
11	$\text{Br}_2\text{O}_4 \rightarrow 2\text{BrO}_2^*$	$7.4\text{E}+4 \text{ s}^{-1}$	22
12	$2\text{BrO}_2^* \rightarrow \text{Br}_2\text{O}_4$	$1.4\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	22
13	$\text{Ce}^{3+} + \text{BrO}_2^* + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce}^{4+}$	$6.2\text{E}+4 \text{ M}^{-2} \text{ s}^{-1}$	22 <sup>c</sup>
14	$\text{HBrO}_2 + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} + \text{BrO}_2^* + \text{H}^+$	$7.0\text{E}+3 \text{ M}^{-1} \text{ s}^{-1}$	22 <sup>c</sup>
2. Reactions Involving Organic Species			
a. Reactions Not Consuming or Producing Radicals			
15	$\text{MA} \rightarrow \text{ENOL}$	$3.0\text{E}-3 \text{ s}^{-1}$	25, 38
16	$\text{ENOL} \rightarrow \text{MA}$	$200.0 \text{ s}^{-1}$	25, 38
17	$\text{ENOL} + \text{Br}_2 \rightarrow \text{BrMA} + \text{Br}^- + \text{H}^+$	$1.91\text{E}+6 \text{ M}^{-1} \text{ s}^{-1}$	39 <sup>d</sup>
18	$\text{MA} + \text{HOBr} \rightarrow \text{BrMA} + \text{H}_2\text{O}$	$8.2 \text{ M}^{-1} \text{ s}^{-1}$	39
19	$\text{BrMA} + \text{HOBr} \rightarrow \text{Br}_2\text{MA} + \text{H}_2\text{O}$	$0.1 \text{ M}^{-1} \text{ s}^{-1}$	f
20	$\text{TTA} + \text{HOBr} \rightarrow \text{BrTTA} + \text{H}_2\text{O}$	$5.0 \text{ M}^{-1} \text{ s}^{-1}$	39 <sup>a</sup>
21	$\text{BrO}_2\text{MA} + \text{H}_2\text{O} \rightarrow \text{HBrO}_2 + \text{TTA}$	$1.0 \text{ s}^{-1}$	47
22	$\text{BrO}_2\text{TTA} \rightarrow \text{HOBr} + \text{MOA}$	$1.0 \text{ s}^{-1}$	47
23	$\text{BrO}_2\text{TTA} \rightarrow \text{HBrO}_2 + \text{MOA}$	$1.0 \text{ s}^{-1}$	47 <sup>a</sup>
24	$\text{BrTTA} \rightarrow \text{Br}^- + \text{MOA} + \text{H}^+$	$1.0 \text{ s}^{-1}$	
b. Reactions Producing Radicals			
25	$\text{Ce}^{4+} + \text{BrMA} \rightarrow \text{Ce}^{3+} + \text{BrMA}^* + \text{H}^+$	$0.09 \text{ M}^{-1} \text{ s}^{-1}$	39, 48
26	$\text{Ce}^{4+} + \text{MA} \rightarrow \text{Ce}^{3+} + \text{MA}^* + \text{H}^+$	$0.23 \text{ M}^{-1} \text{ s}^{-1}$	39, 57
27	$\text{Ce}^{4+} + \text{TTA} \rightarrow \text{Ce}^{3+} + \text{TTA}^* + \text{H}^+$	$0.66 \text{ M}^{-1} \text{ s}^{-1}$	39, 57
28	$\text{HOBr} + \text{MOA} \rightarrow \text{Br}^* + \text{OA} + \text{}^*\text{COOH}$	$140.0 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>a,b</sup>
29	$\text{Ce}^{4+} + \text{MOA} + \text{H}_2\text{O} \rightarrow \text{Ce}^{3+} + \text{OA} + \text{}^*\text{COOH} + \text{H}^+$	$10.0 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>a,b</sup>
30	$\text{HOBr} + \text{OA} \rightarrow \text{Br}^* + \text{}^*\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$	$140.0 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>b</sup>
31	$\text{Ce}^{4+} + \text{OA} \rightarrow \text{Ce}^{3+} + \text{}^*\text{COOH} + \text{CO}_2 + \text{H}^+$	$10.0 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>b</sup>
32	$\text{BrO}_3^- + \text{OA} + \text{H}^+ \rightarrow \text{BrO}_2^* + \text{}^*\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$	$1.6\text{E}-5 \text{ M}^{-2} \text{ s}^{-1}$	30 <sup>b</sup>
c. Reactions Consuming Radicals			
33	$2\text{Br}^* \rightarrow \text{Br}_2$	$1.0\text{E}+8 \text{ M}^{-1} \text{ s}^{-1}$	30
34	$\text{Br}^* + \text{BrMA}^* \rightarrow \text{Br}_2\text{MA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	f
35	$2\text{BrMA}^* + \text{H}_2\text{O} \rightarrow \text{BrMA} + \text{BrTTA}$	$1.0\text{E}+8 \text{ M}^{-1} \text{ s}^{-1}$	
36	$\text{BrMA}^* + \text{MA}^* + \text{H}_2\text{O} \rightarrow \text{MA} + \text{BrTTA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
37	$\text{BrMA}^* + \text{TTA}^* + \text{H}_2\text{O} \rightarrow \text{TTA} + \text{BrTTA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
38	$\text{BrMA}^* + \text{Ce}^{4+} + \text{H}_2\text{O} \rightarrow \text{Ce}^{3+} + \text{BrTTA} + \text{H}^+$	$1.0\text{E}+7 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>a,b</sup>
39	$\text{BrMA}^* + \text{BrO}_2^* + \text{H}_2\text{O} \rightarrow \text{HBrO}_2 + \text{BrTTA}$	$5.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
40	$\text{BrMA}^* + \text{}^*\text{COOH} \rightarrow \text{BrMA} + \text{CO}_2$	$5.0\text{E}+8 \text{ M}^{-1} \text{ s}^{-1}$	
41	$2\text{MA}^* + \text{H}_2\text{O} \rightarrow \text{MA} + \text{TTA}$	$3.2\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	13
42	$\text{MA}^* + \text{TTA}^* + \text{H}_2\text{O} \rightarrow 2\text{TTA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
43	$\text{MA}^* + \text{}^*\text{COOH} \rightarrow \text{MA} + \text{CO}_2$	$2.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
44	$\text{MA}^* + \text{Br}^* \rightarrow \text{BrMA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
45	$\text{MA}^* + \text{Ce}^{3+} + \text{H}^+ \rightarrow \text{MA} + \text{Ce}^{4+}$	$1.7\text{E}+4 \text{ M}^{-2} \text{ s}^{-1}$	57
46	$\text{MA}^* + \text{BrO}_2^* \rightarrow \text{BrO}_2\text{MA}$	$5.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	14
47	$2\text{TTA}^* \rightarrow \text{TTA} + \text{MOA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	13 <sup>a</sup>
48	$\text{TTA}^* + \text{}^*\text{COOH} \rightarrow \text{TTA} + \text{CO}_2$	$2.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
49	$\text{TTA}^* + \text{Br}^* \rightarrow \text{BrTTA}$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
50	$\text{TTA}^* + \text{Ce}^{3+} + \text{H}^+ \rightarrow \text{TTA} + \text{Ce}^{4+}$	$1.7\text{E}+4 \text{ M}^{-2} \text{ s}^{-1}$	57 <sup>a</sup>
51	$\text{TTA}^* + \text{BrO}_2^* \rightarrow \text{BrO}_2\text{TTA}$	$5.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
52	$2\text{}^*\text{COOH} \rightarrow \text{OA}$	$1.2\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	30
53	$\text{}^*\text{COOH} + \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} + \text{CO}_2 + \text{H}^+$	$1.0\text{E}+7 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>b</sup>
54	$\text{}^*\text{COOH} + \text{Br}^* \rightarrow \text{Br}^- + \text{CO}_2 + \text{H}^+$	$1.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	
55	$\text{}^*\text{COOH} + \text{BrO}_2^* \rightarrow \text{HBrO}_2 + \text{CO}_2$	$5.0\text{E}+9 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
d. Reactions Preserving Radicals			
56	$\text{MA}^* + \text{Br}_2 \rightarrow \text{BrMA} + \text{Br}^*$	$1.5\text{E}+8 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>g</sup>
57	$\text{MA}^* + \text{HOBr} \rightarrow \text{TTA} + \text{Br}^*$	$1.0\text{E}+7 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>g</sup>
58	$\text{MA}^* + \text{BrO}_3^- + \text{H}^+ \rightarrow \text{TTA} + \text{BrO}_2^*$	$40.0 \text{ M}^{-2} \text{ s}^{-1}$	14 <sup>e</sup>
59	$\text{MA}^* + \text{TTA} \rightarrow \text{MA} + \text{TTA}^*$	$1.0\text{E}+5 \text{ M}^{-1} \text{ s}^{-1}$	
60	$\text{TTA}^* + \text{MA} \rightarrow \text{TTA} + \text{MA}^*$	$1.0\text{E}+5 \text{ M}^{-1} \text{ s}^{-1}$	
61	$\text{MA}^* + \text{BrMA} \rightarrow \text{MA} + \text{BrMA}^*$	$1.0\text{E}+5 \text{ M}^{-1} \text{ s}^{-1}$	h
62	$\text{BrMA}^* + \text{MA} \rightarrow \text{BrMA} + \text{MA}^*$	$5.0\text{E}+2 \text{ M}^{-1} \text{ s}^{-1}$	
63	$\text{TTA}^* + \text{BrMA} \rightarrow \text{TTA} + \text{BrMA}^*$	$2.0\text{E}+5 \text{ M}^{-1} \text{ s}^{-1}$	
64	$\text{BrMA}^* + \text{TTA} \rightarrow \text{BrMA} + \text{TTA}^*$	$5.0\text{E}+3 \text{ M}^{-1} \text{ s}^{-1}$	
65	$\text{TTA}^* + \text{Br}_2 \rightarrow \text{BrTTA} + \text{Br}^*$	$1.0\text{E}+8 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
66	$\text{TTA}^* + \text{HOBr} \rightarrow \text{MOA} + \text{Br}^* + \text{H}_2\text{O}$	$1.0\text{E}+7 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
67	$\text{TTA}^* + \text{BrO}_3^- + \text{H}^+ \rightarrow \text{MOA} + \text{BrO}_2^* + \text{H}_2\text{O}$	$40.0 \text{ M}^{-2} \text{ s}^{-1}$	14 <sup>a,e</sup>
68	$\text{BrMA}^* + \text{Br}_2 \rightarrow \text{Br}_2\text{MA} + \text{Br}^*$	$1.0\text{E}+6 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a,f</sup>

TABLE I (Continued)

		rate constant <sup>f</sup>	reference
69	$\text{BrMA}^* + \text{HOBr} \rightarrow \text{BrTTA} + \text{Br}^*$	$1.0\text{E}+5 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
70	$\text{BrMA}^* + \text{BrO}_3^- + \text{H}^+ \rightarrow \text{BrO}_2^* + \text{BrTTA}$	$40.0 \text{ M}^{-2} \text{ s}^{-1}$	14 <sup>a,e</sup>
71	$^*\text{COOH} + \text{BrMA} \rightarrow \text{Br}^- + \text{MA}^* + \text{CO}_2 + \text{H}^+$	$1.0\text{E}+7 \text{ M}^{-1} \text{ s}^{-1}$	
72	$^*\text{COOH} + \text{Br}_2 \rightarrow \text{Br}^- + \text{Br}^* + \text{CO}_2 + \text{H}^+$	$1.5\text{E}+8 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
73	$^*\text{COOH} + \text{HOBr} \rightarrow \text{Br}^* + \text{CO}_2 + \text{H}_2\text{O}$	$2.0\text{E}+7 \text{ M}^{-1} \text{ s}^{-1}$	14 <sup>a</sup>
74	$^*\text{COOH} + \text{BrO}_3^- + \text{H}^+ \rightarrow \text{BrO}_2^* + \text{CO}_2 + \text{H}_2\text{O}$	$2.1\text{E}+3 \text{ M}^{-2} \text{ s}^{-1}$	30
75	$\text{Br}^* + \text{MA} \rightarrow \text{Br}^- + \text{MA}^* + \text{H}^+$	$1.0\text{E}+5 \text{ M}^{-1} \text{ s}^{-1}$	
76	$\text{Br}^* + \text{TTA} \rightarrow \text{Br}^- + \text{TTA}^* + \text{H}^+$	$1.0\text{E}+6 \text{ M}^{-1} \text{ s}^{-1}$	
77	$\text{Br}^* + \text{BrMA} \rightarrow \text{Br}^- + \text{BrMA}^* + \text{H}^+$	$5.0\text{E}+6 \text{ M}^{-1} \text{ s}^{-1}$	
78	$\text{Br}^* + \text{MOA} + \text{H}_2\text{O} \rightarrow \text{Br}^- + \text{OA} + ^*\text{COOH} + \text{H}^+$	$2.0\text{E}+3 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>a</sup>
79	$\text{Br}^* + \text{OA} \rightarrow \text{Br}^- + ^*\text{COOH} + \text{CO}_2 + \text{H}^+$	$2.0\text{E}+3 \text{ M}^{-1} \text{ s}^{-1}$	30
80	$\text{BrO}_2^* + \text{OA} \rightarrow \text{HBrO}_2 + ^*\text{COOH} + \text{CO}_2$	$1.0\text{E}+2 \text{ M}^{-1} \text{ s}^{-1}$	30 <sup>e</sup>

<sup>a</sup> Adjusted by analogy to the reference given. <sup>b</sup> Modified in this work to fit experimental data. <sup>c</sup> Adjusted in this work for  $[\text{H}^+] = 1.29 \text{ M}$  in  $1 \text{ M H}_2\text{SO}_4$ . <sup>d</sup> Calculated from the reference given using enolization equilibrium constant  $1.5 \times 10^{-5}$ . <sup>e</sup> Value used here is lower than the upper limit given in the reference. <sup>f</sup>  $\text{Br}_2\text{MA}$  is not a dynamic variable of the model. <sup>g</sup> Products of the reaction are not specified in the reference. <sup>h</sup> This reaction was first suggested by Noyes and Jwo.<sup>56</sup> <sup>i</sup> Abbreviations: MA  $\equiv \text{CH}_2(\text{COOH})_2$ ; MA\*  $\equiv ^*\text{CH}(\text{COOH})_2$ ; ENOL  $\equiv (\text{HOOC})\text{CH}=\text{C}(\text{OH})_2$ ; BrMA  $\equiv \text{BrCH}(\text{COOH})_2$ ; BrO<sub>2</sub>MA  $\equiv \text{OBrOCH}(\text{COOH})_2$ ; Br<sub>2</sub>MA  $\equiv \text{CBr}_2(\text{COOH})_2$ ; BrMA\*  $\equiv ^*\text{CBr}(\text{COOH})_2$ ; TTA  $\equiv \text{HCOH}(\text{COOH})_2$ ; TTA\*  $\equiv ^*\text{COH}(\text{COOH})_2$ ; BrTTA  $\equiv \text{BrCOH}(\text{COOH})_2$ ; BrO<sub>2</sub>TTA  $\equiv \text{OBrOCOH}(\text{COOH})_2$ ; MOA  $\equiv \text{CO}(\text{COOH})_2$ ; OA  $\equiv (\text{COOH})_2$ . <sup>j</sup> 2.3E+9 represents  $2.3 \times 10^9$ .

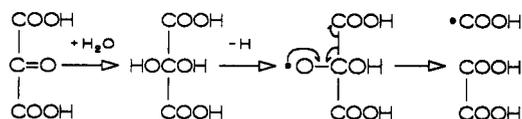


Figure 1. Suggested route of oxidation of  $\text{CO}(\text{COOH})_2$  to  $(\text{COOH})_2$  and  $^*\text{COOH}$  via the hydrate form of the ketone.

carbon<sup>31</sup> and in general with the electropositivity of the carbon atom.<sup>31</sup>

iv. For equilibria such as  $\text{R} + \text{Q} \rightleftharpoons \text{R}^* + \text{Q}$ , the equilibrium constant reflects primarily the relative stabilities of  $\text{R}^*$  and  $\text{Q}^*$  and is shifted toward the more stable radical.

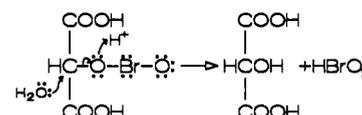
v. Most of the radicals formed in the BZ system are resonance-stabilized. Their relative stabilities are related to the number of possible resonance structures for each radical.

This comparison assigns a special position to  $\text{BrMA}^*$ . This is the only radical in the system with four resonance structures, one having the unpaired electron on the bromine atom. An X-ray crystallographic study<sup>34</sup> of solid-phase  $\text{BrMA}^*$  found 19% of the unpaired electron on Br. We assume in the presence of substantial  $\text{BrMA}^*$  that  $\text{BrMA}^*$  is the dominant organic radical in the system.

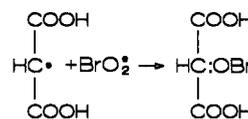
There are four subprocesses in the organic subset that need to be discussed in detail: the oxidation of MA to  $\text{CO}_2$ , the possibility of a special mechanistic role for  $^*\text{COOH}$ , the reaction between  $\text{MA}^*$  and  $\text{BrO}_2^*$ , and the bromination reactions of organic intermediates.

Excluding  $\text{HCOOH}$  and  $\text{OCHCOOH}$ , the major stable intermediates that must be considered are: tartronic acid (2-hydroxymalonic acid or TTA), mesoxalic acid (2-oxomalonic acid or MOA), and oxalic acid (OA). Tartronic acid is readily oxidized to MOA via  $\text{TTA}^*$ . However, a problem occurs in the oxidation of MOA to oxalic acid if it is assumed that  $\text{HOCCOCOO}^*$  is an intermediate as such radicals usually decarboxylate to a radical with one less carbon atom. In the case of the mesoxalic acid this yields glyoxylic acid, which is not found. However, ketones such as MOA are known to exist in the form of a hydrate ( $\text{HOCC}(\text{OH})_2\text{COOH}$ ) in aqueous solution. Hydrogen abstraction from such a hydrate is expected<sup>33</sup> to be from an alcoholic OH rather than from  $-\text{COOH}$ . The resulting  $-\text{O}^*$  radical may then decompose into  $^*\text{COOH}$  and  $(\text{COOH})_2$ . This pathway is shown in Figure 1.

All oxidations of organic intermediates by this path lead to  $^*\text{COOH}$ , which becomes an intermediate whose fate must be carefully considered. Its thermodynamics<sup>35</sup> is different from that of other organic radicals occurring in this system. The standard potential<sup>35</sup>  $E^\circ(\text{CO}_2/\text{CO}_2^-) = -1.8 \text{ V}$  suggests it will act as a reducing agent donating its unpaired electron rather than as an



Route I



Route II

Figure 2. Suggested mechanisms for the decomposition of  $(\text{COOH})_2\text{H-COBrO}$  formed by the reaction of malonyl radical with  $\text{BrO}_2^*$ . The two routes are estimated (ref 17) to have approximately equal rates in  $1 \text{ M H}_2\text{SO}_4$ , while route II is assumed to be dominant in  $3 \text{ M H}_2\text{SO}_4$  (refs 15 and 16). See text for details.

oxidizing agent by abstracting a hydrogen. Besides avoiding the formation of  $\text{HCOOH}$ , there is another important consequence of this nature of  $^*\text{COOH}$ .  $\text{BrMA}$  is known<sup>36</sup> to be a good electron acceptor, both oxidizing  $\text{I}^-$  in acidic solution and giving a cathodic polarographic wave. Therefore, it is feasible that  $^*\text{COOH}$  rapidly reduces  $\text{BrMA}$ , yielding  $\text{MA}^*$  and  $\text{Br}^-$  and strengthening the FKN negative feedback loop.

The reaction of  $\text{BrO}_2^*$  with  $\text{MA}^*$  to form  $\text{MABrO}_2$  that may decompose to either  $\text{HBrO}_2 + \text{TTA}$  or  $\text{HOBr} + \text{MOA}$  is the basis of  $\text{MA}^*$  control. According to Försterling et al.<sup>17</sup> the rates of the two routes are approximately equal in  $1 \text{ M H}_2\text{SO}_4$ , while the reduction of  $\text{BrO}_2^*$  to  $\text{HOBr}$  is dominant in  $3 \text{ M H}_2\text{SO}_4$ . Although there is no direct evidence for either of the two routes, we suggest the mechanism outlined in Figure 2. The decomposition of  $\text{MABrO}_2$  to  $\text{HBrO}_2$  and TTA (route I in Figure 2) proceeds by  $\text{H}_2\text{O}$  attack on the central MA carbon atom. This route diminishes in importance as the activity of water decreases<sup>37</sup> with increasing  $[\text{H}_2\text{SO}_4]$  relative to that leading to  $\text{HOBr}$  and MOA (route II in Figure 2), which involves the loss of the acidic proton from the central carbon with the simultaneous formation of a carbon-oxygen double bond. Thus  $\text{MA}^*$  control is expected to be more important at high  $[\text{H}_2\text{SO}_4]$ , as is observed. Further work is needed to support this hypothesis.

The proposed mechanism includes a number of reactions describing the bromination of various intermediates. It normally has been assumed that MA derivatives are brominated by  $\text{Br}_2$  and

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that the direct reactions of HOBr are oxidative. Of course, HOBr also can lead indirectly to bromination if there is enough Br<sup>-</sup> available to convert it to Br<sub>2</sub>. Bromination by Br<sub>2</sub> proceeds<sup>38</sup> via the enol of MA. However, the work of Pachtl<sup>39</sup> indicates that HOBr may also directly brominate MA. The reactive species was assumed<sup>39</sup> to be MA itself and not its enol. We have included both bromination mechanisms with the enolization rate independent of acid concentration as reported by Leopold and Haim.<sup>38</sup> Kinetic studies of the HOBr/Br<sub>2</sub> + MA reaction suggest that the second bromination of MA to yield Br<sub>2</sub>MA is much slower than the first bromination. The BrMA + HOBr reaction is included as a BrMA sink, but Br<sub>2</sub>MA is not treated as a dynamic variable as its chemistry is unknown. This omission is important only late in the reaction when most MA has been removed by oxidation or bromination.

There is little information available on the bromination of TTA. We assume that TTA is brominated only by HOBr and at a rate comparable to that of MA. The bromination product is assumed to be 2-bromohydroxymalonic acid (BrTTA), which decomposes into MOA and Br<sup>-</sup> as suggested<sup>40</sup> for similar bromohydrin intermediates in uncatalyzed bromate oscillators. It is assumed that MOA is unreactive with Br<sub>2</sub> and is oxidized by HOBr in the same way as is OA.

### Selection of Rate Constant Values

The final model consists of 80 elementary reactions and their rate constants. The source of each rate constant is given in Table I, but in some cases the actual basis for the value chosen is not obvious.

The Field and Försterling<sup>22</sup> values of the rate constants of the inorganic part of the FKN mechanism are for 1 M H<sub>2</sub>SO<sub>4</sub> and assume the activity of H<sup>+</sup> to be 1.0 M as calculated using the value of the second dissociation constant of H<sub>2</sub>SO<sub>4</sub>,  $K_2 = 0.012 \text{ M}^{-1}$ . However, calculations<sup>37</sup> based on measurements of the total concentration of sulfur-containing species yield  $[\text{H}^+]_{\text{total}} = [\text{H}_2\text{SO}_4^*] + [\text{H}_3\text{O}^+] + [\text{H}_2\text{O}_2^*] + [\text{H}_7\text{O}_3^*] + [\text{H}_9\text{O}_4^*] \approx 1.29 \text{ M}$  in 1 M H<sub>2</sub>SO<sub>4</sub>. It is not clear which value should be used when evaluating kinetic data in concentrated sulfuric acid solutions. Only experimental data on the [H<sub>2</sub>SO<sub>4</sub>] dependence of rate constants can solve the problem in such a complicated system. In the absence of such experiments, the Raman based<sup>37</sup> value  $[\text{H}^+] = 1.29 \text{ M}$  is assumed in 1 M H<sub>2</sub>SO<sub>4</sub> and the Field-Försterling rate constants were reevaluated on this basis.  $[\text{H}^+] = 1.29 \text{ M}$  was then used in the simulations reported here. This procedure resulted in an increase in  $\Delta_r G^\circ(\text{HBrO}_2)$  from  $\approx -0.4$  to  $-0.14 \text{ kJ/mol}$ . Table I contains these revised values, except for reaction 3, where the modified rate constant  $k_3 \approx 4.4 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$  is somewhat too high compared to measurements.<sup>20a,21b</sup> We choose to use  $k_3 = 2.0 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ .

Some other rate constants were also measured in 1 M H<sub>2</sub>SO<sub>4</sub> and include [H<sup>+</sup>]. In Table I  $k_1$ ,  $k_{45}$ , and  $k_{74}$  were obtained by dividing the value reported for 1 M H<sub>2</sub>SO<sub>4</sub> by 1.29 M.

The rate constant of the enolization of malonic acid was measured by Leopold and Haim<sup>38</sup> in a NaClO<sub>4</sub>/HClO<sub>4</sub> medium. The enolization equilibrium constant ( $k_{15}/k_{16}$ ) is not known (ref 38 suggests it to be  $<10^{-4}$ ). The value  $1.5 \times 10^{-5}$  is suggested by the data of Edelson et al.<sup>25</sup> and was used here. After finishing the work, we became aware that Hansen and Ruoff<sup>41</sup> found  $k_{15} = 0.0011$  in 1 M D<sub>2</sub>SO<sub>4</sub>. This value is very close to that used here, and with the uncertainty in the enolization equilibrium constant, it did not seem useful to redo the simulations.

Pachtl<sup>39</sup> used low values of [Br<sub>2</sub>]<sub>0</sub> (where reactions 15 and 16 are at equilibrium) to obtain the rate of bromination of MA. He assumed attack of Br<sub>2</sub> on MA itself, but we assume that it is the enol which is brominated and calculate  $k_{17}$  by dividing Pachtl's rate constant by  $k_{15}/k_{16}$ .

The experimental results of Field and Boyd<sup>30</sup> on the BrO<sub>3</sub><sup>-</sup> + OA and the BrO<sub>3</sub><sup>-</sup> + Ce(III) + OA reactions allow a subset of the mechanism to be tested and the adjustment of some parameters. The values of  $k_{30}$ ,  $k_{31}$ ,  $k_{32}$ , and  $k_{53}$  were obtained in this way. The rate constants of the uninvestigated but analogous reactions involving MOA were made equal to the appropriate rate constant values with OA.

Diffusion control rate constants of about  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  were assumed for reactions between two radicals. Some differentiation was introduced on the basis of the stability of the radicals involved; e.g.,  $k_{40}$  is less than  $k_{43}$  as BrMA\* is more stable than MA\*. Field and Boyd<sup>30</sup> found in the OA-acetone BZ reaction that reaction 55 between BrO<sub>2</sub>\* and \*COOH was not necessary to reproduce their experimental data. However, we have assigned the value  $k_{55} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  to that reaction to make its rate comparable to that between BrO<sub>2</sub>\* and MA\*.

There are no data available for H abstraction processes involving MA\* such as the three equilibria represented by reactions 59–64. The rate constants for these reactions were chosen to be a self-consistent set on the basis of the stabilities of the radicals involved. We assume that the equilibrium constant for  $\text{MA}^* + \text{TTA} \rightleftharpoons \text{MA} + \text{TTA}^*$  is about 1. Although TTA has a more easily abstracted acidic  $\alpha$ -hydrogen than does MA, the resulting TTA\* is more reactive than MA\* because of the electron-withdrawing -OH group.<sup>31</sup> Similar reasoning on the basis of the rules discussed above suggests that the equilibrium constants for the reactions  $\text{MA}^* + \text{BrMA} \rightleftharpoons \text{BrMA}^* + \text{MA}$  and  $\text{TTA}^* + \text{BrMA} \rightleftharpoons \text{TTA} + \text{BrMA}^*$  should be greater than 1. The forward rate constants were adjusted on the basis of H atom abstraction rate constants available in the literature. Hydroxyl radical abstracts hydrogen<sup>42</sup> from MA at a specific rate of  $\approx 2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and the rate constant of the reaction between MA\* and ascorbate ion in neutral solution<sup>31</sup> is  $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . We assume these values supply an upper limit on the values of  $k_{59}$  and  $k_{60}$ . The specific rate of H abstraction by CH<sub>3</sub>\* from lactic acid<sup>43</sup> ( $k = 1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) supplies a lower limit. We choose the values  $k_{59} = k_{60} = 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , which allows estimates to be made of  $k_{61}$ ,  $k_{62}$ ,  $k_{63}$ , and  $k_{64}$ . Significant (e.g., 10-fold) increases in the forward rates of these reactions diminish the contribution of MA\* control by diverting MA\* from reaction with BrO<sub>2</sub>\*.

The reasons for inclusion of reaction 71 as a major sink for \*COOH were discussed earlier. The value  $k_{71} = 10^7 \text{ M}^{-1} \text{ s}^{-1}$  was chosen to reproduce observed induction period lengths. The only analogous value we know of is  $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for the liberation<sup>44</sup> of I<sup>-</sup> from 3-iodotyrosine by \*COOH at pH = 3.

Reactions 75–77 are H atom abstraction reactions by Br\* for which little kinetic data are available. The value of  $k_{75}$  was set equal to  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{76}$  and  $k_{77}$  were assigned relative to this value considering the acidity of the hydrogen abstracted and the stability of the resulting organic radical.

### Simulation Results

Dissolved O<sub>2</sub> may have<sup>15,45,46</sup> a dramatic effect on the behavior of the BZ reaction. As our model does not include reactions involving O<sub>2</sub>, we test it mainly by application to experiments in which O<sub>2</sub> is excluded.

The model is tested first on the BrO<sub>3</sub><sup>-</sup> + OA and the BrO<sub>3</sub><sup>-</sup> + Ce(III) + OA reactions investigated by Field and Boyd.<sup>30</sup> Parts A and B of Figure 3 show, respectively, the experimental and simulated absorbance curves for the BrO<sub>3</sub><sup>-</sup> + OA reaction, and parts A and B of Figure 4 show, respectively, the experimental and simulated absorbances during the BrO<sub>3</sub><sup>-</sup> + Ce(III) + OA reaction. The length of the induction period in Figure 4 depends on the initial [Br<sup>-</sup>], which we did not adjust. The simulated

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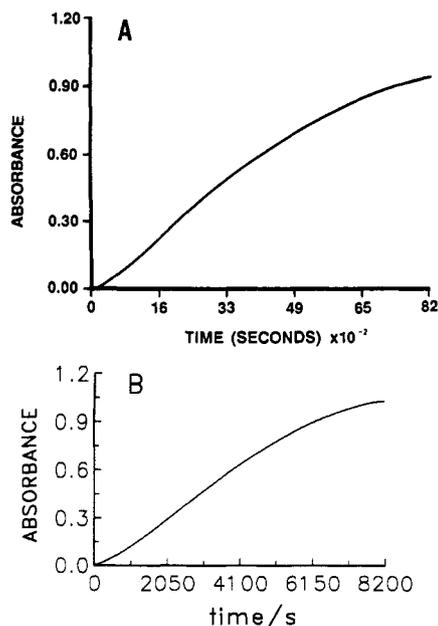
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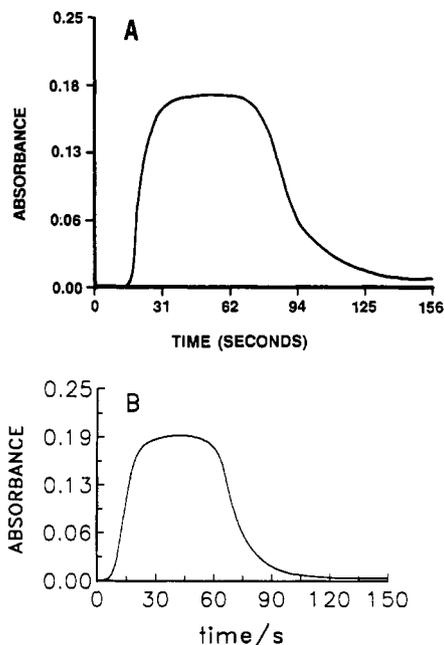
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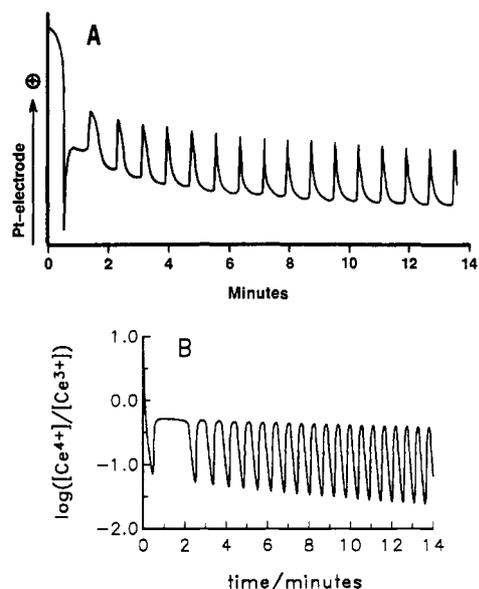
**Figure 3.** (A) Experimental absorbance vs time curve during the reaction between  $\text{BrO}_3^-$  and  $(\text{COOH})_2$  in 1 M  $\text{H}_2\text{SO}_4$  from ref 30. Initial concentrations:  $[\text{BrO}_3^-]_0 = 0.0133 \text{ M}$ ;  $[(\text{COOH})_2]_0 = 0.0702 \text{ M}$ . (B) Simulation of the same system assuming  $[\text{H}^+]_0 = 1.29 \text{ M}$ .



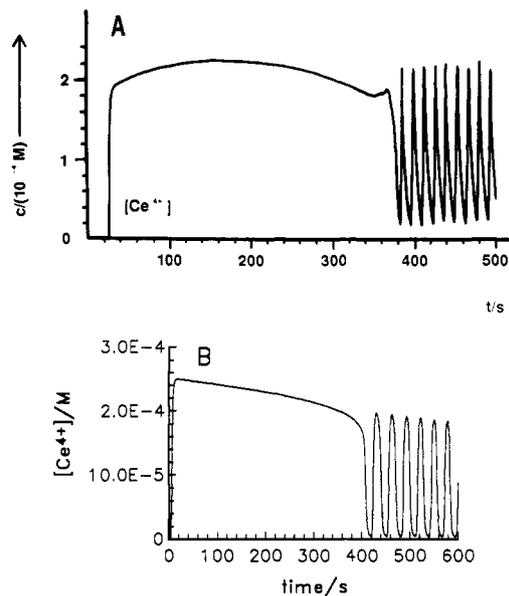
**Figure 4.** (A) Experimental absorbance vs time curve during the  $\text{Ce(III)}-\text{BrO}_3^--(\text{COOH})_2$  reaction in 1 M  $\text{H}_2\text{SO}_4$  from ref 30. Initial concentrations:  $[\text{Ce(III)}]_0 = 0.00024 \text{ M}$ ;  $[\text{BrO}_3^-]_0 = 0.016 \text{ M}$ ;  $[(\text{COOH})_2]_0 = 0.009 \text{ M}$ . (B) Simulation of the same system assuming  $[\text{H}^+]_0 = 1.29 \text{ M}$ .

absorbance curves were calculated by using the entire mechanism in Table I and absorption coefficients due to Field and Boyd.<sup>30</sup> Very good agreement between experiment and simulation was obtained by adjustment of a few rate constants as indicated in Table I.

Ruoff and Noyes<sup>46</sup> found that dissolved  $\text{O}_2$  has a dramatic effect on BZ systems when  $\approx 6 \times 10^{-2} \text{ M}$   $\text{HOBr}$  initially is added to the reaction mixture. Figure 5A shows such an experiment in which the reaction mixture is purged with Ar. The oscillations persist for 16 h, much longer than in the presence of  $\text{O}_2$ . The induction period is almost eliminated by the added  $\text{HOBr}$ , suggesting that  $\text{HOBr}$  rapidly brominates MA. The simulation in Figure 5B reproduces the lack of an induction period as well as the period of  $\approx 50\text{--}60 \text{ s}$ . The shape of the simulated oscillations does not



**Figure 5.** (A) Experimental Pt-electrode potential trace measured in an  $\text{O}_2$ -free BZ system in 1 M  $\text{H}_2\text{SO}_4$  (ref 46). Initial concentrations:  $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$ ;  $[\text{CH}_2(\text{COOH})_2]_0 = 0.28 \text{ M}$ ;  $[\text{Ce(IV)}]_0 = 0.0005 \text{ M}$ ;  $[\text{HOBr}]_0 = 0.06 \text{ M}$ . (B) Simulation of the same system assuming  $[\text{H}^+]_0 = 1.29 \text{ M}$ .

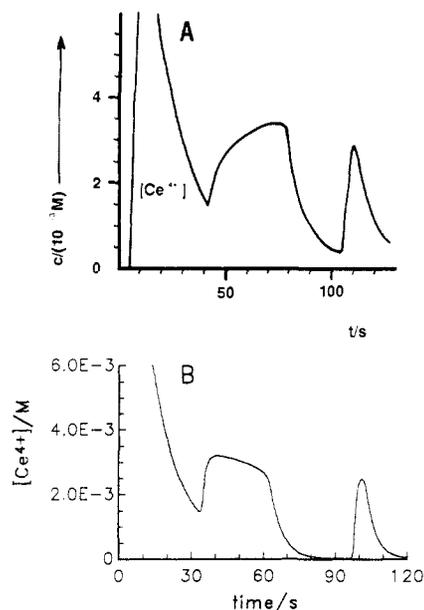


**Figure 6.** (A) Experimental  $[\text{Ce(IV)}]$  vs time curve measured in an  $\text{O}_2$ -free BZ system in 1 M  $\text{H}_2\text{SO}_4$  (ref 47). Initial concentrations:  $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$ ;  $[\text{CH}_2(\text{COOH})_2]_0 = 0.6 \text{ M}$ ;  $[\text{Ce(III)}]_0 = 0.001 \text{ M}$ ;  $[(\text{COOH})_2]_0 = 10^{-6} \text{ M}$ . (B) Simulation of the same system assuming  $[\text{H}^+]_0 = 1.29 \text{ M}$ .

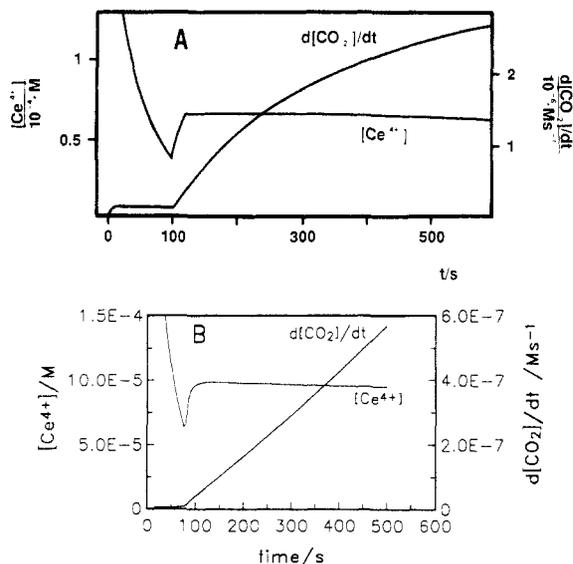
agree as well, with the oscillator spending too long in the oxidized state. The simulated oscillations persist for 4.25 h, which is less than found experimentally but quite satisfactory as the model regards  $\text{Br}_2\text{MA}$  as an inert product and thus does not reproduce the latter stages of the reaction accurately.

The BZ experiments due to Försterling and co-workers are ideal for testing our model as they are carried out with  $\text{N}_2$  or  $\text{H}_2$  purging. Parts A and B of Figure 6 show, respectively, experimental (Murányi and Försterling<sup>47</sup>) and simulated  $[\text{Ce(IV)}]$  traces. The lengths of the induction periods agree well, but the simulated oscillatory period is about twice as long as the experimental. This discrepancy may be attributable<sup>30</sup> to a difference in kinetic behavior resulting from coordination state between freshly oxidized  $\text{Ce(IV)}$  and  $\text{Ce(IV)}$  in equilibrium with a 1 M  $\text{H}_2\text{SO}_4$  medium,

(47) Murányi, Sz.; Försterling, H.-D. *Z. Naturforsch.* **1990**, *45a*, 135.

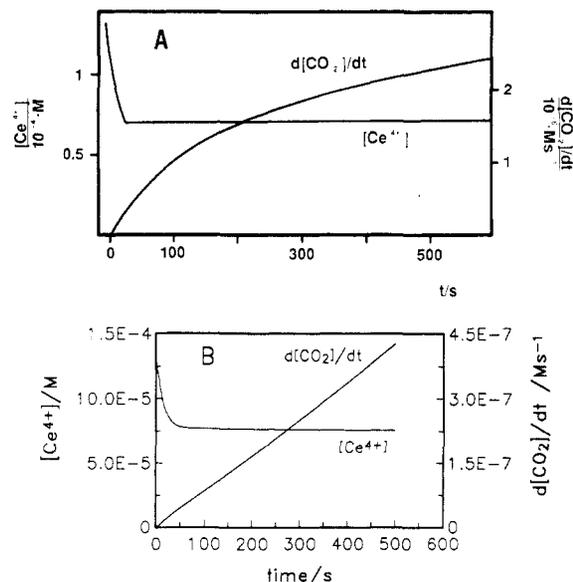


**Figure 7.** (A) Experimental [Ce(IV)] vs time curve measured in an  $O_2$ -free BZ system in 1 M  $H_2SO_4$  (ref 17). Initial concentrations:  $[BrO_3^-]_0 = 0.1$  M;  $[CH_2(COOH)_2]_0 = 0.4$  M;  $[Ce(IV)]_0 = 0.02$  M. (B) Simulation of the same system assuming  $[H^+]_0 = 1.29$  M.

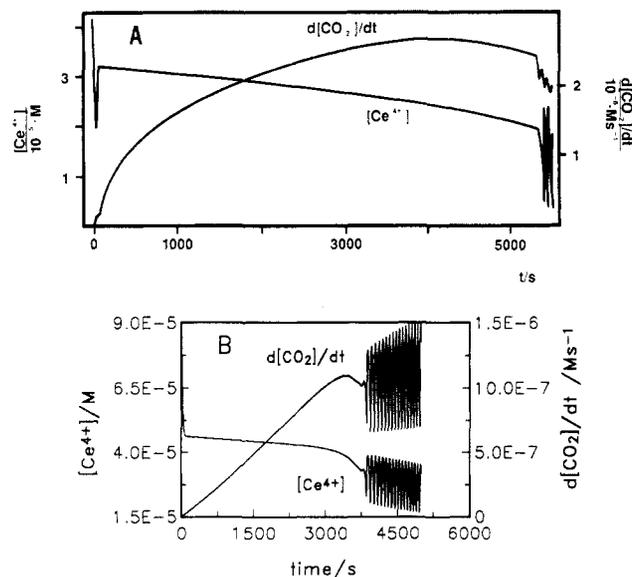


**Figure 8.** (A) Experimental [Ce(IV)] and  $d[CO_2]/dt$  vs time curves measured in an  $O_2$ -free BZ system with high  $[MA]_0/[BrO_3^-]_0$  in 1 M  $H_2SO_4$  (refs 39 and 48). Initial concentrations:  $[BrO_3^-]_0 = 0.03$  M;  $[CH_2(COOH)_2]_0 = 0.1$  M;  $[Ce(IV)]_0 = 0.000345$  M. (B) Simulation of the same system assuming  $[H^+]_0 = 1.29$  M.

as we discuss below. In simulations of this and other BZ experiments where the catalyst initially is in its reduced (Ce(III)) form, one has to assume some impurity in the system so that the reaction can start. We assumed contamination by a small amount ( $10^{-6}$  M) of oxalic acid. Another approach could have been the assumption<sup>15</sup> of a small amount of bromine dioxide in equilibrium with the acidic bromate. We did not attempt to simulate in detail the  $Cl^-$ -perturbation experiments reported in the same<sup>47</sup> paper as we consider the reaction between  $Cl^-$  and  $HBrO_2$  to be only a partial description of the chemistry involved. However, a few simulations using slightly higher  $[Cl^-]_0$  gave results similar to the Radicalator<sup>17,47</sup> for the initial part of the reaction and considerably better results later in the reaction where the Radicalator is unable to reproduce the oscillations. Figure 7 shows a good fit of another Försterling experiment,<sup>17</sup> in which  $[Ce(IV)]_0$  is very high and generates a high  $[MA^*]$  in the initial stages of the reaction. The discrepancy in the simulated shape of the first, wide, oxidized peak may again result from the coordination state of the Ce(IV). As



**Figure 9.** (A) Experimental [Ce(IV)] and  $d[CO_2]/dt$  vs time curves measured in an  $O_2$ -free BZ system with low  $[MA]_0/[BrO_3^-]_0$  in 1 M  $H_2SO_4$  (refs 39 and 48). Initial concentrations:  $[BrO_3^-]_0 = 0.3$  M;  $[CH_2(COOH)_2]_0 = 0.1$  M;  $[Ce(IV)]_0 = 0.000132$  M. (B) Simulation of the same system assuming  $[H^+]_0 = 1.29$  M.



**Figure 10.** (A) Experimental [Ce(IV)] and  $d[CO_2]/dt$  vs time curves measured in an  $O_2$ -free BZ system in 1 M  $H_2SO_4$  (refs 39 and 48). Initial concentrations:  $[BrO_3^-]_0 = 0.1$  M;  $[CH_2(COOH)_2]_0 = 0.1$  M;  $[Ce(IV)]_0 = 0.0001$  M. (B) Simulation of the same system assuming  $[H^+]_0 = 1.29$  M.

opposed to the Radicalator,<sup>17</sup> both the initial stages and the oscillations themselves are adequately reproduced.

The model also may be tested by its ability to reproduce the measured rate of  $CO_2$  evolution. Försterling et al.<sup>39,48</sup> measured simultaneously [Ce(IV)] spectrophotometrically and  $d[CO_2]/dt$  by  $H_2$  purging followed by reduction of  $CO_2$  to methane, which was quantitatively monitored by a flame-ionization method. Figure 8A shows these quantities at very high  $[MA]_0/[BrO_3^-]_0$ , where the inhibitory effect of  $MA^*$  on the  $HBrO_2$  autocatalysis is expected to be important. The initial 100 s of the experiment is characterized by a low, steady  $CO_2$  formation rate which greatly increases later in the reaction. The simulations exhibited in Figure 8B show similar trends. The early minimum in [Ce(IV)] is reproduced, although the time scale and the concentrations deviate

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somewhat from the experimental. The sharp increase in  $d[\text{CO}_2]/dt$  as radical inhibition becomes less important at  $\approx 80$  s is reproduced qualitatively, although the measured rates are about 4 times larger than calculated. Figure 9 shows the analogous results when  $[\text{MA}]_0/[\text{BrO}_3^-]_0$  is small. Agreement between the experimental and simulated behavior of  $[\text{Ce(IV)}]$  is considerably better than in Figure 8.

Both  $[\text{Ce(IV)}]$  and  $d[\text{CO}_2]/dt$  also were measured by Försterling et al.<sup>39,48</sup> in another experiment. Parts A and B of Figure 10 show, respectively, experimental and simulated traces, which are characterized by an apparent radical inhibition in the very early stages of the reaction and a very long ( $\approx 5200$  s) induction period followed by normal oscillations. The model reproduces the long ( $\approx 3500$  s) induction period, the maximum in  $d[\text{CO}_2]/dt$ , and the regular BZ oscillations, but it fails to simulate the initial radical inhibition. Accumulation of BrMA (not shown) also was measured during the induction period, and its rate of formation is quantitatively reproduced in the simulations.

## Discussion

These results allow elucidation of some details of the BZ reaction. It is indicated that inhibition of the  $\text{HBrO}_2$  autocatalysis by organic radicals produced by Ce(IV) occurs and is especially important at high  $[\text{MA}]_0/[\text{BrO}_3^-]_0$  and in the initial stages of the reaction before significant amounts of brominated organic materials accumulate. However,  $\text{Br}^-$  control seems more important at later stages of the reaction when  $[\text{BrMA}]$  is high.

Alternative control intermediates were suggested originally to explain the effect of addition<sup>7</sup> of  $\text{Ag}^+$  to the BZ reaction. Several simulations were carried out with a continuous input of  $\text{Ag}^+$  and assuming that  $\text{Ag}^+$  removes  $\text{Br}^-$  at a nearly diffusion-controlled rate.<sup>8</sup> Low input rates of  $\text{Ag}^+$  shortened the oscillatory period, but higher input rates suppressed oscillations in both  $[\text{Br}^-]$  and  $[\text{Ce(IV)}]/[\text{Ce(III)}]$ . No radical-controlled oscillations were seen.

Field and Boyd<sup>30</sup> suggested that freshly oxidized Ce(IV) in the  $\text{BrO}_3^-$ -OA-Ce(IV)/Ce(III)-acetone system may not have the equilibrium  $\text{HSO}_4^-$  coordination states expected in 1 M  $\text{H}_2\text{SO}_4$  and may oxidize OA much faster than the equilibrated species does. Difficulties encountered by us suggest that similar situation arises in the classic BZ system. It was not possible using measured<sup>39,48</sup> rate constants for the oxidation of organic compounds by Ce(IV) equilibrated with 1 M  $\text{H}_2\text{SO}_4$  to simulate adequately phenomena occurring both at the beginning and at later stages of the reaction. All discrepancies encountered involve overdominance of oxidized states and could be decreased by assuming a larger rate constant for the oxidation of organic matter by freshly oxidized Ce(IV). It is not clear how important this detail is for the complete understanding of the BZ reaction itself. However, experimental studies of the BZ reaction often focus on fine details such as bifurcation sequences,<sup>49,50</sup> deterministic chaos,<sup>49,50</sup> and effects of stirring noise,<sup>51</sup> and it is possible that complex formation between Ce(IV) and  $\text{HSO}_4^-$  ion may play a role here.

Its sensitivity to assumed rate constant values helps to characterize the chemical features of the mechanism. However, the number of reactions and variables in this model does not allow a detailed analysis to be easily carried out. Techniques<sup>52</sup> exist for the analysis and simplification of complex mechanisms via investigation of the instantaneous derivatives of the reaction rates with respect to the rate constants. Such an analysis of this model will be the subject of a subsequent paper.<sup>53</sup> However, some observations can be made now.

The length of the induction period of Figure 6B increases as  $k_{17}$  increases. A smaller value of this parameter generally gives better agreement with the experiment. The enolization constant

of MA is incorporated in  $k_{17}$ , and there are no experimental data available for it. An estimate of its upper limit has been given<sup>38</sup> that is about 6 times higher than the value<sup>25</sup> used here. As  $k_{17}$  is calculated by dividing an experimental specific rate by this equilibrium constant, a value for  $k_{15}/k_{16}$  closer to the estimated maximum  $10^{-4}$  would improve the agreement between experiment and simulation.

The ratio  $k_{22}/k_{21}$  and the value of  $k_{71}$  are critical to the behavior of the model, these reactions being associated with the delayed, negative feedback loop. In agreement with Försterling et al.<sup>17</sup> in 1 M  $\text{H}_2\text{SO}_4$ ,  $k_{22}/k_{21} \approx 1$  is needed to simulate the experiments in Figures 7A, 8A, and 9A. An increase in this ratio also shortens the induction period in Figure 6B. Reaction 71 is a  $\text{Br}^-$ -regeneration step, and higher values of  $k_{71}$  shorten the computed induction period, but it does not have a major effect on the initial stages of the reaction when there is little BrMA. This suggests that reaction 71 is an important  $\text{Br}^-$ -producing process and that an experimental study of it is desirable. If this reaction is not included in  $^*\text{COOH}$  and  $\text{BrO}_2^*$  (reaction 55) becomes as important a  $\text{HBrO}_2$ -producing step as reaction 13.

The rate of oxidation of BrMA by  $\text{MA}^*$  also has a major effect in situations where  $\text{MA}^*$  inhibition of the  $\text{HBrO}_2$  autocatalysis is important. Values of  $k_{61}$  higher than  $\approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$  make the oxidized plateau in Figure 7B disappear and  $\text{Br}^-$ -controlled oscillations begin immediately after the first Ce(IV) consumption period. We suggest that  $k_{61}$  must be in the range  $10^5$ – $10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Comparison of resonance structures suggests that  $\text{BrMA}^*$  is the most stable radical in the system, and we have assumed it to be the dominant radical species. However, experimental tests of this assumption are needed.

It is clear that BrMA has a special role in the BZ system. In the light of the possible inhibition of the  $\text{HBrO}_2$  autocatalysis by organic radicals, the  $\text{BrMA}^*$  formed by the oxidation of BrMA may become a major inhibiting (i.e., controlling) species. By the cascade of reactions 39–24–3 every  $\text{BrMA}^*$  removes one  $\text{BrO}_2^*$ , which is a more effective inhibition than that of reactions 46–21–22. Furthermore,  $\text{BrMA}^*$  could react with  $\text{BrO}_2^*$  as  $\text{MA}^*$  does in reaction 46, resulting in  $\text{HOBr}$ ,  $\text{CO}_2$ , and  $\text{BrCOCOOH}$ . This latter compound is unstable and would react with water producing  $\text{Br}^-$  and OA. This way both a  $\text{BrO}_2^*$  is removed and another inhibitor,  $\text{Br}^-$ , is produced. Preliminary results of the simulation of a system where initially both MA and BrMA are present indicate that in certain cases this assumption would improve the performance of the mechanism significantly.

## Conclusion

The model derived here reproduces semiquantitatively several experiments performed with the oscillatory Belousov–Zhabotinskii reaction and with its subsets in 1 M  $\text{H}_2\text{SO}_4$ . It incorporates the most recent mechanistic suggestions as well as previous revisions of the original FKN mechanism. Inhibition of the autocatalytic bromate–bromous acid reaction by radicals produced by Ce(IV) oxidation of MA and its derivatives seems to be needed to explain several phenomena occurring during the early stages of the reaction. However, BZ oscillations in 1 M sulfuric acid medium still seem to be primarily bromide ion controlled. Furthermore, the introduction of radical inhibition does not support the claim of radical control of the oscillations in the presence of  $\text{Ag}^+$ .

Several suggestions are made about the mechanistic details of the organic subset of this complicated system that may help in designing experiments to clarify further details of the organic chemistry involved.

When a chemical mechanism of this size with many unknown parameters is assembled, it is always dubious if the conclusions drawn are actually relevant to the real system studied. However, we suggest that the model presented here, though not complete, does represent a significant step forward in understanding the chemistry of the Belousov–Zhabotinskii reaction.

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### Computations

A VAX 8600 computer was used for all numerical integrations. Simulations were carried out with the use of the program SIMULATE, which was developed by one of us<sup>54</sup> based on the numerical integrator ROW4S.<sup>55,56</sup> Usually a relative error tolerance of  $10^{-3}$

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was used; spot checks with relative error tolerance of  $10^{-4}$  gave identical results.

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## Period Lengthening near the End of Oscillations in Chemical Systems

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In many oscillating systems, the period of oscillations rises sharply with the change of the control parameter just before the oscillations end, and the system collapses to a stable steady state. This increase in period is usually interpreted as an approach to a homoclinic orbit, in which the period will be in fact infinite. In this paper a few oscillating chemical models are examined near the "end of oscillations". It is found that, although some models do show the period lengthening appropriate for an approach to a homoclinic orbit, others show a much sharper increase, indicating that other period lengthening mechanisms may be operating. The period lengthening may, in some cases, be very dramatic, and periods of up to  $\sim 10^5$  s have been calculated. The experimental and computational implications of such long periods are discussed.

### Introduction

As a parameter or constraint of the system changes, the properties such as amplitude and period of limit cycle oscillations will, in general, change too. At some critical parameter, the oscillations will stop and the system will fall into a stable steady state. Just before this bifurcation it sometimes happens that the period rises sharply as seen for example in Figure 1. In this figure the period of the limit cycle of the Oregonator model,<sup>1</sup> with flow,<sup>2,3</sup> is plotted vs the stoichiometric factor  $f$  as a control parameter. Similar results were obtained by Gaspar et al.,<sup>3</sup> by Rovinski,<sup>4</sup> and by Bar-Eli.<sup>5</sup> Different models were used, and all gave similar increase in period as the parameter approaches its critical value, beyond which there are no more oscillations, and the system will be at a steady state.

On the experimental side, Gaspar and Galambosi<sup>3c</sup> obtained period lengthening in BZ reaction with oxalic acid. Maselko<sup>6</sup> has examined  $Mn^{2+}$ -catalyzed BZ reaction and obtained a sharp rise in period before the end of oscillations. Likewise, Crowley and Epstein<sup>7</sup> examined coupled CSTR's containing BZ oscillators and obtained similar period lengthening both in their experiments and in their calculations. Such an increase in period is usually interpreted by the approach of the limit cycle to a homoclinic orbit possessing an infinite period.<sup>8</sup>

In order to test this assumption, we have examined the rate of increase of the period in a few well-known models of chemical oscillators. In some cases the rate of increase does indeed fit the one expected for a homoclinic orbit (vide infra), but in others this rate is much greater, indicating that another mechanism may be operating.

### Theory

Physical oscillations, i.e., stable limit cycles, may end or start in a variety of ways, as shown schematically in Figure 2.

1. *Supercritical Hopf Bifurcation*<sup>9,10</sup> (Figure 2A, Point H1). This will result in small-amplitude oscillations with period close to  $2\pi/\omega$ , where  $\omega$  is the imaginary part of an eigenvalue whose real part is zero. As can be seen from the figure, no hysteresis is expected in this case.

2. *Subcritical Hopf Bifurcation* (Figure 2A, Point H2). This point is a source of an unstable limit cycle which coalesces with the stable one, originating at H1, at the right of point H2. The period behavior near this point is not dictated by any theory; however, in two examples discussed below, an increase of period, as in Figure 1, is observed. A region of hysteresis between a stable limit cycle and a stable steady state should exist in this case; between point H2 and the arrow, indicating the end of oscillations (point E), the system can be either in the stable steady state or in the limit cycle. The terms loop-loop bifurcation or stable-unstable limit cycle bifurcation seem appropriate, since two limit cycles, one stable and the other unstable, destroy each other,

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