Supplementary Information

"Kinetics and Mechanisms of Bromine Chloride Reactions with Bromite and Chlorite Ions"

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Table S1. Stoichiometry of the $HOBr/BrO_2^-$ and $BrCl/BrO_2^-$ Reactions [a]

$[Cl^-]$, mM	$[BrO_3^-]/[BrO_2^-]$
0.0	0.97(6)
19.1	1.01(2)

[a] Conditions: $[HOBr]_T$ = 1.52 mM, $[BrO_2^-]$ = 0.54 mM, $p[H^+]$ = 6.9, $[PO_4]_T$ = 20 mM, 25.0 °C, flow rate = 1.0 mL/min, 100 mA current, and 9.0 mM Na_2CO_3. Errors represent the standard deviation of measurements from three identical solutions.

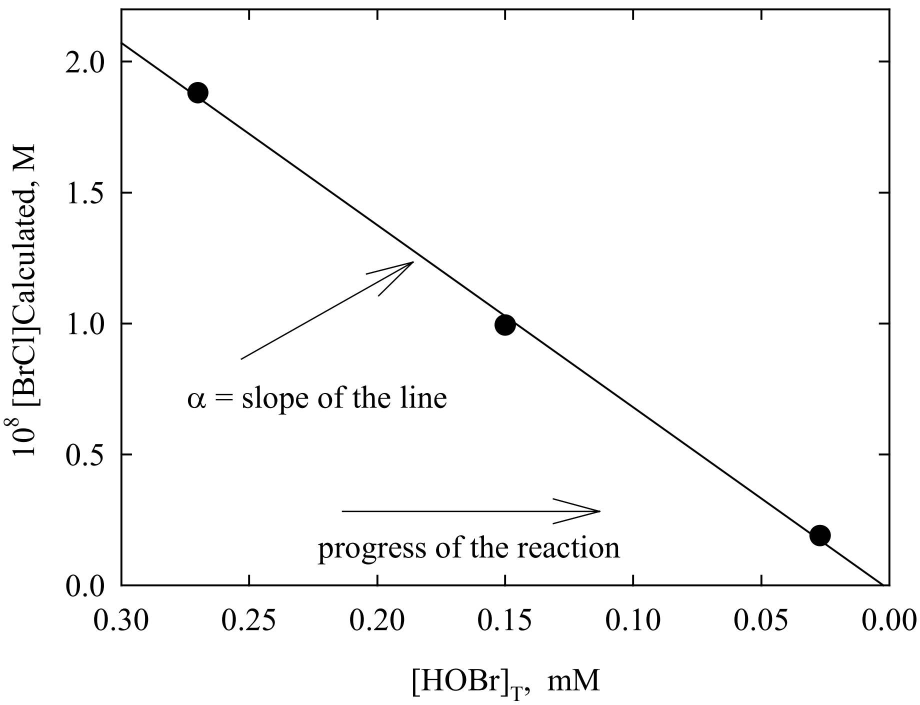

Figure S1. The ratio $[BrCl]/[HOBr]_T = \alpha$ is nearly constant during the $BrCl/ClO_2^-$ reaction if the Br^- formed is taken into account with all the involved equilibria from Table 1. HOBr is consumed during the reaction and the Br^- formed affects the BrCl concentration. The data points are at 10%, 50%, and 90% of the reaction. Conditions: $[HOBr]_T = 0.3$ mM, $p[H^+] = 6.04$, and $[Cl^-] = 0.01$ M. The plot is presented in a descending order in HOBr concentration to reflect the loss of HOBr during the course of the reaction.

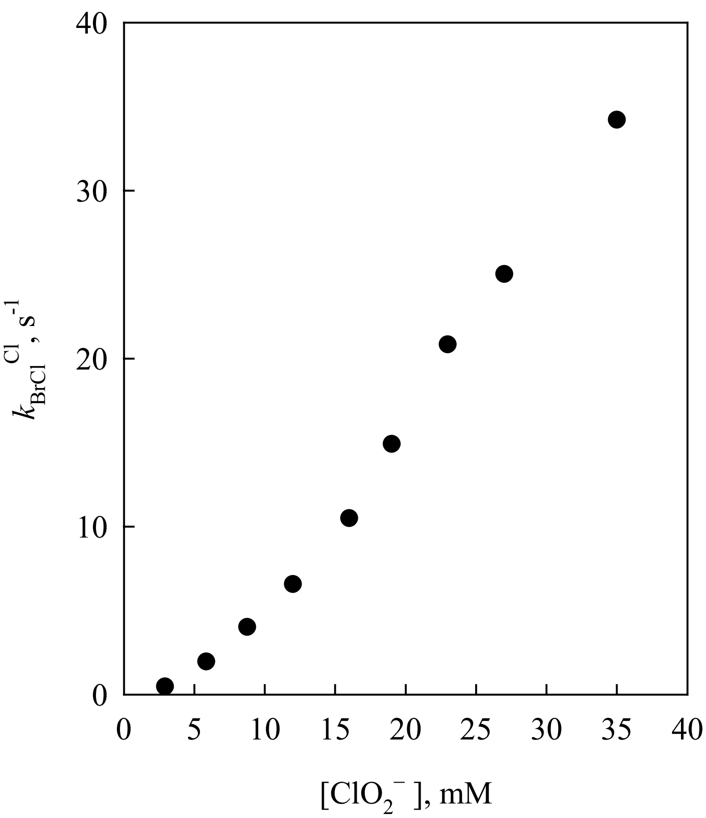

Figure S2. Dependence of k_{BrCl}^{Cl} on chlorite ion concentration for the $BrCl/ClO_2^-$ reaction. Conditions: 37.6 mM Cl^-, $[HOBr]_T$ = 0.305 mM, $[PO_4]_T$ = 5.0 mM, p[H^+] = 6.01, 25.0 °C, and μ = 1.0 M.

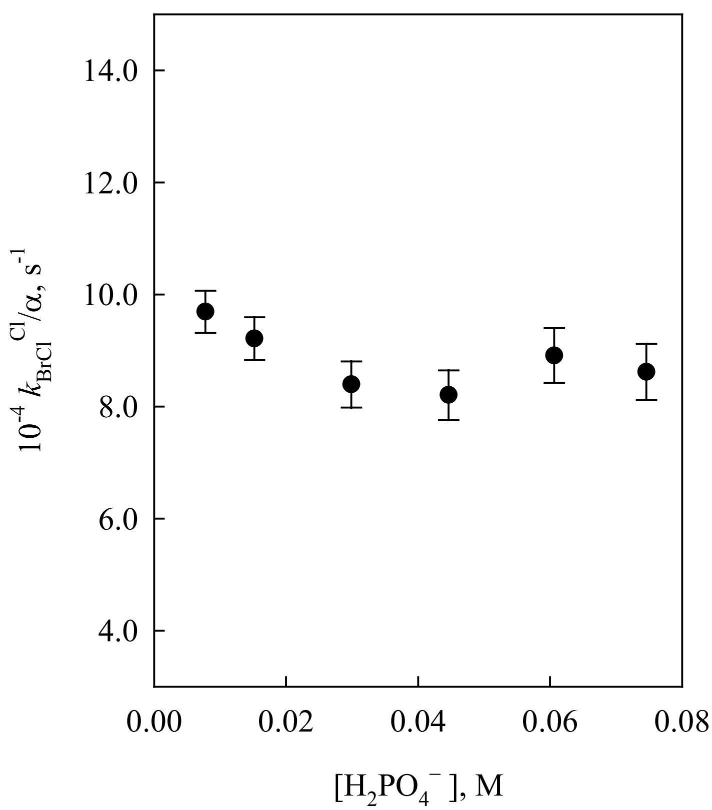

Figure S3. Lack of a buffer effect for the $BrCl/ClO_2^-$ reaction after accounting for the α term. 25.0 mM ClO_2^-, $p[H^+] = 5.75$, 19.1 mM Cl^-, $[HOBr]_T = 0.169$ mM, 25.0 °C, $\mu = 1.0$ M, and $\lambda = 359$ nm.

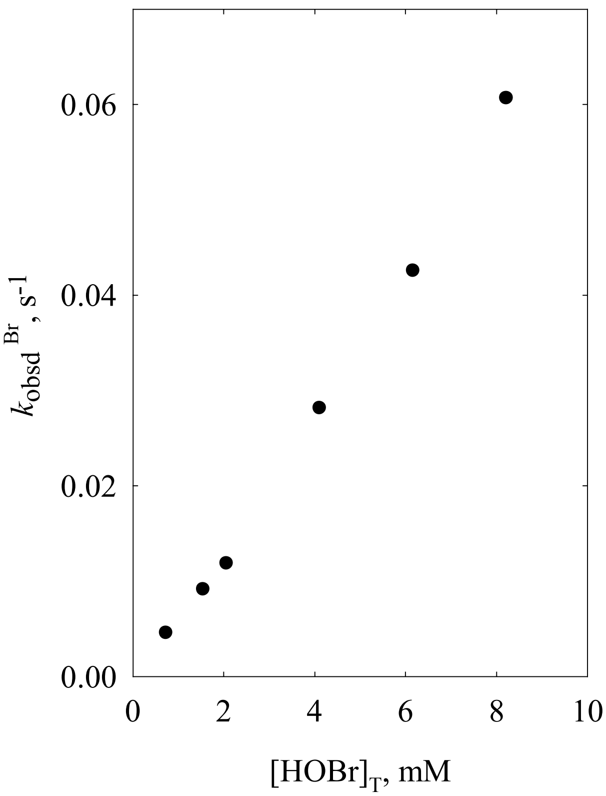

Figure S4. Effect of increasing $[HOBr]_T$ on the BrO_2^-/HOBr reaction. $[BrO_2^-]$ = 70 μM, $p[H^+]$ = 5.91, $[PO_4]_T$ = 80 mM, 25.0 ^oC, μ = 1.0 M, and λ = 240 nm.

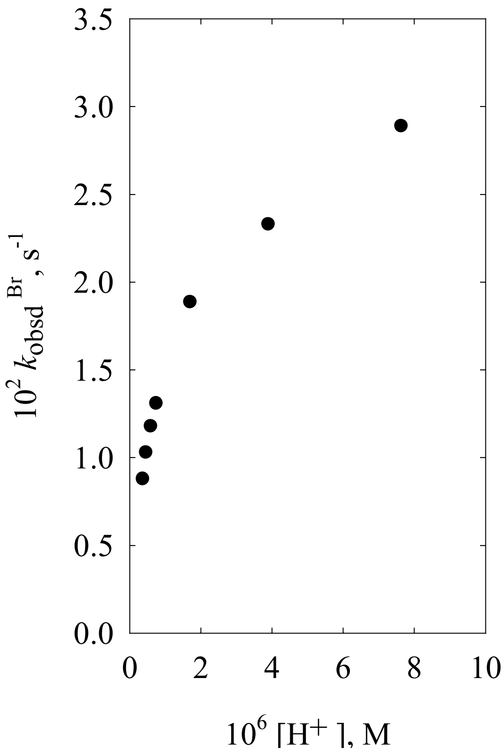

Figure S5. Dependence of BrO_2^-/HOBr reaction on proton concentration. $[HOBr]_T$ = 2.87 mM, $[BrO_2^-]$ = 0.1 mM, $[PO_4]_T$ = 80 mM, 25.0 °C, μ = 1.0 M, and λ = 245 nm.

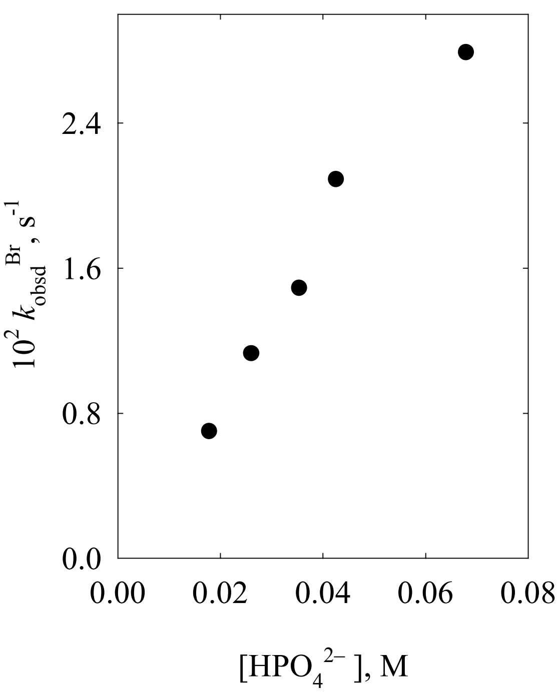

Figure S6. Dependence of BrO_2^-/HOBr reaction on phosphate buffer. $[HOBr]_T$ = 2.78 mM, p[H^+] = 5.99, [BrO_2^-] = 0.1 mM, 25.0 ^{o}C, μ = 1.0 M, and λ = 245 nm.

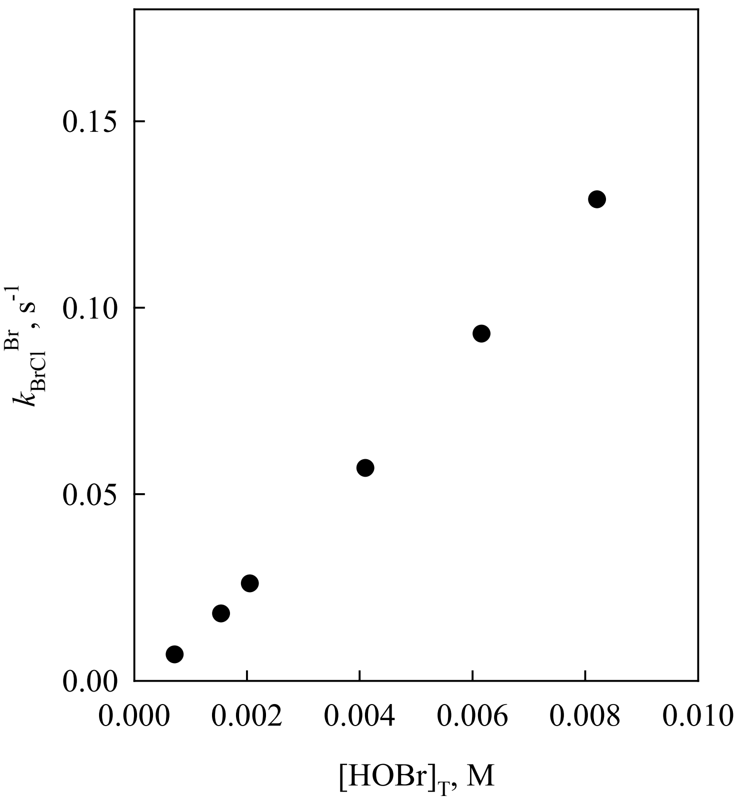

Figure S7. Dependence of the $BrCl/BrO_2^-$ reaction on $[HOBr]_T$. Conditions: $[BrO_2^-]$ = 0.07 mM, p$[H^+]$ = 5.91, $[Cl^-]$ = 20 mM, $[PO_4]_T$ = 80 mM, 25.0 ^oC, μ = 1.0 M, and λ = 240 nm.

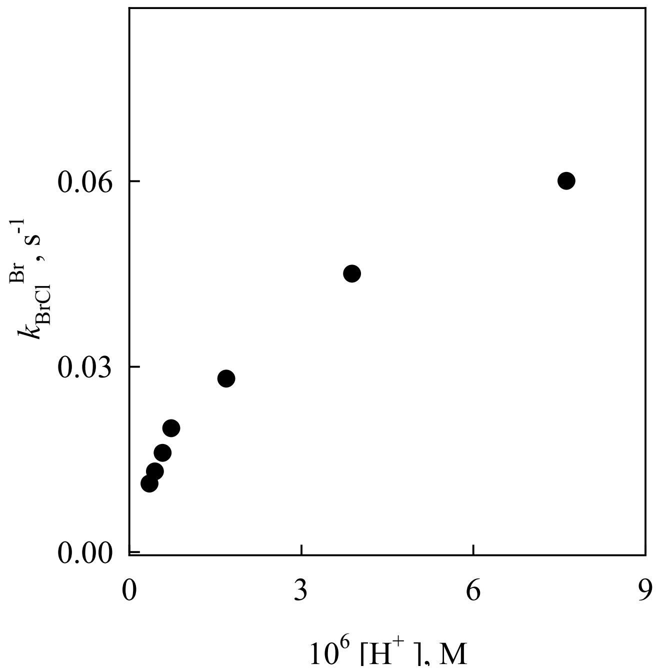

Figure S8. Acid effect on the $BrCl/BrO_2^-$ reaction before introducing the α term. Conditions: $[HOBr]_T$ = 2.87 mM, $[Cl^-]$ = 15.3 mM, $[BrO_2^-]$ = 0.1 mM, $[PO_4]_T$ = 80 mM, 25.0 °C, μ = 1.0 M, and λ = 245 nm.

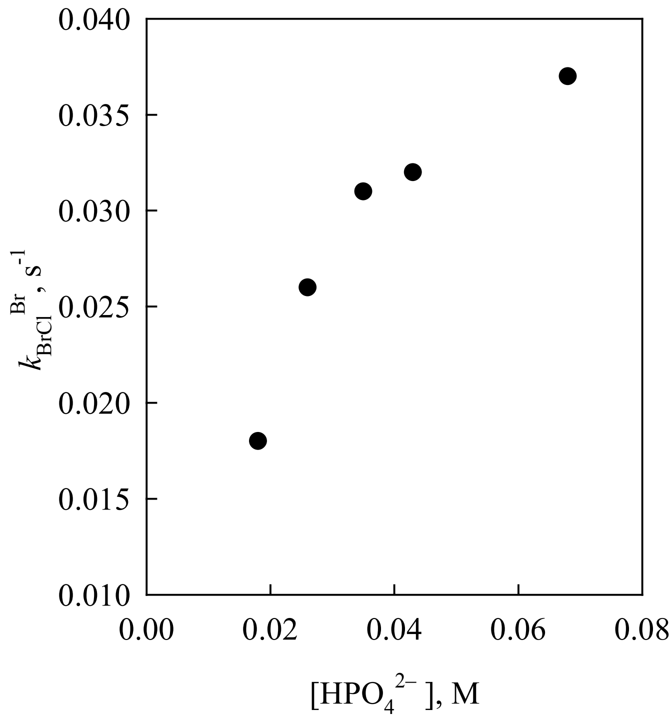

Figure S9. The rate of the $BrCl/BrO_2^-$ reaction is accelerated by the basic form of phosphate buffer, before accounting for the α term: $[HOBr]_T$ = 2.78 mM, p[H^+] = 5.99, [Cl^-] = 15.3 mM, [BrO_2^-] = 0.1 mM, 25.0 °C, μ = 1.0 M, and λ = 245 nm.

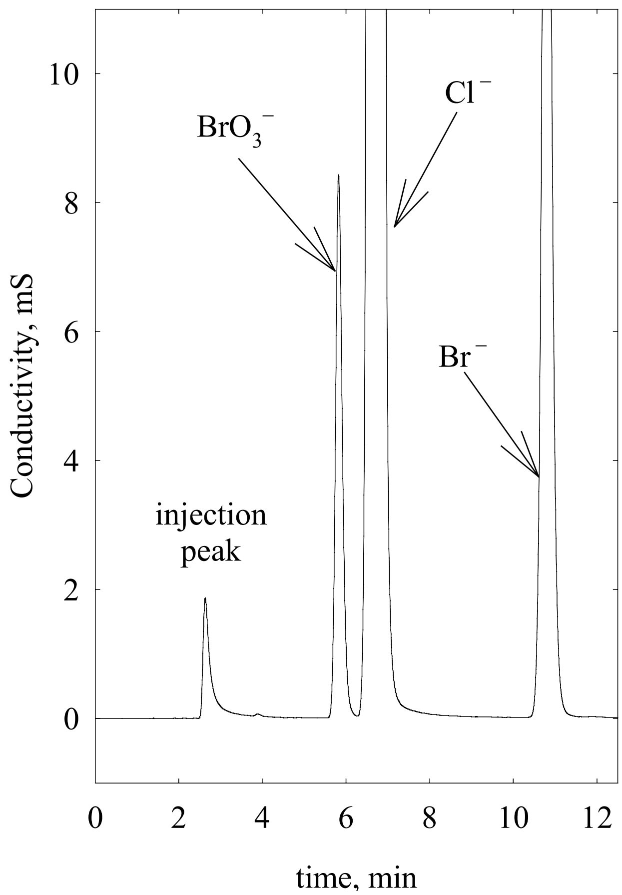

Figure S10. Ion chromatogram of the products of $BrCl/BrO_2^-$ reaction: $[HOBr]_T = 1.52$ mM, $[BrO_2^-] = 0.54$ mM, $[Cl^-] = 19.1$ mM, $p[H^+] = 6.9$, $[PO_4]_T = 20$ mM, and 25.0 °C. Flow rate = 1.0 mL/min, 100 mA current, and 9.0 mM Na_2CO_3. The $[BrO_3^-]$ equals 0.545 mM, leading to stoichiometry of 1.01(2) for $BrO_3^- : BrO_2^-$. A large excess of Na_2SO_3 was used to react with the residual HOBr present in the system.

Appendix S1. Equilibrium Calculations in Accord with Table 1

Solving the concentrations of twelve species using twelve equations, whether bromide is initially present or absent:

eq (1) through eq (12)

equilibrium constants:

$$K_1^{\mathrm{BrCl}} = \frac{[\mathrm{BrCl_2^-}]}{[\mathrm{BrCl}][\mathrm{Cl^-}]} \qquad [\mathrm{BrCl_2^-}] = K_1^{\mathrm{BrCl}}[\mathrm{Cl^-}][\mathrm{BrCl}] \tag{1}$$

$$K_{\mathrm{h1}} = \frac{[\mathrm{HOBr}][\mathrm{Cl^-}][\mathrm{H^+}]}{[\mathrm{BrCl}]} \qquad [\mathrm{HOBr}] = \frac{K_{\mathrm{h1}}[\mathrm{BrCl}]}{[\mathrm{Cl^-}][\mathrm{H^+}]} \tag{2}$$

$$K_{\mathrm{h2}} = \frac{[\mathrm{HOBr}][\mathrm{Br^-}][\mathrm{H^+}]}{[\mathrm{Br_2}]} \qquad [\mathrm{Br_2}] = \frac{K_{\mathrm{h1}}[\mathrm{Br^-}][\mathrm{BrCl}]}{K_{\mathrm{h2}}[\mathrm{Cl^-}]} \tag{3}$$

$$K_4^{\mathrm{Br2}} = \frac{[\mathrm{Br_3^-}]}{[\mathrm{Br_2}][\mathrm{Br^-}]} \qquad [\mathrm{Br_3^-}] = \frac{K_4^{\mathrm{Br2}}K_{\mathrm{h1}}[\mathrm{Br^-}]^2[\mathrm{BrCl}]}{K_{\mathrm{h2}}[\mathrm{Cl^-}]} \tag{4}$$

$$K_3^{\mathrm{Br2}} = \frac{[\mathrm{Br_2Cl^-}]}{[\mathrm{Br_2}][\mathrm{Cl^-}]} \qquad [\mathrm{Br_2Cl^-}] = \frac{K_3^{\mathrm{Br2}}K_{h1}[\mathrm{Br^-}][\mathrm{BrCl}]}{K_{\mathrm{h2}}} \tag{5}$$

$$K_7^{HOBr} = \frac{[\mathrm{HOCl}][\mathrm{Br^-}]}{[\mathrm{HOBr}][\mathrm{Cl^-}]} \qquad [\mathrm{HOCl}] = \frac{K_7^{\mathrm{HOBr}}K_{\mathrm{h1}}[\mathrm{BrCl}]}{[\mathrm{H^+}][\mathrm{Br^-}]} \tag{6}$$

$$K_{\mathrm{h3}} = \frac{[\mathrm{HOCl}][\mathrm{Cl^-}][\mathrm{H^+}]}{[\mathrm{Cl_2}]} \qquad [\mathrm{Cl_2}] = \frac{K_7^{\mathrm{HOBr}}K_{\mathrm{h1}}[\mathrm{Cl^-}][\mathrm{BrCl}]}{K_{\mathrm{h3}}[\mathrm{Br^-}]} \tag{7}$$

Appendix S1, continued

$$K_5^{Cl2} = \frac{[Cl_3^-]}{[Cl_2][Cl^-]} \qquad [Cl_3^-] = \frac{K_5^{Cl2} K_7^{HOBr} K_{h1}[Cl^-]^2[BrCl]}{K_{h3}[Br^-]} \quad (8)$$

$$K_a^{HOCl} = \frac{[H^+][OCl^-]}{[HOCl]} \qquad [OCl^-] = \frac{K_a^{HOCl} K_7^{HOBr} K_{h1}[BrCl]}{[H^+]^2[Br^-]} \quad (9)$$

$$K_a^{HOBr} = \frac{[H^+][OBr^-]}{[HOBr]} \qquad [OBr^-] = \frac{K_a^{HOBr} K_{h1}[BrCl]}{[H^+]^2[Cl^-]} \quad (10)$$

bromine balance:

$$[BrCl]_T = [BrCl] + [BrCl_2^-] + [Br^-]_i + \Delta[Br^-] + 2[Br_2Cl^-] + 2[Br_2] + 3[Br_3^-] + [HOBr] + [OBr^-] \quad (11)$$

$[Br^-]_i$ is the initial Br^- concentration while $\Delta[Br^-]$ is the change of $[Br^-]$ at equilibrium.

oxidizing power balance:

$$[BrCl]_T^{ox} = [BrCl] + [BrCl_2^-] + [Br_2Cl^-] + [Br_2] + [Br_3^-] + [HOBr] + [Cl_2] + [Cl_3^-] + [HOCl] + [OCl^-] \quad (12)$$

eq(11) – eq(12):

$$[Br^-]_i = [Br_2Cl^-] + [Br^-]i + \Delta[Br^-] + [Br_2] + 2[Br_3^-] - [Cl_2] - [Cl_3^-] - [HOCl] - [OCl^-] \quad (13)$$

Appendix S1, continued

put eqs (1) through (10) into eq (13):

$$[\mathrm{BrCl}] = \frac{n_1}{n_2 + n_3} \quad (14)$$

$$n_1 = -K_{h2}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2(\Delta[\mathrm{Br}^-]^2 + \Delta[\mathrm{Br}^-][\mathrm{Br}^-]_i)$$

$$n_2 = K_3^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2(\Delta[\mathrm{Br}^-]^2 + 2\Delta[\mathrm{Br}^-][\mathrm{Br}^-]_i + [\mathrm{Br}^-]_i^2)$$
$$+ K_{h1}K_{h3}[\mathrm{H}^+]^2(\Delta[\mathrm{Br}^-]^2 + 2\Delta[\mathrm{Br}^-][\mathrm{Br}^-]_i + [\mathrm{Br}^-]_i^2)$$
$$+ 2K_4^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{H}^+]^2(\Delta[\mathrm{Br}^-]^3 + 3\Delta[\mathrm{Br}^-]^2[\mathrm{Br}^-]_i + 3\Delta[\mathrm{Br}^-][\mathrm{Br}^-]_i^2 + [\mathrm{Br}^-]_i^3)$$

$$n_3 = -(K_7^{\mathrm{HOBr}}K_{h1}K_{h2}[\mathrm{Cl}^-]^2[\mathrm{H}^+]^2 + K_5^{\mathrm{Cl2}}K_7^{\mathrm{HOBr}}K_{h1}K_{h2}[\mathrm{Cl}^-]^3[\mathrm{H}^+]^2$$
$$+ K_7^{\mathrm{HOBr}}K_{h1}K_{h2}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+] + K_a^{\mathrm{HOCl}}K_7^{\mathrm{HOBr}}K_{h1}K_{h2}K_{h3}[\mathrm{Cl}^-])$$

put eq (14) and eq (1) through (10) into eq (11):

$$X_4\Delta[\mathrm{Br}^-]^4 + X_3\Delta[\mathrm{Br}^-]^3 + X_2\Delta[\mathrm{Br}^-] + X_1\Delta[\mathrm{Br}^-] + X_0 = 0 \quad (15)$$

$$X_4 = K_4^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{H}^+]^2$$

$$X_3 = K_3^{Br2}K_{h1}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2 + K_{h1}K_{h3}[\mathrm{H}^+]^2 + [\mathrm{Br}^-]_i K_4^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{H}^+]^2$$
$$+ 2K_4^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{H}^+]^2[\mathrm{BrCl}]_T$$

$$X_2 = K_{h1}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2 + K_1^{\mathrm{BrCl}}K_{h2}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2 + 4[\mathrm{Br}^-]_i K_{h1}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2$$
$$+ [\mathrm{Br}^-]_i K_{h1}K_{h3}[\mathrm{H}^+]^2 - 3[\mathrm{Br}^-]_i^2 K_4^{\mathrm{HOBr}}K_{h1}K_{h3}[\mathrm{H}^+]^2 + K_{h1}K_{h2}K_{h3}[\mathrm{H}^+]$$
$$+ K_a^{\mathrm{HOBr}}K_{h1}K_{h2}K_{h3} + K_3^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{Cl}^-][\mathrm{H}^+]^2[\mathrm{BrCl}]_T + K_{h1}K_{h3}[\mathrm{H}^+]^2[\mathrm{BrCl}]_T$$
$$+ 6[\mathrm{Br}^-]_i K_4^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{H}^+]^2[\mathrm{BrCl}]_T - 3[\mathrm{Br}^-]_i K_3^{\mathrm{Br2}}K_{h1}K_{h3}[\mathrm{H}^+]^2[\mathrm{Cl}^-]$$

Appendix S1, continued

$$X_1 = K_{h2}K_{h3}[Cl^-][H^+]2[Br^-]_i + K_1^{BrCl}K_{h2}K_{h3}[Cl^-]^2[H^+]^2[Br^-]_i - K_3^{Br2}K_{h1}K_{h3}[H^+]^2[Cl^-][Br^-]_i$$

$$+ K_{h1}K_{h3}[H^+]^2[Br^-]_i^{\,2} - 5K_4^{Br2}K_{h1}K_{h3}[H^+]^2[Br^-]_i^{\,3} + K_{h1}K_{h2}K_{h3}[H^+][Br^-]_i$$

$$+ K_a^{HOBr}K_{h1}K_{h2}K_{h3}[Br^-]_i + 2K_3^{Br2}K_{h1}K_{h3}[H^+]^2[Cl^-][BrCl]_T[Br^-]_i$$

$$+ 2K_{h1}K_{h3}[H^+]^2[BrCl]_T[Br^-]_i + 6K_4^{Br2}K_{h1}K_{h3}[H^+]^2[BrCl]_T[Br^-]_i^{\,2}$$

$$- 2K_{h1}K_{h3}[H^+]^2[Cl^-][Br^-]_i^{\,2} + K_7^{HOBr}K_{h1}K_{h2}[Cl^-]^2[H^+]^2$$

$$+ K_5^{Cl2}K_7^{HOBr}K_{h1}K_{h2}[Cl^-]^3[H^+]^2 + K_7^{HOBr}K_{h1}K_{h2}K_{h3}[Cl^-][H^+]$$

$$+ K_a^{HOCl}K_7^{HOBr}K_{h1}K_{h2}K_{h3}[Cl^-]$$

$$X_0 = K_3^{Br2}K_{h1}K_{h3}[H^+]^2[Cl^-][BrCl]_T[Br^-]_i^{\,2} + K_{h1}K_{h3}[H^+]^2[BrCl]_T[Br^-]_i^{\,2}$$

$$+ 2K_4^{Br2}K_{h1}K_{h3}[H^+]^2[BrCl]_T[Br^-]_i^{\,3} - K_3^{Br2}K_{h1}K_{h3}[H^+]^2[Cl^-][Br^-]_i^{\,3}$$

$$- K_{h1}K_{h3}[H^+]^2[Br^-]_i^{\,3} - 2K_4^{Br2}K_{h1}K_{h3}[H^+]^2[Br^-]_i^{\,4}$$

$$- K_7^{HOBr}K_{h1}K_{h2}[Cl^-]^2[H^+]^2[BrCl]_T - K_5^{Cl2}K_7^{HOBr}K_{h1}K_{h2}[Cl^-]^3[H^+]^2[BrCl]_T$$

$$- K_7^{HOBr}K_{h1}K_{h2}K_{h3}[Cl^-][H^+][BrCl]_T - K_a^{HOCl}K_7^{HOBr}K_{h1}K_{h2}K_{h3}[Cl^-][BrCl]_T$$

$$+ K_7^{HOBr}K_{h1}K_{h2}[Cl^-]^2[H^+]^2[Br^-]_i + K_5^{Cl2}K_7^{HOBr}K_{h1}K_{h2}[Cl^-]^3[H^+]^2[Br^-]_i$$

$$+ K_7^{HOBr}K_{h1}K_{h2}K_{h3}[Cl^-][H^+][Br^-]_i + K_a^{HOCl}K_7^{HOBr}K_{h1}K_{h2}K_{h3}[Cl^-][Br^-]_i$$

This 4^{th} power equation, eq (15), of $\Delta[Br^-]$ can be solved by MathCad 8 after dividing all terms by X_4. Then, [BrCl] can be determined by eq (14). Subsequently, concentrations of all other species can be determined by eqs (1) through (10).