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COMMENTS

Comment on “Kinetics and Mechanism of Nitrite Oxidation by HOBr/BrO$^-$ in Atmospheric Water and Comparison with Oxidation by HOCl/ClO$^-$”

Robert H. Becker,[†] Kara E. Huff Hartz,[‡] and
Dale W. Margerum*

*Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907-2084*

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Lahoutifard et al. recently reported the kinetics of the HOBr/NO$_2^-$ reaction system in NaCl and Na$_2$SO$_4$ media at varying ionic strengths.[1] They measured the kinetics of this reaction system and proposed a reaction mechanism in which HOBr and NO$_2^-$ are in equilibrium with BrNO$_2$. The rate-determining step in the proposed mechanism is the BrNO$_2$/NO$_2^-$ reaction to produce N$_2$O$_4$ and Br$^-$. They also compared the oxidations of NO$_2^-$ via HOCl, HOBr, Cl$_2$, and Br$_2$.

We address the overlooked complexities of this reaction system under the conditions set by Lahoutifard et al. when NaCl is used for ionic strength control. HOBr and Cl$^-$ react in a reversible, [H$^+$]-dependent equilibrium to produce bromine chloride (BrCl) as well as HOCl and Br$^-$ (eqs 1 and 2).[2] BrCl is a well-known and important species in many areas, including wastewater treatment[3,4] and Arctic ozone chemistry.[2,5]

$$\mathrm{HOBr} + \mathrm{Cl}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{BrCl} + \mathrm{H_2O} \qquad K_1 = 7.7 \times 10^3\ \mathrm{M}^{-2} \quad (1)$$

$$\mathrm{BrCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{HOCl} + \mathrm{Br}^- + \mathrm{H}^+ \qquad K_2 = 8.7 \times 10^{-10}\ \mathrm{M}^2 \quad (2)$$

Because Lahoutifard et al. used Cl$^-$ concentrations as large as 2 M, the BrCl and BrCl$_2^-$ concentrations may be large enough to influence spectral as well as kinetic observations at the pH values used in the study. HOCl and Br$^-$ are also in equilibrium with HOBr and Cl$^-$,[2] and under the conditions of high [Cl$^-$] (ranging to 2 M) in this study, millimolar concentrations of HOCl and Br$^-$ can be present. Furthermore, BrCl, HOCl, HOBr, and Cl$^-$ are in equilibrium with several other species, such as BrCl$_2^-$ and Br$_2$Cl$^-$. In basic solutions, Br$^-$, OCl$^-$, and HOCl can have appreciable concentrations even at higher pH values.

Evidence of species such as BrCl and HOCl is shown in their Figure 1a.[1] This spectrum does not resemble that of HOBr as they suggested (where $\epsilon = 95$ M^{-1} cm^{-1} at $\lambda_{\max} = 260$ nm).[6] We believe that the large absorbance observed below 300 nm is primarily due to BrCl$_2^-$, which is in equilibrium with BrCl at high chloride concentrations.[2] The molar absorptivity of BrCl$_2^-$ at 232 nm is 37 200 M^{-1} cm^{-1}, and we calculate that the absorbance is 0.56 at this wavelength due to BrCl$_2^-$ under the 1.0 M Cl$^-$ conditions of Lahoutifard et al.[2] This accounts for a significant part of the band labeled (a). We calculate this absorbance after the subtraction of the approximately 0.05 background absorbance shown in the figure, the origin of which is unknown.

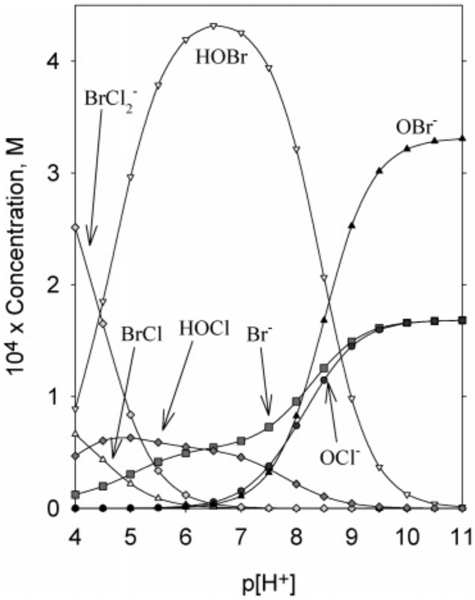

Figure 1. Conditions: [Br]$_T$ = 0.50 × 10^{-3} M, where [Br]$_T$ = ([Br$^-$] + [BrCl] + [BrCl$_2^-$] + 2[Br$_2$Cl$^-$] + 2[Br$_2$] + 3[Br$_3^-$] + [HOBr] + [OBr$^-$]), and [NaCl] = 1.0 M, 25.0 °C. Cl$_2$, Cl$_3^-$, Br$_2$, Br$_3^-$, and Br$_2$Cl$^-$ are minor species under these conditions and are not shown in the graph for clarity.

As shown by Liu and Margerum,[2] at least 13 species can be present in an aqueous solution with conditions comparable to that of the equilibrium conditions of Lahoutifard et al. Figure 1 (generated from equations given in ref 7) shows the main species in equilibrium at p[H$^+$] 4−11 and 0.5 mM [Br]$_T$ (where [Br]$_T$ = [Br$^-$] + [BrCl] + [BrCl$_2^-$] + 2[Br$_2$Cl$^-$] + 2[Br$_2$] + 3[Br$_3^-$] + [HOBr] + [OBr$^-$]). These concentrations are representative of those used by Lahoutifard et al. Figure 1 is constructed by assuming negligible initial bromide; however, Br$^-$ and HOCl are generated by the reaction mixture (eq 2). This distribution will also vary considerably with [Br]$_T$. When [Br]$_T$ is low, the system will equilibrate with more HOCl and OCl$^-$ present, whereas at higher [Br]$_T$, the HOBr/OBr$^-$ species are favored. As shown by our equilibrium distribution in Figure 1, HOCl/OCl$^-$ are major species that were not considered by Lahoutifard et al., and these species will influence the kinetics measured in their study.

This complex equilibrium system causes the unusual trend in the pK_a determination of HOBr in NaCl media as a function of ionic strength (0.0 to 2.0 M) reported by Lahoutifard et al. in their Figure 2.[1] The trend shown is contrary to the Debye−Hückel−Brønsted−Davies equation.[8,9] At ionic strengths from 0 to 1 M, the pK_a would be expected to decrease, as is the case for their Na$_2$SO$_4$ solutions. In the NaCl solutions, as [Cl$^-$] increases, more and more [OBr$^-$] is shifted toward BrCl$_2^-$, an unreactive species. When titrating with acid to generate HOBr,

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* Corresponding author. E-mail: margerum@purdue.edu.

[†] Current address: ExxonMobil Research and Engineering Co., Paulsboro, NJ 08066.

[‡] Current address: Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213.

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as was done by Lahoutifard et al., it would appear that the pK_a increases as the ionic strength of the NaCl solution increases. In fact, the influence of other species in the solution is appreciable. This causes the loss of OBr^-, which would cause the pK_a to appear to increase as [NaCl] increases. For these reasons, we believe that the pK_a values measured in NaCl are not accurate.

Finally, they make comparisons between the oxidations of NO_2^- via Cl_2, Br_2, HOBr, and HOCl (Lahoutifard et al., Figure 8).[1] In their mechanism, they show that HOBr is in rapid preequilibrium with $BrNO_2$ and the $BrNO_2/NO_2^-$ reaction is observable (i.e., the rate-determining step).[1] This is the same as the Br_2/NO_2^- system proposed by Pendlebury and Smith,[10] where Br_2 and $BrNO_2$ are preequilibrium species and $BrNO_2$ reacts with NO_2^- in the rate-determining step. The chlorine analogues[11,12] are similar in that HOCl, Cl_2, and $ClNO_2$ are all preequilibrium species in the $HOCl/NO_2^-$ or Cl_2/NO_2^- systems and that the rate-determining step is the $ClNO_2/NO_2^-$ reaction. Lahoutifard et al. suggest, by plotting initial rates versus pH in their Figure 8, that the rate of NO_2^- oxidation by HOCl, Cl_2, Br_2, or HOBr can be observed and that each of the four species will have vastly different initial rates when reacting with NO_2^-.[1] Because these species are in rapid preequilibrium with either $BrNO_2$ or $ClNO_2$, which react to oxidize NO_2^- in the rate-determining step, this suggestion cannot be correct.

By using the equilibrium between HOBr and Br_2[13] (the same applies to the chlorine analogues),[14] one can demonstrate mathematically that the rates of the Br_2/NO_2^- system and the $HOBr/NO_2^-$ system are the same, as must be the case because they each have the same rate-determining step. The large differences in the $HOBr/NO_2^-$ and Br_2/NO_2^- reaction rates (indicated in Figure 8 by Lahoutifard et al.) merely represent the differences in the species distribution of HOBr and Br_2 at the pH values shown. Although they apply these rates to gas-phase chemistry, where equilibria may not hold, their aqueous-phase assumptions necessitate that the HOX and X_2 (X = Br and Cl) species are in rapid preequilibrium. Comparisons between the $BrNO_2/NO_2^-$ reaction and the $ClNO_2/NO_2^-$ reaction are warranted and informative. However, the comparisons between like-halogen systems, which they also discussed, are not helpful because all rates represent the same reaction ($XNO_2 + NO_2^- \rightarrow N_2O_4 + X^-$ where X = Br and Cl) with only differing equilibrium concentrations.

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