

Comment on “Oscillations in the Bromomalonic Acid/Bromate System Catalyzed by $[\text{Ru}(\text{bipy})_3]^{2+}$ ”

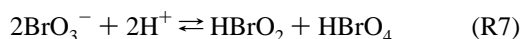
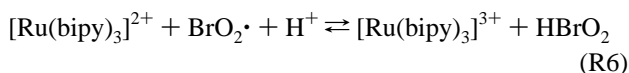
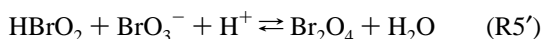
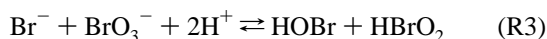
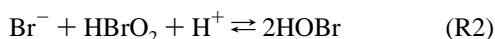
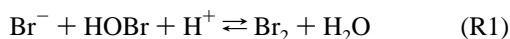
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In a recent study about the autocatalytic reaction between $[\text{Ru}(\text{bipy})_3]^{2+}$ and bromate in 1 M sulfuric acid, a mechanism involving seven reactions, some of them reversible, was proposed to explain the time evolution of $[\text{Ru}(\text{bipy})_3]^{2+}$ concentrations for different initial bromate concentrations.¹ This reaction set is basically that proposed by Noyes, Field, and Thompson² (NFT) for the oxidation of cerium(III) by acidic bromate. The NFT mechanism can explain the bistability found in the $\text{Ce}^{3+}-\text{BrO}_3^-$ system and the bistability and oscillations found in a stirred flow reactor (CSTR) for the minimal bromate oscillator, $\text{Ce}^{3+}-\text{BrO}_3^- - \text{Br}^-$ and $\text{Mn}^{2+}-\text{BrO}_3^- - \text{Br}^-$.^{3–10} The NFT set of reactions is the inorganic core of the mechanism proposed by Field, Körös, and Noyes¹¹ (FKN) to explain the Belousov–Zhabotinsky (BZ) reaction. The NFT mechanism has been discussed, revised, and updated as a consequence of simulations and experimental results obtained from kinetics studies on specific reactions and from experimental work with oscillating systems related to the minimal bromate oscillator and to the BZ system.^{12–22}

Starting with the minimal bromate oscillator catalyzed by $[\text{Ru}(\text{bipy})_3]^{2+}$, exchanging the cerium by ruthenium complexes and keeping the numbering of the reactions according to ref 15, we have the sequence



What we want to point out is the inclusion of (R7) in this reaction set. Gao and Försterling¹ included this reaction based on the instability of acidic bromate evidenced by $\text{BrO}_2\cdot$ formation in a 10 M sulfuric acid solution of bromate.²³

Using ΔG_f° for BrO_3^- , HBrO_2 , and HBrO_4 equal to 1.7, 6.8, and 122.09 kJ/mol, we calculate the equilibrium constant for (R7) as 1×10^{-22} .^{24,25} Ignoring the deviation from ideality, we calculate the equilibrium concentration for HBrO_4 and

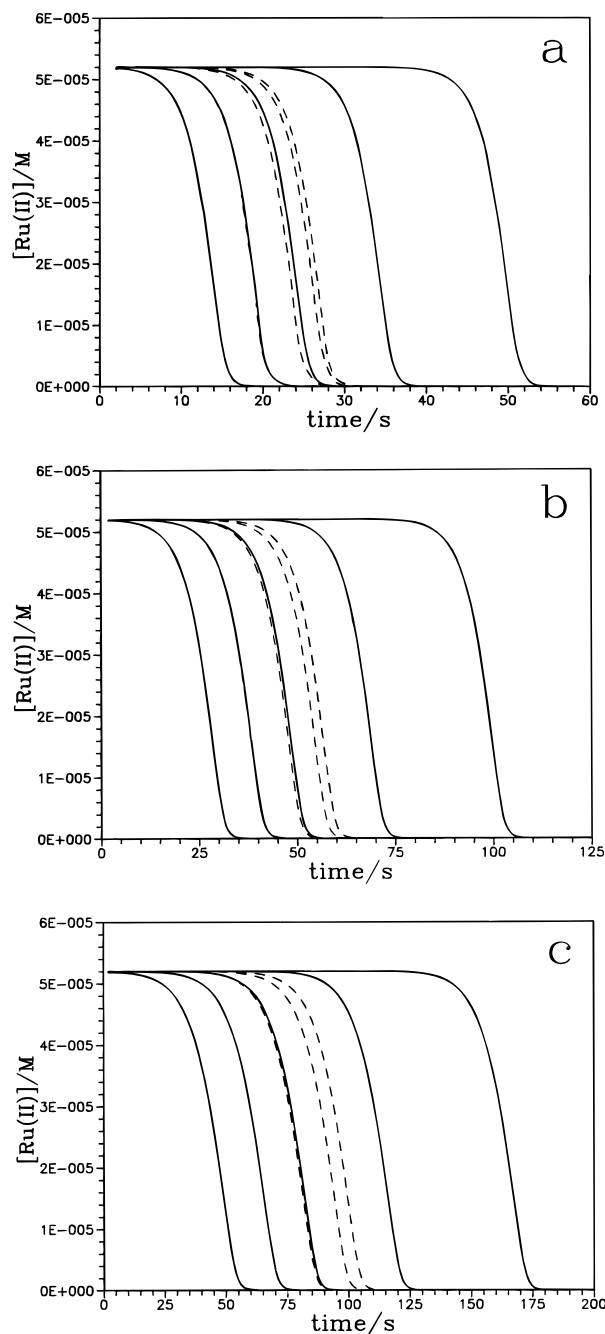


Figure 1. Numerical integration results of the mechanism given by eqs R1–R7 (dashed lines) at initial $[\text{BrO}_3^-]$ of (a) 1×10^{-2} M, (b) 5×10^{-3} M, and (c) 3×10^{-3} M and initial concentration for H_2SO_4 and $[\text{Ru}(\text{bipy})_3]^{2+}$ equal to 1 and 5.2×10^{-5} M, respectively. Rate constants are the same as used by Gao and Försterling.¹ Solid lines corresponds to (R7) turned off. Each solid line, from left to right, corresponds to background concentrations of 1×10^{-8} , 1×10^{-9} , 1×10^{-10} , 1×10^{-12} , and 1×10^{-15} M, respectively. Results obtained with (R7) turned on for the background concentration 1×10^{-8} , 1×10^{-9} , 1×10^{-10} , 1×10^{-11} , and 1×10^{-15} M are shown, from left to right, as dashed lines. There are five dashed lines too, but the first two (1×10^{-8} and 1×10^{-9} M) superimpose the solid lines calculated using these same background concentrations.

HBrO_2 as equal to 2×10^{-11} M in a 10 M H_2SO_4 and 0.2 M bromate solution (concentrations used in the Försterling and Murányi experiment²³). At 1 M sulfuric acid and 3×10^{-3} M bromate concentrations, $[\text{HBrO}_4]_{\text{eq}}$ and $[\text{HBrO}_2]_{\text{eq}}$ are calculated as 3×10^{-14} M. It means that, ignoring the activation energy barrier, equilibrium concentrations of the products of (R7) are in the range of trace amounts.

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One piece of information that is usually omitted when reporting kinetics simulations are the initial concentration values used for species not present at the reaction beginning. It is a well-known fact that the algorithms used in the numerical integration of mechanistic models can produce a divide-by-zero condition when exact zero values are attributed to some concentration values. As a solution to this problem, it is usually to set an arbitrary "background" concentration in the range of 1×10^{-10} M for all the species not initially present.

Figure 1 shows the numerical integration results of the mechanism (R1)–(R7) (dashed lines) using the rate constants given by Gao and Försterling and starting at different background concentrations in the range from 1×10^{-8} to 1×10^{-15} , for the three initial bromate concentrations given in Figure 3 of their paper. Results obtained turning off (R7) are presented as solid lines.

The numerical integrations were performed on a 486/33 MHz PC-compatible microcomputer using a program written in Turbo Pascal to solve autonomous ordinary differential equation systems by a semiimplicit Runge–Kutta method.²⁶

Our results show that background concentrations can affect the calculated concentration–time curves, depending on the mechanism considered. Comparing our Figure 1 with Figure 3 from the Gao and Försterling paper, we can estimate that the background concentration probably used by these authors was 1×10^{-10} M.

As shown in Figure 1, (R1)–(R6) and (R1)–(R7) mechanisms produce quite the same results if background concentrations are equal to or greater than 1×10^{-10} M. If background concentrations are lower than 1×10^{-10} , the results from each mechanism will differ greatly. In addition, mechanism (R1)–(R7) will give the same concentration–time curves if background concentration is set lower than or equal to 1×10^{-15} M.

Our conclusion is that one cannot say whether (R7) is occurring to produce the trace amounts of HBrO_2 necessary to start the autocatalytic reaction between $[\text{Ru}(\text{bipy})_3]^{2+}$ and acidic bromate. The agreement between simulation and experimental results using a background concentration of 1×10^{-10} M was

fortuitous. To increase the confidence on simulation results, one must specify the initials concentrations of impurities. Considering the influence of the Br^- concentrations in (R1)–(R3), this species appears to be one of the most important impurities to be evaluated in the reagents.

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