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Oscillations in the Bromomalonic Acid/Bromate System Catalyzed by $[Ru(phen)_3]^{2+}$

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We investigated the oscillatory behavior of a BZ system with bromomalonic acid and bromate as substrates and with $[Ru(phen)_3]$ SO_4 as a catalyst. The observed oscillations can be well modeled with a theory based on two different feedback loops originally developed for a corresponding BZ system with $[Ru(bipy)_3]$ SO_4 as a catalyst. Furthermore, we have reexamined the decomposition of acidic bromate. We conclude that the products of this reaction are HOBr and O_2 rather than HOBr and perbromate; the rate constant for the decomposition reaction turns out to be 1000 times smaller for 1 M sulfuric acid solution than expected from earlier experiments performed with 3 M sulfuric acid solutions.

1. Introduction

Recently we presented a model of the BZ reaction involving two different negative feedback loops: (i) removal of $HBrO_2$ by Br^- and (ii) removal of $BrO_2^\bullet$ by organic radicals.[1] We applied this model successfully to a BZ system with bromomalonic acid as organic substrate and $[Ru(bipy)_3]^{2+}$ as a catalyst. However, we come into difficulties with the ferroin catalyzed BZ system: in this case the negative feedback loop is not sufficient to inhibit the autocatalytic reaction properly.[2] To obtain more insight into the role of the catalyst in the BZ reaction we performed experiments with $[Ru(phen)_3]^{2+}$, where the ligand phenanthroline is identical with the ligand in ferroin.

2. Chemicals and Experimental Methods

H_2SO_4 (96%, Fluka p.a.) was used without further purification. $NaBrO_3$ (Fluka p.a.) was recrystallized twice from water. Bromomalonic acid was prepared following the prescription of Försterling et al.[3,4] All solutions were prepared with doubly distilled water.

$[Ru(phen)_3]Cl_2$ (Aldrich) was converted into its sulfato salt: a saturated aqueous solution (about 1.05 g of the chloride salt in 7 mL of water) was prepared; 1 mL of 5 M H_2SO_4 was added dropwise, and the sulfato salt precipitated. The sulfato salt was separated by filtering and further purified by washing with diethyl ether. For the preparation of $[Ru(III)(phen)_3]_2$ $(SO_4)_3$ the $[Ru(II)(phen)_3]SO_4$ salt was dissolved in 5 M H_2SO_4 and oxidized by addition of PbO_2. The remaining solid PbO_2 was separated by filtration. Due to the fact that $[Ru(III)(phen)_3]^{3+}$ is not stable in 1 M H_2SO_4 at room temperature, the stock solutions used in the experiment were all freshly prepared in 5 M H_2SO_4 and kept in an ice bath.

The spectroscopic experiments were carried out in an optical cell (path length 2.0 cm; volume 12 mL) at a temperature of 20° C. Nitrogen gas was bubbled through the solution in the cell before starting the reaction (for 15 min) and during the reaction to exclude oxygen. The kinetics was measured by monitoring the absorbance change with a single beam spectrophotometer at 450 nm (absorption maximum of $[Ru(phen)_3]^{2+}$); the concentration was calculated using the extinction coefficients $\epsilon_{450}^{Ru(II)} = 16500\ M^{-1}\ cm^{-1}$ and $\epsilon_{450}^{Ru(III)} = 145\ M^{-1}\ cm^{-1}$. The absorption spectra were measured with a Hewlett-Packard HP8452A diode array spectrophotometer.

The measurement of oxygen in acidic bromate solutions was performed with an oxygen sensitive electrode (Clark type electrode EO16, WTW). There was one difficulty with this electrode, namely, that the membrane was not chemically resistant against the acidic bromate. Therefore, the oxygen content of the samples was measured after the addition of 8 M NaOH solution (leading to an excess of 0.1 M NaOH).

The numerical integration of the set of 18 kinetic differential equations was performed with the program DIFFGL, which is based on Gear's method.[5]

3. Experiments and Simulations

3.1. Autocatalytic Reaction. We studied the autocatalytic reaction of $[Ru(phen)_3]^{2+}$ with bromate in 1 M sulfuric acid. In our experiment we purged a sulfuric acid solution with nitrogen for 15 min before starting the reaction, and during the reaction a flow of nitrogen through the solution was maintained. The reaction was started by adding bromate (dissolved in water) and $[Ru(phen)_3]SO_4$ (dissolved in 1 M H_2SO_4) simultaneously to a solution of 1M sulfuric acid. Bromate was used in great excess over $[Ru(phen)_3]^{2+}$. The results are shown in Figures1 and 2.

The simulations were performed by using the reaction schemes R1−R7 (Table 1). Compared with the simulation of the $[Ru(bipy)_3]^{2+}$ system[1] this reaction scheme differs only in the rate constant for reaction R6

$$[Ru(phen)_3]^{2+} + BrO_2^\bullet + H^+ \rightarrow [Ru(phen)_3]^{3+} + HBrO_2 \quad (R6)$$

which was slightly reduced from $k_6 = 4 \times 10^6\ M^{-2}\ s^{-1}$ to $k_6 = 3.7 \times 10^6\ M^{-2}\ s^{-1}$. The initial concentrations of BrO_2 and

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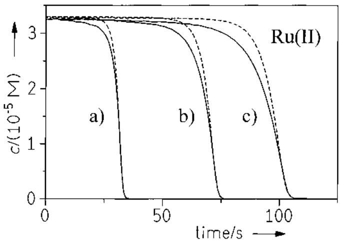


Figure 1. Autocatalytic oxidation of $[Ru(phen)_3]^{2+}$ (initial concentration 3.3×10^{-5} M) by acidic bromate. Solid lines: experiments with (a) $[BrO_3^-]_0 = 1.0 \times 10^{-2}$ M, (b) $[BrO_3^-]_0 = 5.0 \times 10^{-3}$ M, (c) $[BrO_3^-]_0 = 3.3 \times 10^{-3}$ M. Dashed lines: simulated from reactions (R1−R7) with the same initial concentrations of BrO_3^- and of $[Ru(phen)_3]^{2+}$ as in the experiments, and with $[Br^-]_0 = 1 \times 10^{-6}$ M.

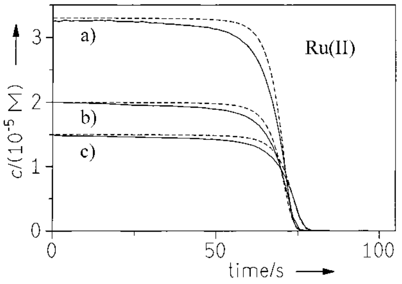


Figure 2. Autocatalytic oxidation of $[Ru(phen)_3]^{2+}$ by acidic bromate (initial concentration 5×10^{-3} M). Solid lines: experiments with (a) $[Ru^{2+}]_0 = 3.3 \times 10^{-5}$ M, (b) $[Ru^{2+}]_0 = 2.0 \times 10^{-5}$ M, (c) $[Ru^{2+}]_0 = 1.5 \times 10^{-5}$ M. Dashed lines: simulated from reactions (R1−R7) with the same initial concentrations of BrO_3^- and of $[Ru(phen)_3]^{2+}$ as in the experiments, and with $[Br^-]_0 = 1 \times 10^{-6}$ M.

$HBrO_2$ were set to zero. To reproduce the observed induction time it was necessary to start with nonzero initial concentrations of bromide. The region of the exponential decay and the final part of the experimental curves can be well modeled but there are some deviations between simulations and experiments in the induction period. The agreement is not as good as with $[Ru(bipy)_3]^{2+}$ as a catalyst,[1] but it seems to be satisfactory for the present approach.

3.2. Reduction of $[Ru(phen)_3]^{3+}$ by Bromomalonic Acid. The rate determining step of the reduction of $[Ru(phen)_3]^{3+}$ by bromomalonic acid (BrMA) is reaction R8:

$$\mathrm{BrMA} + [\mathrm{Ru(phen)_3}]^{3+} \rightarrow \mathrm{BrMA}^{\bullet} + [\mathrm{Ru(phen)_3}]^{2+} + \mathrm{H}^+ \quad (\mathrm{R8})$$

Previously it was assumed that the bromomalonyl radicals $BrMA^{\bullet}$, produced in R8, disproportionate to bromomalonic acid and bromotartronic acid.[1,3] Bromotartronic acid is not stable and decomposes into mesoxalic acid and bromide ion, which is most important in the first negative feed back loop of the BZ reaction. Recently we[6] found that in the reduction of Ce^{4+} by BrMA the bromomalonyl radicals disappear by recombination rather than by disproportionation:

$$2\mathrm{BrMA}^{\bullet} + \mathrm{H_2O} \rightarrow \mathrm{BrEETRA} + \mathrm{Br}^- + \mathrm{CO_2} \quad (\mathrm{R9})$$

The products of the recombination are bromoethenetricarboxylic acid (BrEETRA), carbon dioxide, and bromide ion.

We measured the kinetics of the reduction of $[Ru(phen)_3]^{3+}$ using different initial concentrations of BrMA. The formation of $[Ru(phen)_3]^{2+}$ was followed spectroscopically at 450 nm after the injection of $[Ru(phen)_3]_2(SO_4)_3$ (dissolved in 1M sulfuric acid) into a solution of BrMA in 1 M H_2SO_4 (Figure 3). The experimental curves can be well modeled with reactions R8 and R9 using the rate constants $k_8 = 94.2$ M^{-1} s^{-1}, $k_{-8} = 1.5 \times 10^5$ M^{-2} s^{-1}, and $k_9 = 1 \times 10^8$ M^{-1} s^{-1}. The forward reaction rate constant k_8 is larger by a factor of 1.7, the reverse constant k_{-8} is 20% larger compared with the corresponding rate constant for the $[Ru(bipy)_3]^{3+}$ complex.[1]

3.3. Oscillatory Behavior. The oscillations were followed spectroscopically at 450 nm. A nitrogen stream was applied through the solution to exclude oxygen from the air. The reaction was started by the injection of $[Ru(bipy)_3]^{2+}$ into a solution of bromate and bromomalonic acid. Oscillations start immediately after the injection of $[Ru(bipy)_3]^{2+}$ without any induction period (Figure 4). Additional experiments with different initial concentrations of bromomalonic acid and bromate were carried out to test the model (Figure 5).

The simulation is based on the reaction scheme R1-R16 (Table 1), including two negative feedback loops: (i) removal of $HBrO_2$ by bromide (reaction R2) and (ii) removal of $BrO_2^{\bullet}$ by $BrMA^{\bullet}$ radicals (Reaction R13). Compared with the simulation of the $[Ru(bipy)_3]^{2+}$ system,[1] changes have been made in reactions R6, R8, and R9, as discussed above. When using R14 with the original rate constant $k_{14} = 0.62$ s^{-1}, we failed to observe oscillations: the system remains in the reduced state after completing one cycle. Apparently, the bromide produced during the oxidation of BrMA by Ru(III) does not fall below its critical concentration and the autocatalytic reaction cannot start again. It turned out that a small change of k_{14} from 0.62 to 0.5 s^{-1} (thus reducing the rate of formation of bromide) is enough to obtain oscillatory behavior.

It can be seen that the simulated curves and the period time (Figure 5) are comparable with those in the experiment (simulation 1). As in the work of Gao et al.,[1] a model without radical control (i.e., omitting reactions R13−R16 from the reaction scheme) fails to reproduce the observed oscillatory behavior (simulation 2); in this case the system remains in the oxidized state indicating that the autocatalytic reaction cannot be stopped by the inhibitor bromide without the help of bromomalonyl radicals.

4. Discussion

We demonstrated that our previous model developed for the BZ reaction with bromomalonic acid as a substrate[1] is also working well if we replace the ruthenium bipyridyl complex by the corresponding phenanthroline complex. It turned out, however, that the inhibition by bromide is too strong when using the original rate constant $k_{14} = 0.62$ s^{-1}: the autocatalytic reaction cannot restart after the first cycle and the system remains in the reduced state. Decreasing k_{14} to 0.50 s^{-1} was sufficient to switch the system into the oscillatory regime. This is only a 20% change of this rate constant. We checked that this small change does not significantly affect the oscillatory behavior of the original ruthenium bipyridyl catalyzed system.

It should be pointed out that most rate constants in the 18 reactions summarized in Table 1 are derived from direct measurements and thus have fixed values in the model. Only k_{14} and k_{15} have been introduced as adjustable parameters, in analogy to earlier investigations on the Ce^{4+}/malonic acid oscillating system.[15]

There is a problem with reaction R7, the spontaneous formation of $HBrO_2$ from acidic bromate. In a previous work[11] we observed the formation of $BrO_2^{\bullet}$ in strongly acidic (3 M) solutions of bromate. To account for this observation we postulated reaction R7, a disproportionation of bromate into bromous acid and perbromate. The rate constant $k_7 = 7 \times 10^{-7}$ M^{-3} s^{-1} was chosen such that the observed steady-state

TABLE 1: Reaction Scheme for the Bromomalonic Acid−$Ru(phen)_3^{2+}$−Acidic Bromate Oscillatory System[a]

	reaction	$k_{forward}$	$k_{reverse}$	ref
R1	$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O$	$8 \times 10^9\ M^{-2}\ s^{-1}$	$80\ s^{-1}$	1, 8
R2	$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr$	$2.5 \times 10^6\ M^{-2}\ s^{-1}$	$2 \times 10^{-5}\ M^{-1}\ s^{-1}$	1, 8
R3	$Br^- + BrO_3^- + 2H^+ \rightleftharpoons HOBr + HBrO_2$	$1.2\ M^{-3}\ s^{-1}$	$3.2\ M^{-2}\ s^{-1}$	1, 8, 9
R4a	$HBrO_2 + H^+ \rightleftharpoons H_2BrO_2^+$	$2 \times 10^6\ M^{-1}\ s^{-1}$	$1 \times 10^8\ s^{-1}$	1, 10
R4b	$HBrO_2 + H_2BrO_2^+ \rightarrow HOBr + BrO_3^- + 2H^+$	$1.7 \times 10^5\ M^{-1}\ s^{-1}$		1, 10
R5a	$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O$	$48\ M^{-2}\ s^{-1}$	$3.2 \times 10^3\ s^{-1}$	1, 9
R5b	$Br_2O_4 \rightleftharpoons 2BrO_2^\bullet$	$7.5 \times 10^4\ s^{-1}$	$1.4 \times 10^9\ M^{-1}\ s^{-1}$	1, 9
R6	$Ru^{2+} + BrO_2^\bullet + H^+ \rightarrow Ru^{3+} + HBrO_2$	$3.7 \times 10^6\ M^{-2}\ s^{-1}$		*b*
R7	$2BrO_3^- + 2H^+ \rightarrow HBrO_2 + HBrO_4$	$7 \times 10^{-7}\ M^{-3}\ s^{-1}$		1, 11
R7a	$2BrO_3^- + 2H^+ \rightarrow 2HBrO_2 + O_2$	$6 \times 10^{-10}\ M^{-3}\ s^{-1}$		*b*
R8	$BrMA + Ru^{3+} \rightleftharpoons Ru^{2+} + BrMA^\bullet + H^+$	$94\ M^{-1}\ s^{-1}$	$1.5 \times 10^5\ M^{-2}\ s^{-1}$	*b*
R9	$2BrMA^\bullet + H_2O \rightarrow BrEETRA + Br^- + CO_2$	$1 \times 10^8\ M^{-1}\ s^{-1}$		1, 12, 6
R10	$BrMA \rightleftharpoons enol$	$1.2 \times 10^{-2}\ s^{-1}$	$800\ s^{-1}$	1, 13
R11	$enol + Br_2 \rightarrow Br_2MA + H^+ + Br^-$	$3.5 \times 10^6\ M^{-1}\ s^{-1}$		1, 13
R12	$enol + HOBr \rightarrow Br_2MA + H_2O$	$1.1 \times 10^6\ M^{-1}\ s^{-1}$		1[c], 13
R13	$BrMA^\bullet + BrO_2^\bullet \rightarrow Q$	$4 \times 10^9\ M^{-1}\ s^{-1}$		1, 14[d]
R14	$Q \rightarrow Q_1 + Br^- + H^+$	$0.5\ s^{-1}$		1[e]
R15	$Q \rightarrow HBrO_2 + BrTA$	$0.46\ s^{-1}$		1
R16	$BrTA \rightarrow Br^- + H^+ + MOA$	$1.5\ s^{-1}$		1

[a] The values refer to a temperature of 20 °C. To account for the acidity of sulfuric acid we use the H^+ concentration reported by Robertson and Dunford.[7] For example, $[H^+] = 1.29$ M for 1 M sulfuric acid. [b] This work. [c] Erroneously, in ref 1 the much smaller value $6.6 \times 10^4\ M^{-1}\ s^{-1}$ was used. However, the change to $1.1 \times 10^6\ M^{-1}\ s^{-1}$ does not affect the kinetics of the oscillatory system. That is because HOBr reacts much faster with bromide than with BrMA forming bromine which disappears in reaction R11. [d] In analogy to the reaction of $MA^\bullet$ with $BrO_2^\bullet$. [e] Slightly reduced from 0.62 to $0.5\ s^{-1}$.

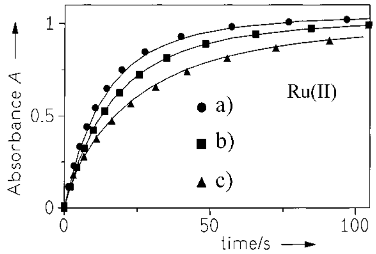


Figure 3. Reduction of $[Ru(phen)_3]^{3+}$ by bromomalonic acid (concentration of $[Ru(phen)_3]^{2+}$ versus time curves). Solid lines: experiments with (a) $[BrMA]_0 = 8.0 \times 10^{-4}$ M, $[Ru(III)]_0 = 3.2 \times 10^{-5}$ M, (b) $[BrMA]_0 = 6.0 \times 10^{-4}$ M, $[Ru(III)]_0 = 3.1 \times 10^{-5}$ M, (c) $[BrMA]_0 = 4.0 \times 10^{-4}$ M, $[Ru(III)]_0 = 3.1 \times 10^{-5}$ M. Dots, squares, and triangles: simulated with $k_8 = 94.2\ M^{-1}\ s^{-1}$, $k_{-8} = 1.1 \times 10^6\ M^{-2}\ s^{-1}$, and $k_9 = 1 \times 10^8\ M^{-1}\ s^{-1}$.

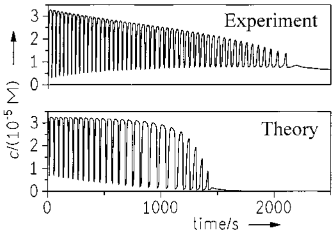


Figure 4. Oscillating system. Concentration c of $[Ru(phen)_3]^{2+}$ versus time curves. Top: experiment. Bottom: simulation. Initial concentrations: $[BrMA]_0 = 0.01$ M; $[Ru(II)]_0 = 3.3 \times 10^{-5}$ M; $[BrO_3^-]_0 = 0.1$ M; $[H_2SO_4] = 0.9$ M.

concentration of $BrO_2^\bullet$ in that system was reproduced. Including reaction R7 in the reaction model generated enough bromous acid to restart the autocatalytic reaction in each oscillation cycle in a radical controlled oscillatory system (Radicalator model).[11]

Recently, Pereira and Faria[16] criticized that, for thermodynamic reasons, perbromate cannot be expected as a reaction product during the decomposition of bromate in acidic solution. Moreover, they demonstrated in the case of the $[Ru(bipy)_3]^{2+}$ catalyzed BZ reaction[1] that trace impurities (e.g., bromide ions forming $HBrO_2$ according to reaction R3) are sufficient to generate enough bromous acid for the onset of the autocatalytic reaction.

In principle we agree with these conclusions. However, we cannot completely neglect possible reaction products occurring during the decomposition of acidic bromate when performing simulations on the BZ reaction on a longer time scale. To obtain new information on this decomposition reaction (besides the observed $BrO_2^\bullet$ steady state concentration under highly acidic conditions) we measured the formation of HOBr in bromate dissolved in 1 M sulfuric acid by following the absorbance change at 330 nm (Figure 6). Immediately after preparing the solution we obtain an absorption band with a maximum at 490 nm, indicating the formation of $BrO_2^\bullet$ radicals. Using an initial bromate concentration of 1 M we find a HOBr concentration of 1×10^{-4} M after 40 h of reaction. From reactions R7, R4a, and R4b it can be expected that two $HBrO_2$ molecules formed in the primary decomposition process of bromate disproportionate rapidly to form one HOBr and one $HBrO_3$ molecule. Thus the expected rate of formation of HOBr is

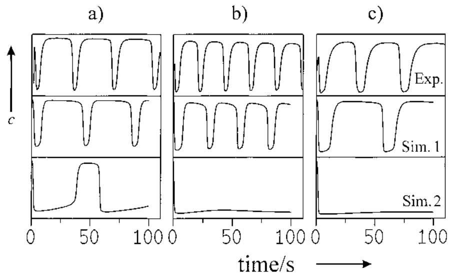
$$\frac{dc_{HOBr}}{dt} = \frac{1}{2}k_7 c^2_{BrO_3^-}\, c^2_{H^+} = 6 \times 10^{-7}\ M\ s^{-1}$$

for $c_{BrO_3^-} = 1$ M and $c_{H^+} = 1.29$ M. Then for $t = 40$ h $= 1.5 \times 10^5$ s we estimate $c_{HOBr} = 0.1$ M. This is 1000 times more than we find in the experiment. Including the decomposition pathways of HOBr (reactions R-2, R-3, R-4a) the calculated concentration of HOBr should be about 0.01 M after 40 h of reaction, and bromine is expected as a second reaction product. However, in the experiment we do not find a significant amount of bromine. This means that the prediction of our model is wrong.

At the same time we searched for another pathway of the decomposition of acidic bromate. Assuming that the decomposition leads to oxygen rather than to perbromate

$$2BrO_3^- + 2H^+ \rightarrow 2HBrO_2 + O_2 \qquad (R7a)$$

we expect one oxygen for two $HBrO_2$. Thus one O_2 should be formed for one HOBr. The result of the measurement (using an oxygen sensitive electrode) is about one-half O_2 per one HOBr. However, regarding the experimental difficulties with the oxygen measurement the amount of oxygen seems to be in



Initial Concentrations

species	case a	case b	case c
$Ru(phen)_3^{2+}$		3.3 × 10^{-5} M	
BrO_3^-	0.1 M	0.2 M	0.1 M
BrMA	0.01 M	0.01 M	0.005 M
H_2SO_4		0.9 M	

Figure 5. Oscillating system. Concentration *c* of $[Ru(phen)_3]^{2+}$ versus time curves (scaling of the ordinate as in Figure 4). Top: experiment. Center: complete model (simulation 1, reactions R1−R16). Bottom: exclusive bromide control model (simulation 2, reactions R1−R12); only one oscillation cycle occurs in case (a), no oscillations occur in cases (b) and (c).

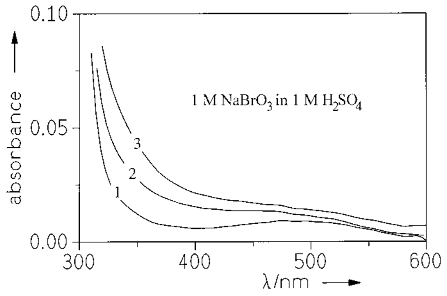


Figure 6. Absorption spectra of a solution of $NaBrO_3$ (1 M) in 1 M sulfuric acid at different times *t* after preparation. Curve 1: $t = 1$ h. Curve 2: $t = 26$ h. Curve 3: $t = 70$ h. Optical path length $d = 10$ cm.

acceptable agreement with the assumption made in R7a. A rate constant $k_{7a} = 6 \times 10^{-10}$ M^{-3} s^{-1} is in accordance with our kinetic data for 1 M sulfuric acid solution. In this case the concentration of HOBr is so small that reactions R-2, R-3, and R-4a do not play a role and no bromine is expected from the model, in accordance with the experiment.

When calculating the steady-state concentration of $BrO_2^\bullet$ in our model we expect $BrO_2^\bullet = 6 \times 10^{-7}$ M. From Figure 6 we obtain $BrO_2^\bullet = 6 \times 10^{-7}$ M (calculated from $A = 6 \times 10^{-3}$, $\epsilon = 1000$ M^{-1} cm^{-1} and $d = 10$ cm), in full agreement with the model.

Reducing rate constant k_7 from 7×10^{-7} M^{-3} s^{-1} to 6×10^{-10} M^{-3} s^{-1} does not affect the simulated oscillatory behavior of the ruthenium catalyzed BZ system (Figures 4 and 5).

According to R7a the reaction rate should increase with the square of the H^+ concentration. However, when increasing the concentration of sulfuric acid from 1 M ($c_{H^+} = 1.29$ M) to 2 M ($c_{H^+} = 2.65$ M) the rate of HOBr formation increases by a factor of 10 than by a factor of 4, as expected from the model. We conclude that acidic bromate decomposes into $HBrO_2$ and elementary oxygen, but the acidity dependence of this reaction needs clarification.

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