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Why the Acidity of Bromic Acid Really Matters for Kinetic Models of Belousov-Zhabotinsky Oscillating Chemical Reactions

Rainer Glaser*, Marco Delarosa and Ahmed Olasunkanmi Salau

Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA

The cerium-catalyzed Belousov-Zhabotinsky oscillating reaction [1-4] and its variants (Fe [5,6], Ru [7,8], Mn [9-11]) are inherently connected to the chemistry of bromine oxoacids $HBrO_x$. The growing interest in nonlinear chemical systems [12-14] has provided strong incentives to study bromine chemistry, and especially the disproportionation of bromous acid has been studied in great detail [15-29]. The bromine chemistry of the Belousov-Zhabotinsky reaction (BZR) involves hypobromous acid HOBr (1), bromous acid HOBrO (2) and bromic acid $HBrO_3$ (3), and the disproportionation reaction of bromous acid (R4) is a key step.

$$H^+ + Br^- + HOBrO \rightleftarrows 2\ HOBr \quad (R2)$$

$$2\ H^+ + Br^- + BrO_3^- \rightleftarrows HOBr + HOBrO \quad (R3)$$

$$2\ HOBrO \rightleftarrows HOBr + H^+ + BrO_3^- \quad (R4)$$

It is generally agreed that hypobromous acid (pK_a(HOBr)=8.59 [30,31]) and bromous acid (pK_a(HOBrO)=3.43 [29]) are not dissociated at pH values typical for the BZR. In contrast, it has been assumed that bromic acid is dissociated under BZR conditions even though the acidity of bromic acid has not been well established. Experimental $pK_a(3)$ values of 1.87 [30], 0.7 [31], and -0.29 [32] were reported and, most recently, Cortes and Faria concluded that $pK_a(3) < -0.5$ [33]. We wrote recently [34] that it will be important to firmly establish $pK_a(3)$ because this value decides whether reactions R3 and R4 should be replaced by reactions R3' and R4', respectively, or whether reactions R3' and R4' need to be considered in addition to reactions R3 and R4.

$$HOBrO_2 \rightleftarrows H^+ + BrO_3^- \quad (A(3))$$

$$H^+ + Br^- + HOBrO_2 \rightleftarrows HOBr + HOBrO \quad (R3') = (R3) + (A(3))$$

$$2\ HOBrO \rightleftarrows HOBr + HOBrO_2 \quad (R4') = (R4) - (A(3))$$

To explore the consequences of the acidity of bromic acid in Belousov-Zhabotinsky reactions, we considered four cases with greatly different concentrations and/or ratios of sulfuric acid and bromate. In Case 1, molar concentrations of H_2SO_4 and of $KBrO_3$ were used as a simple case of $R_0 = [H_2SO_4]_0/[BrO_3^-]_0 = 1$. In Case 2, we simulated the situation with 0.5 M H_2SO_4 and 0.1 M $KBrO_3$ (R_0=5). This case models the concentrations (0.567 M H_2SO_4, 0.089 M $KBrO_3$) we used in our studies of a variant of the ferroin-catalyzed BZR described by Keusch [6,38]. In Case 3, we studied the situation with 1.0 M H_2SO_4 and 0.1 M $KBrO_3$ (R_0 = 10), which closely mimics the Ce-catalyzed BZR [39] reported by Shakhashiri (0.9 M H_2SO_4, 0.075 M $KBrO_3$). Case 4 with 1.5 M H_2SO_4 and 0.05 M $KBrO_3$ (R_0 = 30) closely mimics the Mn-catalyzed BZR [37] reported by Shakhashiri (1.6 M H_2SO_4, 0.06 M $KBrO_3$).

$$H_2O \rightleftarrows H^+ + OH^-,\ K_w \quad (1)$$

$$H_2A \rightleftarrows H^+ + HA^-,\ K_{a1,1} \quad (2)$$

$$HA^- \rightleftarrows H^+ + A^{2-},\ K_{a1,2} \quad (3)$$

$$HB \rightleftarrows H^+ + B^-,\ K_{a2} \quad (4)$$

We evaluated the system of differential equations describing the equilibria of equations 1-4 with Mathematica [41,42]. K_w denotes the ion product of water ($K_w=10^{-14}$). H_2A denotes the diprotic sulfuric acid H_2SO_4 and we employed acidity constants $pK_{a1,1}$=-3 (a lower bound) and $pK_{a1,2}$=+2 for the first and second dissociations of sulfuric acid [43,44]. HB denotes the monoprotic acid $HBrO_3$ and we evaluated the four cases for integer values of pK_{a2} between +3 and -3 to cover the entire range of reported experimental pK_{a2} values (vide supra). The most pertinent results of the simulations are summarized in table 1. In supporting information we provide more extensive tables (Tables S1 – S4) and these also include the results of the simulations without consideration of the second dissociation of sulfuric acid. In the present context it suffices to state that the protonation state of bromate is essentially the same irrespective as to whether the second dissociation of sulfuric acid is considered or neglected.

We begin our analysis of the data in table 1 by examination of the ratio $R_P = [HBrO_3]/[BrO_3^-]$. The measurements of the acidity of bromic acid gave values in the range p$K_a(3)$=0.5 ± 1.5, and we find that the R_P values fall between 1.5 and 0.5 for p$k_a(3)$=0 and they fall between 2.9 and 14.6 for p$K_a(3)$=1. For all cases, neither bromic acid nor bromate is the dominant species (95%, $R_P > 19$, $R_P < 0.05$) over a range of at least three p$K_a(3)$ units. This result leads to the important conclusion that reactions R3' and R4' must be considered in addition to reactions R3 and R4 in kinetic models of the BZ reaction with bromate.

It is qualitatively clear that the equilibrium *pH* value will be more sensitive to the value of p$K_a(3)$ the lower one selects the ratio $R_0 = [H_2SO_4]_0/[BrO_3^-]_0$. The quantitative data in table 1 support this notion in that the values $\Delta pH = pH[pK_a(3)=+3] - pH[pK_a(3)=-3]$ decrease as R_0 increases. For Case 1 with R_0=1 the ΔpH value is as large as one full pH unit. As with Case 1, Case 5 is characterized by R_0=1 but in Case 5 this ratio is realized with much lower (one tenth) initial concentrations of sulfuric acid and bromate. Detailed results for Case 5 are listed in table S5 and the most pertinent data appear in table 1. While ΔpH ≈ 0.6 is significantly reduced in Case 5 as compared to Case 1, the ΔpH value remains large and of a magnitude that allows for experimental approaches to the determination of p$K_a(3)$ via pH measurements as a function of R_0. We explored this notion for p$K_a(3)$=0 and two scenarios: In Scenario 1 the initial concentration of sulfuric acid is fixed to $[H_2SO_4]_0$ = 1.0 M while $[BrO_3^-]_0$ is allowed to vary between 0.0005 and 4 M. In Scenario 2 the initial bromate concentration is fixed to $[BrO_3^-]_0$ = 0.1 M and $[H_2SO_4]_0$ varies from 0.1 M to 5 M. The numerical results are summarized in tables S6 and S7, respectively, and they are illustrated in figure 1. The figure shows in a compelling fashion that variations

***Corresponding author:** Rainer Glaser, Department of Chemistry, University of Missouri, Columbia, USA, E-mail: glaserr@missouri.edu

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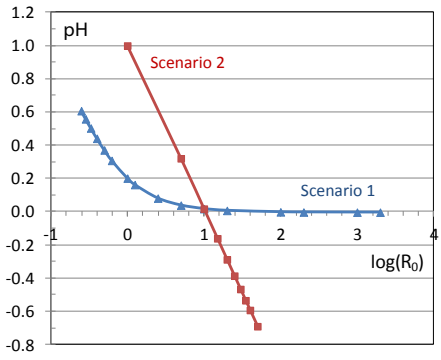

Figure 1: Simulations of *pH* as a function of log(R_0) for Scenario 1 (1.0 M H_2SO_4, variation of $KBrO_3$) and Scenario 2 (variation of H_2SO_4, 0.1 M $KBrO_3$) for $pK_a(3) = 0$.

of R_0 in Scenario 1 result in large *pH* variations Scenario 1 presents a promising approach to measure $pK_a(3)$. We hope that this editorial will encourage such measurements by suitably equipped research groups, and we will be happy to perform the mathematical modeling necessary to extract the value of $pK_a(3)$ from such experimental data sets.

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