ADDITIONS AND CORRECTIONS

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Jennie L. Thomas, Angel Jimenez-Aranda, Barbara J. Finlayson-Pitts,* and Donald Dabdub* : Gas-Phase Molecular Halogen Formation from NaCl and NaBr Aerosols: When Are Interface Reactions Important?

Page 1859. The kinetic salt effect plays an important role in determining the rates of reactions for two ions undergoing a reaction in a solution with high ionic strength.[1] For kinetics modeling, an approximation is needed to estimate how reaction rates change with salt concentration as discussed by Knipping and Dabdub.[2]

Briefly, we present an overview of the interface reaction used to describe halogen production from aerosols. The interface reaction rate is defined by

$$R_{\mathrm{int}} = \left(\frac{r^2}{3D_{\mathrm{g}}} + \frac{4r}{3\upsilon\gamma}\right)^{-1}[\mathrm{A}]_{\mathrm{g}} \qquad (1)$$

where

$$\gamma = \phi\gamma'\beta_{\mathrm{X}}[\mathrm{X}^-]_{\mathrm{aq}} \qquad (2)$$

is the overall surface reaction probability, r is the aerosol radius, and D_g is the gas-phase diffusion coefficient. The mean molecular speed of the colliding gas is represented by υ. γ' denotes the probability that X^- and A react when these species collide, with allowed values from 0 and 1. The expression $\beta_X[X^-]_{aq}$ is the fraction of the droplet surface covered by the X^- halide ion estimated from molecular dynamics simulations[3−5] with a specific β_X parameter (with units of inverse concentration) for each sodium halide. This fraction is always significantly less than one so that γ does not exceed unity.

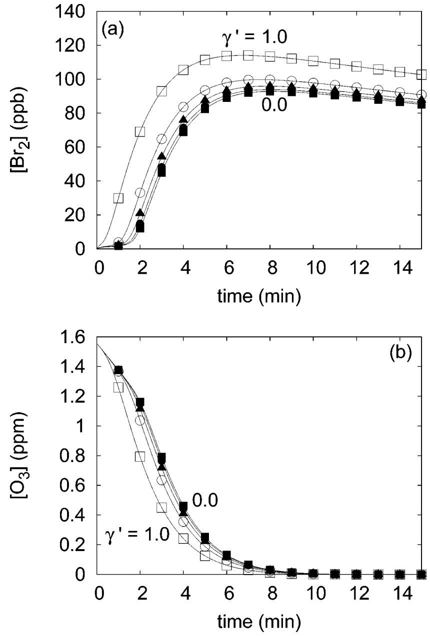

Figure 1. Predicted gas-phase Br_2 and O_3 as a function of γ' for the NaBr + OH case: ■, $\gamma' = 0.0$; ●, $\gamma' = 0.003$; ▲, $\gamma' = 0.01$; ○, $\gamma' = 0.03$; □, $\gamma' = 1.0$. The expression relating γ' to the interface reaction rate is defined in eqs 1 and 2. (Corresponds to Figure 4 in ref 6.)

Due to an error in implementing the kinetic salt effect (KSE), the results from studies using the model of aerosol, gas, and interfacial chemistry (MAGIC) have recently been remodeled with the following minor corrections.

Revisiting the sensitivity study presented by Thomas and coworkers in 2006,[6] the results for NaBr aerosols interacting with OH changes slightly upon correction of the KSE. Figures 1−3 (referred to as Figures 4−6 in the original study) show the corrected results. First, Figure 1a shows the predicted Br_2 concentration versus time for several interface reaction prob-

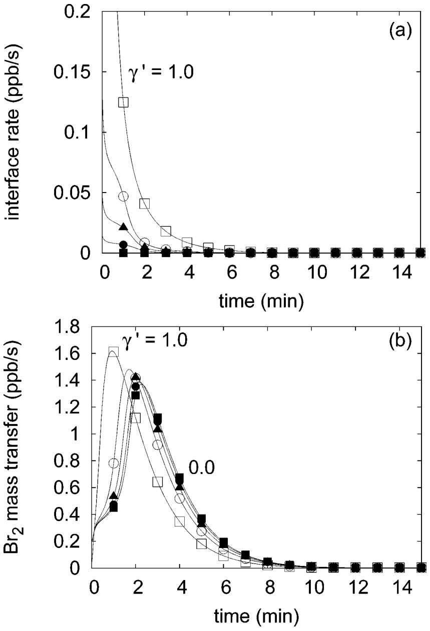

Figure 2. Predicted interface reaction rate and Br_2 mass transfer from the drop as a function of γ' for the NaBr + OH case. Positive mass transfer rate corresponds to net flux towards the gas phase: ■, $\gamma' = 0.0$; ●, $\gamma' = 0.003$; ▲, $\gamma' = 0.01$; ○, $\gamma' = 0.03$; □, $\gamma' = 1.0$. The expression relating γ' to the interface reaction rate is defined in eqs 1 and 2. (Corresponds to Figure 5 in ref 6.)

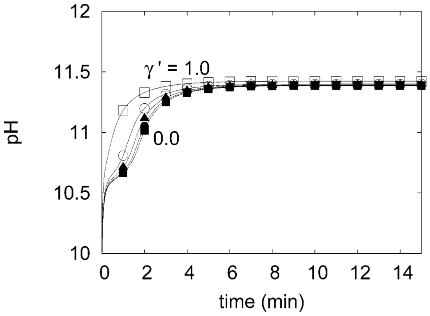

Figure 3. Predicted pH as a function of γ' for the NaBr + OH case: ■, $\gamma' = 0.0$; ●, $\gamma' = 0.003$; ▲, $\gamma' = 0.01$; ○, $\gamma' = 0.03$; □, $\gamma' = 1.0$. The expression relating γ' to the interface reaction rate is defined in eqs 1 and 2. (Corresponds to Figure 6 in ref 6.)

abilities. With correction of the KSE, the aqueous phase chemistry proceeds faster and the interface reaction is predicted to be even less important. The original work concluded that an interface reaction is only important at high interface reaction probabilities, but at longer times the bulk aqueous-phase chemistry dominates the behavior of the system. This conclusion becomes stronger with these corrected results and it is clear that an interface reaction is unlikely to be important for NaBr aerosols upon reaction with OH.

Figure 1b shows the concentration of O_3 versus time as a function of the reaction probability. Ozone destruction is more rapid due to faster Br_2 production in the aqueous phase. This is consistent with the well-known bromine initiated ozone destruction cycle. Figure 2a shows that the interface reaction only proceeds at a significant rate for short reaction times and high reaction probabilities. Br_2 mass transfer is faster out of the aerosol in the new results due to the faster Br_2 forming aqueous-phase chemistry. Finally, Figure 3 shows that pH is predicted to be relatively independent of interface reaction probability, further confirming that an interface reaction is not important for the behavior of this system.

For chloride chemistry,[2,6,7] the aqueous phase does not contribute significantly to chlorine production and there was a negligible difference in Cl_2 production upon correction of the KSE. In the case of NaBr aerosols interacting with O_3,[3,6] the difference in peak Br_2 concentrations is insignificant in the range of realistic interface reaction probabilities.[3] Remodeling Hunt et al.'s 2004 experiments changes the best fit γ by less than the reported error.

In summary, correction of the KSE treatment makes a small change in the predictions for the NaBr + OH[6] system. It does not significantly alter any of the previoius results on OH + NaCl[2,6,7] or on O_3 + NaBr.[3,6]

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References and Notes

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Jerzy L. Gębicki* and Magdalena Maciejewska: Reactions of 2,2′-Azinobis-(3-ethylbenzthiazoline-6-sulfonate) dianion, $ABTS^{2-}$, with $^{\bullet}OH$, $(SCN)_2^{\bullet -}$, and Glycine or Valine Peroxyl Radicals

Page 2122. In this paper reactions 13, 20, and 21 are erroneously written; however, this influences neither the results nor the conclusions. These hydrogen abstraction (from an amino acid molecule) reactions should be written as follows:

$$^{\bullet}OH + Val \rightarrow H_2O + Val^{\bullet} \qquad k_{13} = 1.2 \times 10^{9}\ M^{-1}\ s^{-1} \tag{13}$$

$$^{\bullet}OH + Gly \rightarrow H_2O + GlyC^{\bullet} \qquad k_{20} = 1.0 \times 10^{8}\ M^{-1}\ s^{-1} \tag{20}$$

$$^{\bullet}OH + Gly \rightarrow H_2O + GlyN^{\bullet} \qquad k_{21} = 6.5 \times 10^{7}\ M^{-1}\ s^{-1} \tag{21}$$

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