COMMENTS

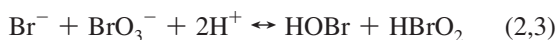## Comment on "Simple KBrO₃, H₂SO₄ Batch Oscillator"

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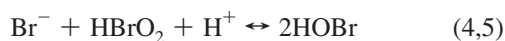
Rachwalska[1] reported oscillations in redox potential at a Pt-electrode in the well-stirred, aqueous, batch system KBrO₃ and H₂SO₄. The KBrO₃ contained ∼0.02% Br⁻ impurity. We are concerned that the experimentally observed oscillations in redox potential result from some form of physical/chemical artifact and should be treated with care. The major cause of our concern is that we see no basis for their occurrence in homogeneous FKN[2] oxybromine chemistry. However, because we have no experimental evidence for our concern, we accept at face value the experimentally observed oscillations.
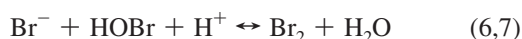
The origin of these oscillations in homogeneous chemical dynamics is supported by Rachwalska[1] using oscillatory simulations based on the FKN chemistry, given below using the author's numbering and rate parameters.
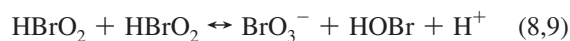
$$Br^- + BrO_3^- + 2H^+ \leftrightarrow HOBr + HBrO_2 \quad (2,3)$$

$$k_2 = 2 \ M^{-3} \ s^{-1} \qquad k_3 = 3.3 \ M^{-1} \ s^{-1}$$

$$Br^- + HBrO_2 + H^+ \leftrightarrow 2HOBr \quad (4,5)$$

$$k_4 = 2.0 \times 10^6 \ M^{-2} \ s^{-1} \qquad k_5 = 2.0 \times 10^{-5} \ M^{-1} \ s^{-1}$$

$$Br^- + HOBr + H^+ \leftrightarrow Br_2 + H_2O \quad (6,7)$$

$$k_6 = 2.3 \times 10^9 \ M^{-2} \ s^{-1} \qquad k_7 = 2.0 \ s^{-1}$$

$$HBrO_2 + HBrO_2 \leftrightarrow BrO_3^- + HOBr + H^+ \quad (8,9)$$

$$k_8 = 3.0 \times 10^3 \ M^{-1} \ s^{-1} \qquad k_9 = 7.5 \times 10^{-9} \ M^{-2} \ s^{-1}$$

$$BrO_3^- + HBrO_2 + H^+ \leftrightarrow Br_2O_4 + H_2O \quad (10,11)$$
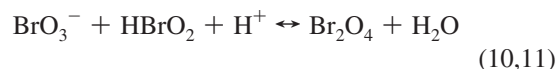
$$k_{10} = 33.0 \ M^{-2} \ s^{-1} \qquad k_{11} = 2200 \ s^{-1}$$

$$Br_2O_4 \leftrightarrow 2BrO_2 \quad (12,13)$$

$$k_{12} = 7.4 \times 10^4 \ s^{-1} \qquad k_{13} = 1.4 \times 10^9 \ M^{-1} \ s^{-1}$$

However, there are a number of inconsistencies in the description of the simulations based on this mechanism and leading to oscillation. It is stated that the rate constants are taken from Field and Försterling[3] (FF). However, several rate constants are significantly different from the FF values. Note that the set of FF rate constants is thermodynamically consistent such that a change in one rate constant should be compensated by changes in another rate constant(s). Furthermore, and most importantly, there are a
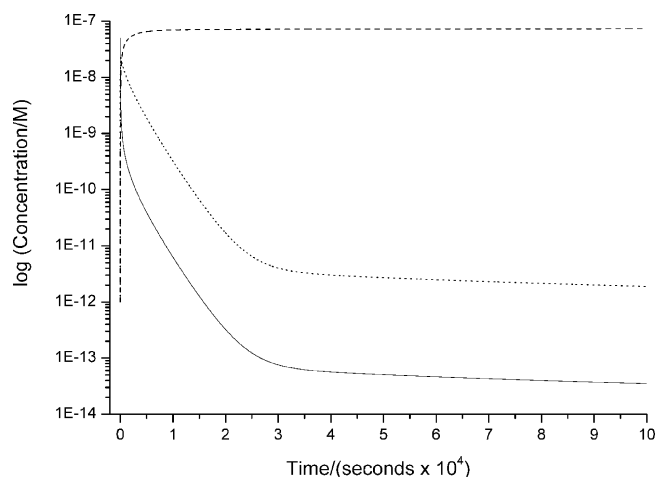

Figure 1. Concentration vs time curves: Br⁻ (—), Br₂ (•••), and HOBr (---), calculated according to eqs 14−21 with the rate constants listed in stoichiometries 2−13. Initial concentrations are the same as in ref 1 [BrO₃⁻]₀ = 0.0125 mol dm⁻³, [H⁺]₀ = 0.64 mol dm⁻³, [Br⁻]₀ = 5.0 × 10⁻⁸ mol dm⁻³. For all other species the initial concentration is 1.0 × 10⁻¹² mol dm⁻³. Integration was performed by XPP, GEAR method with a relative error tolerance 1.0 × 10⁻¹⁰.

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number of discrepancies between the FKN stoichiometries given above and the mass-action rate equations displayed by the author.

The correct FKN mass-action rate equations are given below in the author's notation of $a = [Br^-]$, $b = [BrO_3^-]$, $c = [HOBr]$, $d = [HBrO_2]$, $e = [BrO_2]$, $f = [Br_2]$, $g = [Br_2O_4]$, $h = [H^+]$, and $w = [H_2O]$. Note the author misidentifies f as $[Br]$ rather than $[Br_2]$.

$$da/dt = -2abh^2 + 3.3cd - 2 \times 10^6 adh + 2 \times 10^{-5}c^2 - 2.3 \times 10^9 ach + 2f \quad (14)$$

$$db/dt = -2abh^2 + 3.3cd + 3 \times 10^3 d^2 - 7.5 \times 10^{-9} bch - 33bdh + 2200g \quad (15)$$

$$dc/dt = 2abh^2 - 3.3cd + 2 \times 2 \times 10^6 adh - 2 \times 2 \times 10^{-5}c^2 - 2.3 \times 10^9 ach + 2f + 3 \times 10^3 d^2 - 7.5 \times 10^{-9} bch \quad (16)$$

$$dd/dt = 2abh^2 - 3.3cd - 2 \times 10^6 adh + 2 \times 10^{-5}c^2 - 2 \times 3 \times 10^3 d^2 + 2 \times 7.5 \times 10^{-9} bch - 33bdh + 2200g \quad (17)$$

$$de/dt = 2 \times 7.4 \times 10^4 g - 2 \times 1.4 \times 10^9 e^2 \quad (18)$$

$$df/dt = 2.3 \times 10^9 ach - 2f \quad (19)$$

$$dg/dt = 33bdh - 2200g - 7.4 \times 10^4 g + 1.4 \times 10^9 e^2 \quad (20)$$

$$dh/dt = -2 \times 2abh^2 + 3.3 \times 2cd - 2 \times 10^6 adh + 2 \times 10^{-5}c^2 - 2.3 \times 10^9 ach + 2f + 3 \times 10^3 d^2 - 7.5 \times 10^{-9} bch - 33bdh + 2200g \quad (21)$$

Comparison of eqs 14−21 with the author's equations reveals a number of discrepancies, several of which introduce spurious autocatalyses or nonlinearities into the model.

(1) The d*a*/d*t* Equation

The final term in this equation according to the author is $+2f^2w$. This term should instead be $2f$, with f defined as $[Br_2]$ rather than $[Br]$. Indeed, the author consistently (also in the d*c*/d*t*, d*f*/d*t*, and d*h*/d*t* equations) writes the differential equations as if stoichiometry (6,7) is (6′,7′).

$$Br^- + HOBr + H^+ \leftrightarrow 2Br + H_2O \quad (6′,7′)$$
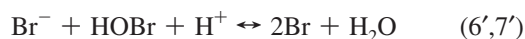
This spurious quadratic term ($2f^2w$) introduces a new nonlinearity. Furthermore, the FKN rate constants are given by all authors we know of (including FF) with the activity of water assumed to be one. Thus there is no need of a *w*-dot equation, and the rates of terms in the author's equations involving water are 55 times too fast.

(2) The d*c*/d*t* Equation

The "+" of the second term (+3.3 cd) should be "−", and this introduces a spurious (first-order) autocatalysis in *c* into the model. The "+" of the fourth term ($+4c^2 \times 10^{-5}$) also should be "−", introducing another spurious (second-order) autocatalysis in *c*. Furthermore, the last term, $-7.5bch \times 10^9$, should be $-7.5bch \times 10^{-9}$! This is a factor of 10^{18} too large and may lead to the unusual concentration axis in Figures 4 and 5. This error is consistent, also appearing in the d*b*/d*t*, d*d*/d*t*, and d*h*/d*t* equations.

(3) The d*h*/d*t* Equation

The first term, $+33bdh$, should be $-33bdh$. This introduces the last spurious (first-order) autocatalysis. The term $-2abh^2$ should be $-4abh^2$. The term $3000d^2$ corresponding to eq 8 is left out of this equation.

We have numerically integrated eqs 14−21 using the author's initial conditions for $[BrO_3^-]$, $[Br^-]$, $[H_2SO_4]$ and found no oscillations. See Figure 1.

Essentially identical results were obtained using MAT-LAB,[4] XPP,[5] and a FORTAN program based on the LSODE[6] integrator. We see no reason to expect oscillations in this mechanism in a batch reactor even with consideration of the Br^- contamination of the $KBrO_3$. The very slow final growth of HOBr and accompanying decline in Br_2 and Br^- may result from the reaction of HOBr with BrO_3^- in reaction 9 followed by reaction 4.

Finally, we wonder what error parameter was used in the simulations. With a spread of perhaps 10^{10} in the values of various chemical species, and the presence of very small concentrations ($\sim 10^{-12}$ mol dm^{-3}), a very tight error parameter would be required to avoid numerical artifacts.

It seems that because of the above listed uncertainties in the simulations reported by the author, the numerical result cannot be taken as support for the purely chemical origin of the observed oscillations. We suggest that the experimental appearance of oscillation is likely an artifact, possibly resulting from metal-ion (e.g., Mn or Fe) impurities on the ppm level in the commercial H_2SO_4 used, atmospheric O_2 introduced by the stirring, or surface phenomena on the Pt electrode. The strong stirring effect observed suggests some physical contribution to the appearance of oscillation.

References and Notes

(1) Rachwalska, M. *J. Phys. Chem A* **2009**, *113*, 1060.
(2) Field, R. J.; Kőrös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
(3) Field, R. J.; Försterling, H.-D. *J. Phys. Chem.* **1986**, *90*, 5400.
(4) http://www.mathworks.com.
(5) http://www.math.pitt.edu/~bard/xpp/xpp.html.
(6) http://www.llnl.gov/CASC/odepack/.