Influence of Oxygen and Organic Substrate on Oscillations and Autocatalysis in the Belousov−Zhabotinsky Reaction

Ludovit Treindl[†] **and Peter Ruoff***

School of Technology and Science, Stavanger College, 4004 Stavanger, Norway

Per Olav Kvernberg

Department of Chemistry, University of Oslo, 0315 Oslo, Norway

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The influence of oxygen in Belousov−Zhabotinsky systems with substituted malonic acid derivatives RMA (R = H, Me, Et, Bu, phenyl, and benzyl) has been studied. A significant influence of oxygen and organic substrate has also been found for the autocatalytic oxidation of the catalyst by bromate. In both the presence and the absence of RMA, oxygen always increases inflection times of the autocatalysis when compared with anaerobic conditions (argon bubbling). In general, period lengths P of RMA−BZ systems increase with increasing Taft σ^* constants of substitutent R and a linear log $P - \sigma^*$ relationship has been found. In aerobic conditions (oxygen bubbling) the MA−BZ system is an exception because malonic acid (MA) BZ period lengths are, at these conditions, significantly lower and deviate from the linear log $P - \sigma^*$ relationship. The deviation appears to be related to the increased release of bromide ion when MA−BZ systems come in contact with oxygen. Model computations indicate that the decrease in inflection time of the autocatalysis is related to the scavenging of BrO_2 radicals, probably by $RMA^\bullet$ and $RMAOO^\bullet$ radicals. The increase of period lengths in RMA−BZ systems with increasing σ^* values appears to be related to the bromination/enolization of the organic substrate as the determined enolization rates of RMA show.

Introduction

The classical[1] Belousov[2]−Zhabotinsky[3] (BZ) reaction is understood as the oscillatory oxidation of a one-electron redox couple (mostly used are Ce(III)/Ce(IV), Mn(II)/Mn(III), ferroin/ferriin, $Ru(bipy)_3^{2+}/Ru(bipy)_3^{3+}$) by bromate ions in acidic media and in the presence of an organic substrate that can be brominated and oxidized.[4,5] The cornerstone work by Field, Körös, and Noyes[4] with the introduction of the Oregonator model[6] showed that the thermodynamics and kinetics of this complicated reaction can be understood as a bromide-controlled on/off switch of the autocatalytic oxidation of the one-electron redox couple by bromate.[7] However, there are still aspects of the BZ reactions that are not completely understood, for example, the influence of oxygen.

Oxygen effects on the BZ reaction and some of its component processes have been described by several authors.[8−28] It has been observed that oxygen both shortens or lengthens induction periods or period lengths.[9,11] At high malonic acid concentrations oxygen is able to completely eliminate oscillations where the remaining reduced steady state shows excitability.[12] It has been very soon recognized that oxygen affects the regeneration of bromide ion, and for a long time it has been believed that oxygen does not influence oxybromine chemistry.[9,11] It has been assumed[12,13] that oxygen accelerates the release of bromide ions during the oxidation of mixtures of BrMA and MA by Ce(IV). This is in agreement with the observation that oxygen shortens the induction period and that the excitable steady state is formed in the Oregonator by an increased *f*-factor.[15,16] The accelerating influence of oxygen when malonic acid (MA) is oxidized by ceric ions has been studied in detail by Noyes and co-workers and has been first explained by the formation of organic peroxy radicals, which increase the rate of initial attack on MA.[14]

The influence of oxygen on the Mn-catalyzed MA−BZ reaction has been studied in detail by Tkac and Treindl.[17] Also in this case it has been found that bromide ions are released more rapidly in the reaction of the Mn(III) with a mixture of MA and BrMA when oxygen is present and that oxygen enhances the rate of Mn(III) consumption at low MA concentration but reduces it at high MA concentrations. A new reaction scheme has been proposed for the influence of oxygen on the oxidation of MA by Mn(III). Its essence is an acceleration of Mn(III) consumption with glyoxylic acid at low MA concentration and regeneration of Mn(III) by oxidation of Mn(II) with MAOOH at high MA concentration. An oxygen-induced excitability of the ethyl ester of 3-oxobutanoic acid−BZ system with the ferroin−ferriin redox catalyst[18] has been described. The oxygen effect has been explained as being due to two competitive reaction steps between peroxomalonic acid (MAOOH) and Mn(III) and Mn(II) ions, respectively.[19]

Oxygen has different effects on BZ systems when the organic substrate is malonic acid (MA) or when it is methylmalonic acid (MeMA). It has been observed that bubbling with oxygen in a MA−BZ system generates a nonoscillatory reduced and excitable steady state that does not change further. With an otherwise identical MeMA system, oxygen inhibits oscillations only temporarily and does so by generating an oxidized steady state.[16,20]

Recently, evidence from electron paramagnetic resonance (EPR) has been presented[21] that peroxymalonyl radicals ($MAOO^\bullet$) are actually formed in the aerobic oxidation of MA by ceric ions. An oxygen-induced enhancement of the primary radical concentration has been proved only very recently.[22] According to Neumann et al.,[22] the observed oxygen-induced increase in radical concentration cannot be explained in the framework of

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[†] Permanent address: Department of Physical Chemistry, Comenius University, 84215 Bratislava, Slovak Republic.

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standard auto-oxidation mechanisms, and therefore, an alternative reaction scheme has been suggested.

Recently, Jwo and co-workers[23−26] focused attention on BZ systems using malonic acid derivatives in combination with various catalysts. They also discussed the role of oxygen in these systems in view of previous explanations.[20] Sun et al.[24] recognized results by Drummond and Waters,[27] which introduced for the first time Mn(II) oxidation by peroxo radicals (MAOO$^\bullet$).

Very recently, Wang et al.[28] studied the oxygen effect in the BZ reaction and observed that the influence of the stirring rate under aerobic conditions is mainly an oxygen effect as considered earlier by Patonay and Noszticzius.[29] Calculations[28] based on a modified Oregonator show that the formation of organic radicals by the oxidized form of the catalyst and the release of bromide ion from organic bromo radicals appear in the MA system to be the most important when dealing with oxygen effects.

The main aim of this work is to study oxygen effects in classical RMA−BZ systems and in the autocatalytic oxidation of the catalyst (Ce(III)) by bromate ion. A better insight into the influence of oxygen effects may also be helpful in understanding some of the phenomena connected with spatial pattern formation, which appear to be often influenced by the presence of oxygen.

Materials and Methods

Sulfuric acid, $Ce(NO_3)_3$, $NaBrO_3$, KBr, malonic acid (MA) and its derivatives methylmalonic- (MeMA), ethylmalonic- (EtMA), butylmalonic- (BuMA), benzylmalonic- (BzMA), and phenylmalonic acid (PhMA) were of commercial analytical quality (Fluka, Aldrich).

Reactions were followed potentiometrically in a thermostated cell at 25.0 °C with a platinum electrode (Metrohm) and with a bromide-ion-selective electrode (Orion). The reference electrode was a Ag/AgCl double junction electrode (Metrohm) with a saturated KCl solution in the inner compartment and a 1 M sulfuric acid solution as the outer electrolyte. The stirring rate was kept constant at 600 rpm using a magnetic stirrer. Oxygen or argon gas was saturated with water (by passing the gas through distilled water in a washing bottle) and was then bubbled through the reacting solution at constant flow rate (1 L/min).

Period lengths were determined from the second oscillation after an induction period. The period of the first oscillation is usually not very reproducible.

RMA enolization rates were obtained by NMR at the University of Oslo with a technique by Hansen and Ruoff.[30]

The data shown in the tables are averages of four independent measurements with a standard deviation of 8%.

Simulation calculations were performed with a double precision version of LSODE.[31]

Experimental Results

BZ Oscillator. We have followed the course of the aerobic (oxygen bubbling) and anaerobic (argon bubbling) BZ reaction in the presence of MA, MeMA, EtMA, BuMA, BzMA, or PhMA. To compare induction periods and period lengths in all these cases, the same initial concentrations of reaction components were always used. Table 1 summarizes the various induction and oscillatory period lengths (second oscillation) for aerobic and anaerobic conditions. Figures 1 and 2 show how the different substrates affect induction periods and oscillations at aerobic conditions and anaerobic conditions. The nature of substituent R in RMA influences the oxygen effect dramatically. In the presence of PhMA (Figure 2) oxygen is necessary for the oscillations to occur, while for BuMA (Figure 1) a very strong inhibiting effect of oxygen can be observed. In the latter case oxygen increases the induction period and the duration of oscillations is essentially diminished.

TABLE 1: Period Length and Induction Period Length for RMA in Atmosphere of Argon or Oxygen[a]

	period of second oscillation, min		
substrate	bubbling oxygen	bubbling argon	σ^* constant
malonic acid	0.5	0.7	+0.49
MeMA	4.9	6.4	0.00
EtMA	9.3	10.0	−0.10
BuMA	7.7	12.05	−0.13
PhMA	1.2		+0.60

	induction period, min	
substrate	bubbling oxygen	bubbling argon
MA	4.8	4.4
MeMA	143	102
EtMA	312	136
BuMA	242	119
PhMA	32	

[a] 1 M H_2SO_4, 2×10^{-3} M $Ce(SO_4)_2$, 0.1 M $NaBrO_3$, 0.2 M substrate.

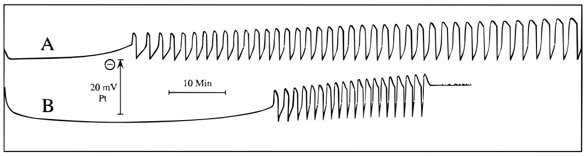

Figure 1. Time dependence of the Pt potential showing the effect of argon (A) and oxygen (B) in the BuMA−BZ oscillating systems. Initial concentrations are $[H_2SO_4] = 1.0$ M, $[Ce(SO_4)_2] = 2 \times 10^{-3}$ M, $[NaBrO_3] = 0.1$ M, and $[BuMA] = 0.2$ M.

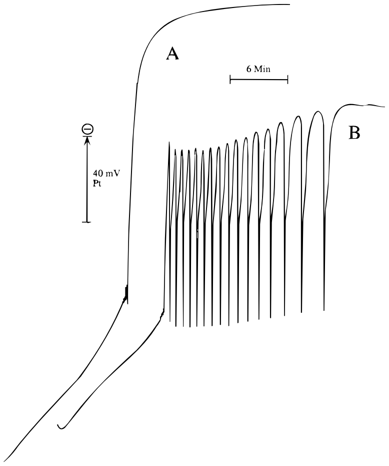

Figure 2. Same system as in Figure 1, but PhMA was used instead of BuMA: (A) argon bubbling; (B) oxygen bubbling.

To look for systematic trends, the influence of substitutent R on induction periods and period length of oscillations was studied in terms of the Taft equation.[32,33] In case of alkyl esters of 3-oxobutanoic acid (and derivatives) as BZ substrates a linear free energy relationship between the rate constant of the Ce(IV) oxidation of these substrates and σ^* was actually found (Figure 3).[34] We find a linear relationship between the logarithm of period length vs σ^*_R (Figure 4). However, MA, BzMA, and PhMA are exceptions. In the case of BzMA no oscillations are observed either in oxygen or in argon atmosphere, while for PhMA, oscillations occur only when oxygen bubbling is used. In case of MA, oxygen leads to much lower period lengths than expected from the alkyl-substituted derivatives. The reason for this is discussed below.

Catalyst Oxidation by Bromate Ion. To explore the influence of oxygen further, we decided to study the kinetics

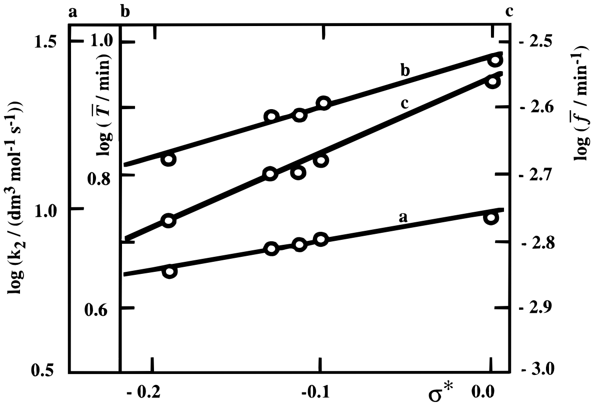

Figure 3. Linear relationship between the logarithm of rate constants of Ce(IV) oxidation of alkyl esters of 3-oxobutanoic acid and Taft constants σ^*. See ref 34 for details.

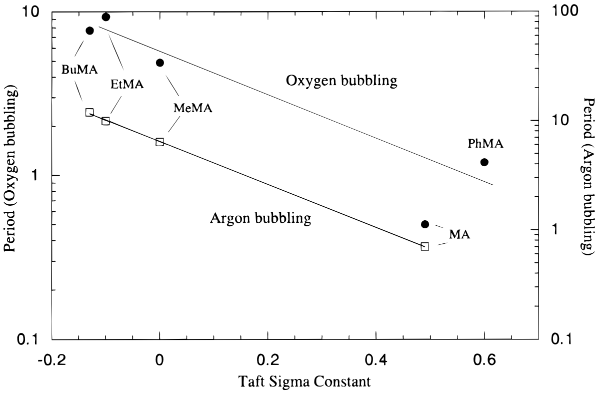

Figure 4. Period of the second oscillation for RMA−BZ systems in aerobic and anaerobic conditions. Initial concentrations are $[H_2SO_4] = 1.0$ M, $[Ce(SO_4)_2] = 2 \times 10^{-3}$ M, $[NaBrO_3] = 0.1$ M, and [RMA] = 0.2 M.

TABLE 2: Inflection Times for Ce(III) Oxidation by Bromate[a]

substrate	condition	inflection time, min
phenyl-MA	argon	12.0
	oxygen	12.8
malonic acid	argon	12.6
	oxygen	14.8
benzyl-MA	argon	15.8
	oxygen	19.8
methyl-MA	argon	15.5
	oxygen	27.6
ethyl-MA	argon	9.2
	oxygen	14.6
butyl-MA	argon	20.8
	oxygen	34.0
no substrate	argon	9.8
	oxygen	16.6

[a] 0.33 M H_2SO_4, 2×10^{-3} M $Ce(NO_3)_3$, 1×10^{-2} M $NaBrO_3$, 2×10^{-2} M substrate.

of the Ce(III) oxidation by bromate ions in the presence and absence of oxygen and organic substrate. Our results clearly show that there is an influence both from oxygen and from the type of organic substrate, if present. If we follow the kinetics of the Ce(III) oxidation by bromate ions in a solution of 0.33 M H_2SO_4 and 2×10^{-3} M Ce(III) and 10^{-2} M BrO_3^-, oxygen increases the inflection times (Table 2, Figure 5A).

Also, the nature of the substituent R in RMA has an influence on the kinetics of the Ce(III) oxidation by bromate (Figure 5B). Table 2 shows inflection times in the presence of RMA derivatives in atmospheres of oxygen or argon. Although inflection times increase if oxygen is used instead of argon, we also observe a prolongation of the oxidized steady state due to the presence of oxygen (Figure 6), indicating both “inhibiting” and “promoting” effects on the oxidized state.

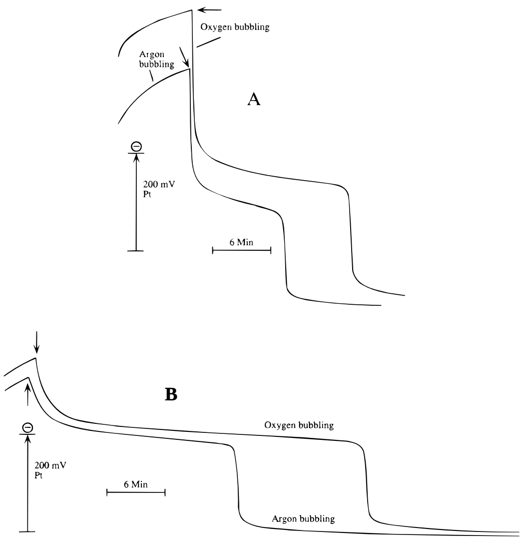

Figure 5. Kinetics of the Ce(III) ions oxidation by bromates in oxygen and in argon. Initial concentrations are $[H_2SO_4] = 0.33$ M and $[Ce(NO_3)_3] = 2 \times 10^{-3}$ M. Arrows indicate addition of 0.01 M $NaBrO_3$. Part A is for no organic substrate present. Part B is same system as in Part A but with 0.02 M BuMA present.

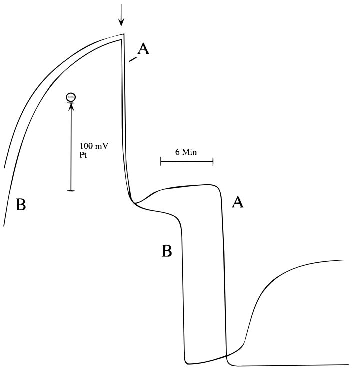

Figure 6. “Inhibiting”and “promoting” effects of oxygen at the beginning of the BZ reaction. Initial concentrations are $[H_2SO_4] = 0.33$ M, $[Ce(NO_3)_3] = 2 \times 10^{-3}$ M, and [MA] = 0.3 M. Arrow indicates addition of 0.01 M $NaBrO_3$. Part A is for bubbling oxygen, and part B is for bubbling argon.

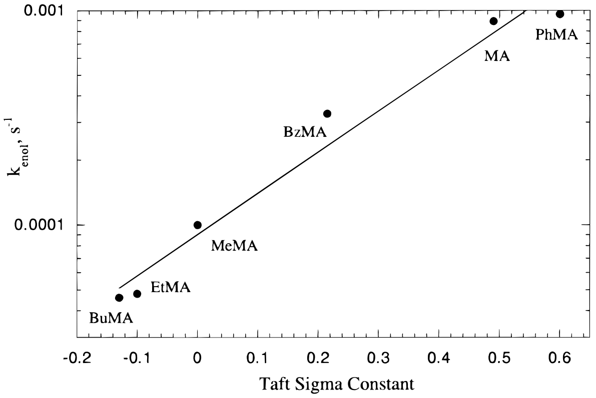

Figure 7. Estimated enolization rate constants of RMA by H/D isotope exchange[30] in 1 M D_2SO_4 as a function of Taft constants σ^* of alkyl groups R. The linear regression coefficient between log k_{enol} and σ^* is 0.961.

Enolization Rate Constants of Organic Substrate. Bromination of the organic substrate is an important process. It proceeds because of the attack of Br_2 on the enol form of the organic substrate. We have estimated the enolization rate constant in 1 M sulfuric acid by a NMR technique earlier[30] applied to MeMA (Figure 7). In fact, $\log(k_{\mathrm{enol}})$ values of RMA enolizations show also a linear dependence with Taft σ^* constants.

Model Calculations

Autocatalytic Oxidation of Catalyst by Bromate Ion. The chemistry of the autocatalytic oxidation of the catalyst by bromate is well understood notably because of the work by Noyes, Field, and Thompson (NFT).[35] To simulate the autocatalysis in the presence of oxygen and RMA derivatives, we consider the following reactions.

The inorganic part of the catalyst oxidation is

$$\mathrm{BrO_3^- + Br^- + 2H^+ \rightleftarrows HBrO_2 + HOBr} \tag{R1}$$

$$\mathrm{HBrO_2 + Br^- + H^+ \rightleftarrows 2HOBr} \tag{R2}$$

$$\mathrm{HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O} \tag{R3}$$

$$\mathrm{BrO_3^- + HBrO_2 + H^+ \rightleftarrows Br_2O_4 + H_2O} \tag{R4}$$

$$\mathrm{Br_2O_4 \rightleftarrows 2BrO_2} \tag{R5}$$

$$\mathrm{BrO_2 + M^{\mathit{n}+} + H^+ \rightleftarrows M^{(\mathit{n}+1)+} + HBrO_2} \tag{R6}$$

$$\mathrm{M^{(\mathit{n}+1)+} + BrO_2 + H_2O \rightleftarrows M^{\mathit{n}+} + 2H^+ + BrO_3^-} \tag{R7}$$

$$\mathrm{2HBrO_2 \rightleftarrows BrO_3^- + HOBr + H^+} \tag{R8}$$

$$\mathrm{Br_2(aq) \rightarrow Br_2(g)} \tag{R9}$$

$$\mathrm{BrO_2 \xrightarrow{O_2}} \tag{R10}$$

Reactions involving organic substrate are

$$\mathrm{M^{(\mathit{n}+1)+} + RMA \rightarrow M^{\mathit{n}+} + RMA^\bullet + H^+} \tag{R11}$$

$$\mathrm{RMA^\bullet + BrO_2 \rightarrow P_1} \tag{R12}$$

$$\mathrm{RMA^\bullet \xrightarrow{O_2} RMAOO^\bullet} \tag{R13}$$

$$\mathrm{RMAOO^\bullet + BrO_2 \rightarrow P_2} \tag{R14}$$

$$\mathrm{2RMA^\bullet + H_2O \rightarrow P_3} \tag{R15}$$

$$\mathrm{M^{(\mathit{n}+1)+} \rightarrow M^{\mathit{n}+}} \tag{R16}$$

$$\mathrm{RMAOO^\bullet + RMA \rightarrow RMA^\bullet + RMAOOH} \tag{R17}$$

$$\mathrm{M^{(\mathit{n}+1)+} + RMAOOH \rightarrow RMAOO^\bullet + M^{\mathit{n}+}} \tag{R18}$$

$$\mathrm{2RMAOO^\bullet \rightarrow P_4} \tag{R19}$$

$$\mathrm{RMAOOH \rightarrow P_5} \tag{R20}$$

Reactions involving brominated organic substrate are

$$\mathrm{Br_2 + R{-}MA \rightarrow R{-}(Br)MA + H^+ + Br^-} \tag{R21}$$

$$\mathrm{MA^\bullet + BrMA \rightarrow MA + BrMA^\bullet} \tag{R22*}$$

$$\mathrm{M^{(\mathit{n}+1)+} + BrMA \rightarrow M^{\mathit{n}+} + BrMA^\bullet} \tag{R23*}$$

$$\mathrm{RMAOO^\bullet + BrMA \rightarrow MAOOH + BrMA^\bullet} \tag{R24*}$$

$$\mathrm{BrMA^\bullet \rightarrow Br^-} \tag{R25*}$$

$$\mathrm{2BrMA^\bullet \rightarrow Br^- + BrMA} \tag{R26*}$$

$$\mathrm{R{-}(Br)MA \rightarrow P_6} \tag{R27}$$

$$\mathrm{BrMA^\bullet + RMA^\bullet \rightarrow Br^-} \tag{R28*}$$

The following rate constants have been used: $k_1 = 1.6$ M^{-3} s^{-1}, $k_{-1} = 3.2$ M^{-1} s^{-1}, $k_2 = 2.5 \times 10^6$ M^{-2} s^{-1}, $k_{-2} = 2.0 \times 10^{-5}$ M^{-1} s^{-1}, $k_3 = 8.0 \times 10^9$ M^{-2} s^{-1}, $k_{-3} = 80$ M^{-1} s^{-1}, $k_4 = 33$ M^{-2} s^{-1} , $k_{-4} = 2.2 \times 10^3$ M^{-1} s^{-1}, $k_5 = 7.5 \times 10^4$ s^{-1}, $k_{-5} = 1.4 \times 10^9$ M^{-1} s^{-1}, $k_6 = 6.2 \times 10^4$ M^{-2} s^{-1}, $k_{-6} = 8.4 \times 10^3$ M^{-1} s^{-1}, $k_7 = 0$ M^{-2} s^{-1}, $k_{-7} = 0$ M^{-3} s^{-1}, $k_8 = 3 \times 10^3$ M^{-1} s^{-1}, $k_{-8} = 1 \times 10^{-8}$ M^{-2} s^{-1}, $k_9 = 0$ s^{-1}, $k_{10} = 0$ s^{-1}, $k_{11} = 0.23$ M^{-1} s^{-1}, $k_{-11} = 2.2 \times 10^4$ M^{-2} s^{-1}, $k_{12} = 5.0 \times 10^9$ M^{-1} s^{-1}, $k_{14} = 5.0 \times 10^9$ M^{-1} s^{-1}, $k_{15} = 3.2 \times 10^9$ M^{-2} s^{-1}, $k_{16} = 0$ s^{-1}, $k_{17} = 0$ M^{-1} s^{-1}, $k_{18} = 0$ M^{-1} s^{-1}, $k_{19} = 0$ M^{-1} s^{-1}, $k_{20} = 0$ s^{-1}, $k_{22} = 100$ M^{-1} s^{-1}, $k_{23} = 30$ M^{-1} s^{-1}, $k_{24} = 5.0 \times 10^9$ M^{-1} s^{-1}, $k_{25} = 7$ s^{-1}, $k_{26} = 1.0 \times 10^8$ M^{-1} s^{-1}, $k_{27} = 4.0 \times 10^{-4}$ s^{-1}, $k_{28} = 1.0 \times 10^9$ M^{-1} s^{-1}. $[\mathrm{BrO_3^-}]_0 = 0.01$ M; $[\mathrm{Br^-}]_0 = 5 \times 10^{-6}$ M; $[\mathrm{M}^{n+}]_0 = 2 \times 10^{-3}$ M, $[\mathrm{H^+}] = 0.33$ M. Rate constants k_{13} and k_{21} have different values that are dependent on the presence/absence of oxygen and the bromination of the organic substrate (see text).

It should be noted that reactions indicated by an asterisk are expected to occur only with malonic acid and bromomalonic acid but not with R-substituted malonic acid derivatives because in processes R22−R24, we regard R$^\bullet$ radicals as unfavorable leaving groups. As a consequence, reactions R25, R26, and R28 are also unlikely to occur when R-substituted malonic acids are used as substrates.[20]

The reactions in addition to the Noyes−Field−Thompson mechanism[35] have been considered in a variety of studies including organic radicals[36−38] and associated oxygen effects.[21,22,28] We have studied the above model with respect to those reactions that have most influence on inflection times.

Presence of Organic Substrate. The inflection time is a complicated function of a variety of parameters. The most important in the model are (i) bromination of the organic substrate (R21), (ii) the creation of $\mathrm{BrO_2}$ scavengers as RMA$^\bullet$ and RMAOO$^\bullet$ radicals (R12, R14), and reactions that indirectly affect the concentration of RMA$^\bullet$ and RMAOO$^\bullet$.

Figure 8 shows calculated inflection times in the absence and presence of organic substrate and oxygen. It is seen that in the presence of RMA (and absence of oxygen), scavenging of $\mathrm{BrO_2}$ by RMA$^\bullet$ leads to an increase in inflection time. When oxygen is purged through the system, the formation of even more reactive RMAOO$^\bullet$ radicals decreases the $\mathrm{BrO_2}$ level further and the inflection time is further increased. Finally, an even larger increase in inflection time can be observed when the rate of bromination is increased.

When the level of MAOO$^\bullet$ is decreased by other reactions (for example, by reactions R17 or R24), the inflection time is expected to decrease. This is shown in Figure 9 when process R24 is “switched on” or “off” (alternatively, one could also have used reaction R17). The dashed line in Figure 9 shows

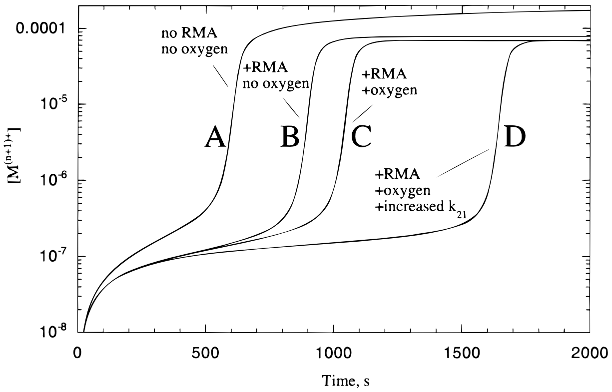

Figure 8. Computations of inflection times using reactions R1−R28: (A) $k_{13} = 0$ M^{-1} s^{-1}, $k_{21} = 0.05$ M^{-1} s^{-1}, [RMA]$_0 = 0$ M; (B) $k_{13} = 0$ M^{-1} s^{-1}, $k_{21} = 0.05$ M^{-1} s^{-1}, [RMA]$_0 = 2 \times 10^{-2}$ M; (C) $k_{13} = 3 \times 10^9$ M^{-1} s^{-1}, $k_{21} = 0.05$ M^{-1} s^{-1}, [RMA]$_0 = 2 \times 10^{-2}$ M; (D) $k_{13} = 3 \times 10^9$ M^{-1} s^{-1}, $k_{21} = 0.1$ M^{-1} s^{-1}, [RMA]$_0 = 2 \times 10^{-2}$ M.

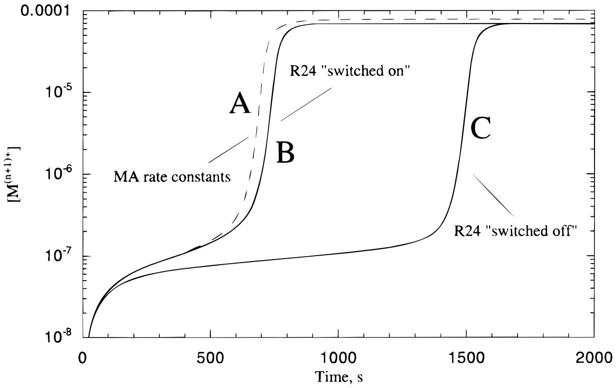

Figure 9. Reactions that influence ROO$^\bullet$ levels, for example, reaction R24, also influence inflection times. Curves B and C have same rate constants as Figure 8 (with $k_{13} = 3 \times 10^9$ M^{-1} s^{-1}, $k_{21} = 0.02$ M^{-1} s^{-1}, [RMA]$_0 = 2 \times 10^{-2}$ M) with the exception that $k_{22} = 0$ M^{-1} s^{-1} and k_{24} has either the value as in Figure 8 (case B) or $k_{24} = 0$ M^{-1} s^{-1} (case C). In curve A we have used values for the malonic acid system[21] $k_{17} = 300$ M^{-1} s^{-1}, $k_{18} = 2.5 \times 10^3$ M^{-1} s^{-1}, $k_{19} = 2.2 \times 10^8$ M^{-1} s^{-1}, $k_{20} = 0.07$ s^{-1}, $k_{22} = 100$ M^{-1} s^{-1}.

the results when rate constants for the malonic acid system is used. Despite the complexity of the model, comparison with experiments shows (Table 2) that computations are still semiquantitative.

Absence of Organic Substrate. Although this appears to be a simpler system than when organic substrate is present, we know little about the mechanism and the species that lead to an increase in inflection time (Figure 5A). BrO_2 is probably captured by oxygen or related species (reaction R10). As expected, calculations show that an increase of k_{10} increases the inflection time.

Small Amplitude Oscillations. In the study of inflection times we assumed that the decay of alkylmalonyl radicals RMA$^\bullet$ (process R15) occurs because of a first-order reaction. In this case the autocatalytic oxidation of M^{n+} shows strictly monotonic behavior (Figure 10A) as observed experimentally. On the other hand, when the rate law of R15 is assumed to be second-order in RMA$^\bullet$, as in radical disproportionation reactions, we observe small-amplitude oscillations (Figure 10B). It may be that these small amplitude oscillations are related to the occurrence of small initial spikes during the induction period in the oscillatory BZ reaction (Figure 1 in ref 36).

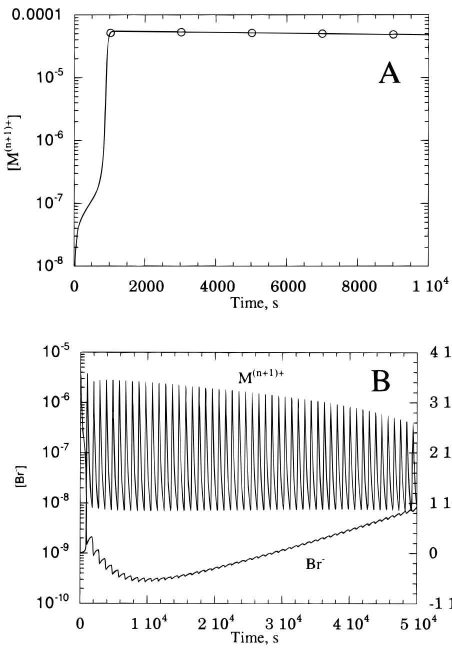

Figure 10. Calculations indicating the influence of reaction order in RMA$^\bullet$ in reaction R15. In part A a first-order decay of RMA$^\bullet$ is assumed. In part B a second-order RMA$^\bullet$ disproportionation is assumed. For simplicity the same numerical value of k_{15} has been assumed for both cases. The rate constants are the same as in Figure 8 (with $k_{13} = 0$ M^{-1} s^{-1}, $k_{21} = 0.02$ M^{-1} s^{-1}, [RMA]$_0 = 2 \times 10^{-2}$ M).

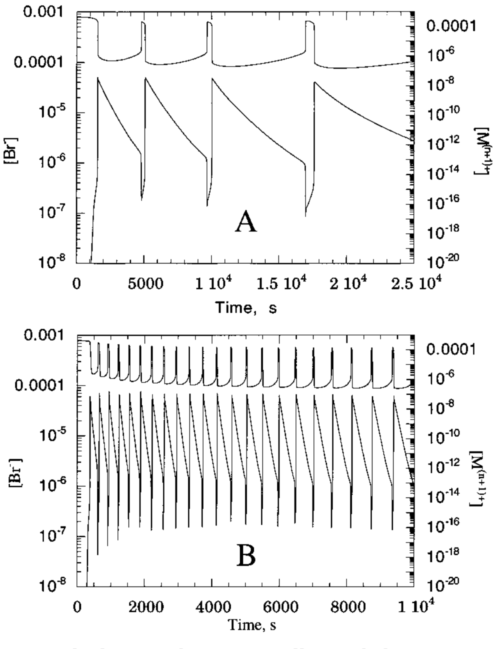

Figure 11. Calculations showing oscillatory behavior in anaerobic conditions ($k_{13} = 0$ M^{-1} s^{-1}) for the malonic acid system: (upper trace) [$M^{(n+1)+}$]; (lower trace) [Br^-]. Initial concentrations are [BrO_3^-]$_0 = 0.1$ M, [RMA]$_0 = 0.2$ M, [Br^-]$_0 = 5 \times 10^{-6}$ M, [M^{n+}]$_0 = 2 \times 10^{-3}$ M, and [H^+] = 1 M. Rate constants are otherwise the same as in Figure 9A. Parts A and B differ only in the bromination rate constant k_{21}: (A) $k_{21} = 0.02$ M^{-1} s^{-1}; (B) $k_{21} = 0.2$ M^{-1} s^{-1}.

BZ Oscillations. Oscillations are obtained by increasing initial reactant concentrations. However, so far the behavior of the model shows no good correlation with the MA−BZ behavior (Figure 11A). By use of the rate constants for the malonic acid system, practically no dependence of oxygen is observed! To increase the number of oscillations, the production of bromide ion has to be increased, for example by increasing k_{21} (Figure 11B).

Discussion

Inflection Times. From the calculations it is seen that BrO_2 and possible reactions with RMA$^\bullet$ and RMAOO$^\bullet$ have a major influence on the inflection time. According to the NFT mechanism,[35] a sufficient number of BrO_2 radicals must accumulate before the autocatalytic oxidation of the catalyst can start. Therefore, conditions that influence the lifetimes of $RMA^•$ and $RMAOO^•$ radicals will play a significant role on BrO_2 kinetics and inflection times. Figures 9 and 10 show this. Although a second-order decay in $RMA^•$ results in small-amplitude oscillations in the oxidized state, these oscillations disappear when the decay becomes first order in $RMA^•$. Since we do not observe such oscillations in our experiments, we wonder how important a second-order term in $RMA^•$ decay actually is. When the substrate concentration is increased (for example, in the study of oscillations), the small-amplitude oscillations also disappear. Perhaps second-order kinetics may sometimes be dominant, since we occasionally observe the appearance of small-amplitude oscillations in an oxidized state.[39,40]

Besides scavenging BrO_2, bromination of the organic substrate and release of the bromide ion also have great influence on inflection times (Figure 8). Because bromination occurs via enolization, the enolization rates (Figure 7) should correspond to reaction R21. However, the determined enolization rate constants do not correlate with experimental inflection times because large bromination rates show in the model increased inflection times, while experiments show the opposite behavior. It appears that organic radical−BrO_2 reactions are more important than bromination. Since the different organic substrates will show different reactivities, a systematic study of the model and of radical stabilities for the different substrate is necessary. This will be the subject of later studies.

Besides oxygen inhibition of inflection times (i.e., the increase of the inflection time and keeping the system in a reduced steady state), there is also a "promoting effect" by which we understand the prolongation of the oxidized steady state in the presence of oxygen (Figure 6). This prolongation can be explained by the idea of Drummond and Waters,[27] which for the first time have taken into consideration the oxidation of the catalyst (Mn(II)) by peroxy radicals. In the presence of oxygen and organic substrate the following reaction steps are assumed to occur:

$$\mathrm{RMA} + \mathrm{M}^{(n+1)+} \rightarrow \mathrm{M}^{n+} + \mathrm{RMA}^\bullet + \mathrm{H}^+ \qquad \text{(R28)}$$

$$\mathrm{RMA}^\bullet \xrightarrow{\mathrm{O}_2} \mathrm{RMAOO}^\bullet \qquad \text{(R13)}$$

$$\mathrm{RMAOO}^\bullet + \mathrm{M}^{n+} + \mathrm{H}^+ \rightleftarrows \mathrm{M}^{(n+1)+} + \mathrm{MAOOH} \qquad \text{(R29)}$$

Although reaction R29 is reversible, oxygen will support the oxidized steady state, which represents another way to produce $M^{(n+1)+}$ besides the main step R6. The importance of process R29 will depend on other reactions, for example, the recombination R19 of $RMAOO^•$ and the reactivity of $RMAOO^•$ toward other species.

BZ Oscillations. When initial concentrations are increased, reactions R1−R28 show oscillations. Unfortunately, only a few oscillations were obtained when rate constants from the malonic acid system[21,28,35−38] were used. The reason for this discrepancy appears to be a lack of an additional but necessary Br^- ion source in the mechanism. This is demonstrated by an increase of k_{21} (Figure 11B). The better but still unrealistic results with increased k_{21} values show that the bromide ion source appears to be related to inorganic bromine species rather than organic bound bromine. The problem of the bromide ion source has been recognized for quite some time and has often been related to the value of the "*f*-factor" in the original Oregonator model.[41] From ^{82}Br-tracer experiments[42] there is evidence that in the malonic acid system the formation of BrMA is a minor part of the total transition from BrO_3^- to Br^- and that most bromide ions originate from bromate via inorganic intermediates (as HOBr) attacked by $RMA^•$ radicals.[20,43]

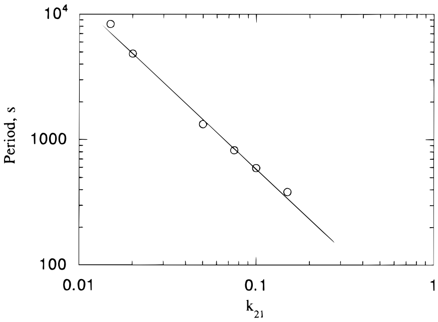

Figure 12. Calculated period length as a function of k_{21}. The rate constants are the same as in Figure 11.

In anaerobic conditions the frequency of oscillations decrease with decreasing enolization rates of the various RMA substrates and shows an excellent agreement with Taft σ^* constants (Figure 4, argon bubbling). This is essentially the behavior predicted by the model, although agreement is only qualitative (Figure 12). Together with the observed correlation between k_{enol} and the Taft constant σ^* (Figure 7) these results indicate that the period in RMA−BZ systems is determined by the bromination of the organic substrate and with enolization as the rate-determining step.

When oxygen is present, period lengths show the same trend when the organic substrate is varied as in anaerobic conditions. However, malonic acid is an exception (Figure 4). In malonic acid there are two abstractable H atoms and in aerobic conditions probably $MAOO^•$ radicals will react more rapidly with brominated organic matter (BrMA) than $MA^•$ radicals. In this way the bromide ion is produced more quickly in aerobic conditions than in anaerobic ones.[20] When substituted malonic acid derivatives are considered, RMABr is not subject to radical attack and the only source of bromide ion appears to be due to the interaction between HOBr and $RMA^•$. Thus, when RMA is considered, peroxy radicals will not react to generate bromide ions either from HOBr or from brominated organic matter, and oxygen will induce an oxidized steady state.[20] In this way and probably also because of processes R28, R13, and R19, increased period lengths for aerobic RMA−BZ systems can be understood because the system will stay longer in the oxidized state (Figure 1).[16] A detailed analysis of the importance of the various proposed processes will be the subject of subsequent work.

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