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

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Becker et al. claim that aqueous chloride media containing bromide contains at least 13 species under conditions comparable to those used in our study and that these equilibria may complicate the analysis of kinetic and equilibrium data. However, under the relevant pH conditions (>6.5) of almost all of our experiments, their Figure 1 shows that only five species have appreciable concentrations: HOBr, OBr^-, Br^-, HOCl, and OCl^-. Of these five, interference from the two Cl(I) species is of concern. Fortunately, the formation of both HOCl and OCl^- is effectively suppressed in the presence of even small amounts of added bromide. For kinetics experiments at pH ≥ 7 (corresponding to 34 of our 36 independent kinetics experiments in chloride media), we prepared Br(I) solutions by the addition of a 10-fold excess of Br^- to a 1 mM solution of OCl^-.[1] Under these conditions, the concentrations of both Cl(I) species are negligible, Figure 1a; therefore, we may neglect their contributions in our kinetic analysis. Although excess bromide was not present in the remaining two kinetics experiments at 6.5 ≤ pH ≤ 7.0 in chloride media, their rate constants are consistent with the rest of our data. (See Figure 6a in ref 2.)

Even in the absence of added Br^-, the formation of other halogen-containing species is suppressed at high Br(I) concentrations. Figure 1b shows the speciation for 20 mM Br(I) in 1 M NaCl, representative of conditions used in our acidimetric titration experiments. HOCl and OCl^- make minor contributions. However, Becker et al. correctly point out that $BrCl_2^-$ contributes to the UV spectrum shown in ref 2, captioned “UV−vis spectra of Br(I) in 1.0 M NaCl: (a) pH = 6”. Because of its much larger extinction coefficient, $BrCl_2$ dominates the spectrum even though its concentration is much smaller than that of HOBr. We used kinetics data across the entire range of pH used (6.5 ≤ pH ≤ 10.0) and [NO_2^-] (0.01−0.04 M) to obtain fitted values of k_1, K_1, K_w, and K_a, where K_a corresponds to the acid dissociation constant for HOBr. For the reasons described above, we maintain that $HOBr^-$ and OBr^- are the only significant X(I) species present in our solutions under these conditions. The fitted values for pK_a, 8.27 and 8.50 in 0.10 M NaCl and 1.0 M NaCl, respectively (Table 1)[2], are slightly lower than those determined independently by acidimetric titration (8.58 and 8.80) in the range of 7 ≤ pH ≤ 11 with and without added bromide. The differences may indeed be caused by a slightly more complex speciation of X(I) in the titration experiments.

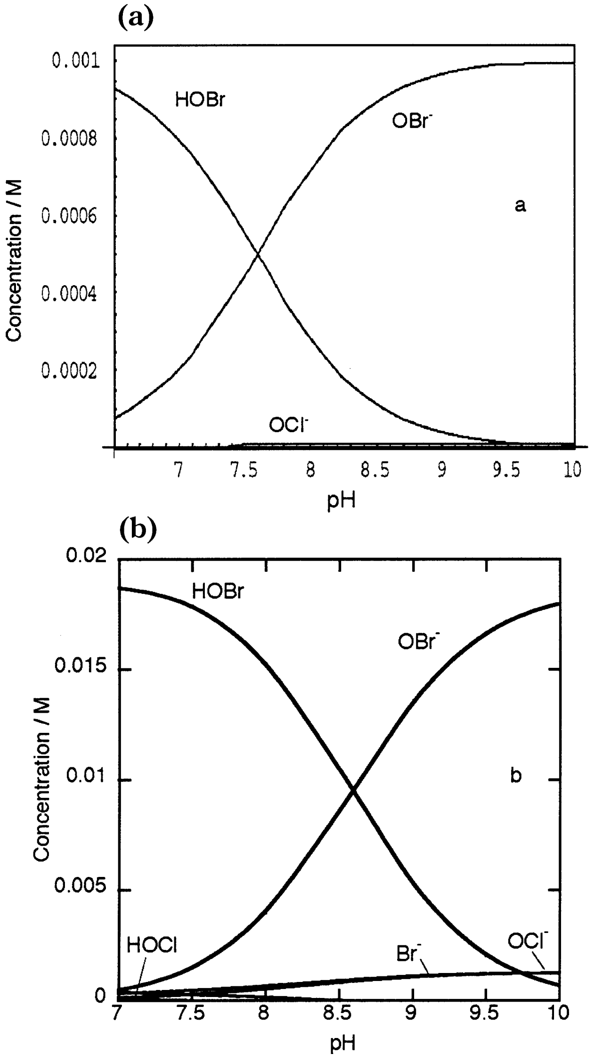

Figure 1. Speciation of (a) 1.0 mM Br(I) in the presence of 9.0 mM Br^-; and (b) 20 mM Br(I) in the absence of added bromide. Calculations were performed with Mathematica, using the same published equilibrium constants as Becker et al. (25 °C, $I = 1.0$ M).[5] Frame a corresponds to conditions used in all but two of our kinetics experiments in chloride media. Frame b corresponds to the conditions used in our acidimetric titrations.

Becker et al. assert that the rates of the HOBr/NO_2^- and Br_2/NO_2^- reactions are mathematically the same and that large differences in the reaction rates “represent the differences in the species distribution of HOBr and Br_2 at the pH values shown”. We agree that both reactions proceed via the same rate-determining step (the reaction of $BrNO_2$ with NO_2^-). The reaction rate is a function of both the rate constant for this step and the concentration of the $BrNO_2$ intermediate. Because the latter varies with Br(I) speciation, the rates are not mathematically the same, indeed, this is the point of our Figure 8.[2] Finally, we made no attempt to apply these solution phase rates to gas-phase chemistry.[2]

We regret that the dominant equilibria involving Br(I) in chloride media were not presented as explicitly as they could have been in our original paper.[3] The calculated speciation is identical to that determined experimentally by Barcellos da Rosa and Zetzsch.[4] Nevertheless, we believe our kinetic experiments and analyses are valid.[3]

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References and Notes

(1) The Experimental Section of our original paper[2] described two methods for the preparation of hypobromite solutions: (1) titration of Br_2 with $AgNO_3$ to yield chloride- and bromide-free BrO^- and (2) addition of aqueous sodium hypochlorite to aqueous bromide, to yield an equimolar amount of hypobromite in the presence of bromide. In the latter method, a mistranslation gave the incorrect impression that bromide was not present in excess, when in fact $[Br^-] = 9[BrO^-]$.

(2) Lahoutifard, N.; Lagrange, P.; Lagrange, J.; Scott, S. L. J *Phys. Chem. A* **2002**, *106*, 11891−11896.

(3) In particular, there is an unfortunate error in the caption to Figure 3 in our paper[2], which should read “Speciation of Br(I) in 1.0 M Na_2SO_4”.

(4) Barcellos da Rosa, M.;Zetzsch, C. *J. Aerosol Sci.* **2001**, *32*, S311−S312.

(5) Liu, Q.; Margerum, D. W. *Environ. Sci. Technol.* **2001**, *35*, 1127−1133.