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Bromamine decomposition revisited: A holistic approach for analyzing acid and base catalysis kinetics

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Abstract

Chloramine chemistry is complex, with a variety of reactions occurring in series and parallel and many that are acid or base catalyzed, resulting in numerous rate constants. Bromide presence increases system complexity even further with possible bromamine and bromochloramine formation. Therefore, techniques for parameter estimation must address this complexity through thoughtful experimental design and robust data analysis approaches. The current research outlines a rational basis for constrained data fitting using Brønsted theory, application of the microscopic reversibility principle to reversible acid or base catalyzed reactions, and characterization of the relative significance of parallel reactions using fictive product tracking. This holistic approach was used on a comprehensive and well-documented data set for bromamine decomposition, allowing new interpretations of existing data by revealing that a previously published reaction scheme was not robust; it was not able to describe monobromamine or dibromamine decay outside of the conditions for which it was calibrated. The current research's simplified model (3 reactions, 17 constants) represented the experimental data better than the previously published model (4 reactions, 28 constants). A final model evaluation was conducted based on representative drinking water conditions to determine a minimal model (3 reactions, 8 constants) applicable for drinking water conditions.

TOC/ABSTRACT ART

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Keywords

monobromamine; dibromamine; haloamines; brønsted; catalysis

INTRODUCTION

Free chlorine is a popular distribution system disinfectant choice in the United States (US),^{1–4} but because of Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules implementation, many US utilities now use combinations of chlorine and chloramines to avoid excessive regulated disinfection by-product formation, including trihalomethanes and haloacetic acids.^{3, 5}

Chloramine chemistry is complex, with a variety of reactions taking place in series and parallel. Some reactions are acid or base catalyzed, which greatly increases the number of rate constants that must be estimated in mechanistic kinetic models of natural waters where carbonate and phosphate are present. When bromide is present in significant concentrations, the system complexity increases even further with possible bromamine and bromochloramine formation under drinking water conditions.⁶ Therefore, it is impossible practically to generate enough experimental data to estimate rate constants in kinetic models solely using data fitting techniques. Thus, a rational basis for constraining the number of parameters that must be calibrated simultaneously is needed. The current research outlines such a holistic approach using Brønsted theory, application of the microscopic reversibility principle to reversible acid or base catalyzed reactions, and characterization of the relative significance of parallel reactions using fictive product tracking. The approach is demonstrated on a comprehensive and well-documented data set for a relatively simple system examining bromamine decomposition.^{7, 8}

The holistic approach allowed new interpretations of existing data, revealing that the reaction scheme employed in previous research was not robust; it was not able to simulate monobromamine (NH_2Br) or dibromamine (NHBr_2) decay outside of the conditions for which it was calibrated (e.g., Figure 1). Thus, a revised reaction scheme for bromamine

decomposition was developed that not only reduces the number of estimated parameters but is also robust in its ability to describe data over a significant range of experimental conditions. As the goal of model development is ultimately its practical application, the revised reaction scheme was further evaluated to arrive at a minimal model applicable to drinking water practice. The revision of the previously published bromamine decomposition reaction scheme and associated new interpretations of existing data is important as the reaction scheme has already been incorporated into models seeking to further extend bromamine chemistry.⁹

EXPERIMENTAL SECTION

Data Set

No new experimental data were generated. Rather, the data set was taken from stopped-flow experiments conducted by Lei, et al.⁷ and Lei⁸. A summary of experimental initial conditions is provided in supporting information (SI), Table S2, and the reader is directed to Lei, et al.⁷ and Lei⁸ for further data set details.

Using absorbance values at 232 nm (A_{232}) and 278 nm (A_{278}) in Appendix A of Lei⁸, NH_2Br and NHBr_2 concentrations were calculated from molar absorptivity ($\epsilon_{\text{NH}_2\text{Br}, 232\text{ nm}} = 82\text{ M}^{-1}\text{ cm}^{-1}$; $\epsilon_{\text{NH}_2\text{Br}, 278\text{ nm}} = 425\text{ M}^{-1}\text{ cm}^{-1}$; $\epsilon_{\text{NHBr}_2, 232\text{ nm}} = 2,000\text{ M}^{-1}\text{ cm}^{-1}$; $\epsilon_{\text{NHBr}_2, 278\text{ nm}} = 715\text{ M}^{-1}\text{ cm}^{-1}$)⁷ and Eq. 1 and Eq. 2 which are appropriate for a 1 cm absorbance cell path length:

$$[\text{NHBr}_2] = \frac{A_{278}\epsilon_{\text{NH}_2\text{Br}, 232\text{ nm}} - A_{232}\epsilon_{\text{NH}_2\text{Br}, 278\text{ nm}}}{\epsilon_{\text{NH}_2\text{Br}, 232\text{ nm}}\epsilon_{\text{NHBr}_2, 278\text{ nm}} - \epsilon_{\text{NHBr}_2, 232\text{ nm}}\epsilon_{\text{NH}_2\text{Br}, 278\text{ nm}}} \quad (1)$$

$$[\text{NH}_2\text{Br}] = \frac{A_{232} - [\text{NHBr}_2]\epsilon_{\text{NHBr}_2, 232\text{ nm}}}{\epsilon_{\text{NH}_2\text{Br}, 232\text{ nm}}} \quad (2)$$

Model Reaction rate expressions and stoichiometry

The bromamine decomposition model of Lei, et al.⁷ served as the starting point for the current research (Table 1) along with the hypobromous acid (HOBr) and ammonia (NH_3) reaction to form NH_2Br ($\text{HOBr} + \text{NH}_3 \rightarrow \text{NH}_2\text{Br}$; $k = 7.5 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$).¹⁰ The model is composed of a general acid-catalyzed NH_2Br disproportionation reaction (Table 1, reaction 1), the associated general acid-catalyzed reverse of reaction 1 (Table 1, reaction -1), and two general base-catalyzed bromamine decomposition reactions (Table 1, reactions 2 and 3). Equilibrium constants of catalytic species were taken from published literature (Table 2) and adjusted to the ionic strength used by Lei, et al.⁷ (0.1 M). Model reactions (Table 1) and required equilibrium equations (Table 2) were implemented into Aquasim.¹¹

Brønsted Theory

Brønsted relationship.—Individual catalysis constants were related by the Brønsted relationship¹² for acid (Eq. 3) and base (Eq. 4) catalysis:

$$\log\left(\frac{k_A}{p}\right) = \log G_A + \alpha \log\left(\frac{qK_a}{p}\right) \quad (3)$$

$$\log\left(\frac{k_B}{p}\right) = \log G_B - \beta \log\left(\frac{pK_a}{q}\right) \quad (4)$$

In Eq. 3 and Eq. 4, k_A and k_B are rate constants for acid and base catalysis, K_a is the respective acid dissociation constant, G_A and α and G_B and β are constants for a similar series of catalysts where α and β have values between 0 and 1, and p and q are statistical correction factors that represent the number of equally bound dissociable protons (p) and equivalent points where protons can attach (q) and were calculated as outlined by Bell¹². When developing the Brønsted relationships, the carbonic acid (H_2CO_3) true concentration was used rather than the sum of dissolved carbon dioxide and carbonic acid ($H_2CO_3^*$), whereas $H_2CO_3^*$ is implemented in the Aquasim model.

Relative catalyst importance.—Because catalysts are typically controlled at relatively constant concentrations in experiments (i.e., buffer concentrations and pH), an analysis of individual catalyst relative importance to the overall reaction rate constant can be made even for complex models with parallel reaction pathways. Such an analysis distinguishes those catalytic species that are likely to be important (and therefore likely estimated from the experimental data) from those catalytic species that are better estimated from a Brønsted relationship. The procedure and an example calculation for determining relative catalyst importance is provided in the SI.

Microscopic Reversibility

Fast, reversible reactions are common when dealing with haloamine chemistry. Application of the microscopic reversibility principle to general acid or base catalysis reactions can substantially reduce the required number of estimated parameters (e.g., Table 1, reactions 1 and -1). Based on the microscopic reversibility principle,¹³ equilibrium constants are used along with either the forward or reverse reaction rate constants to calculate the other rate constant. Equilibrium constant incorporation into the model can be accomplished in at least two ways to decrease the required number of parameters. First, published equilibrium constants determined experimentally or from thermodynamic estimates can be directly used. For example, referring to Table 1, K_1 can be used along with k_1 to calculate k_{-1} , eliminating the need to estimate the individual catalysis constants associated with k_{-1} . Second, published equilibrium constants and their associated uncertainty may be used to constrain the allowable range of equilibrium constants estimated through model fitting to experimental data. The latter method was applied in the current research, using the equilibrium constant

for reactions 1 and -1 (K_1) proposed by Trogolo and Arey¹⁴ ($\log K_1 = -0.5 \pm 1.2$, $K_1 = 0.020$ – 5.0) where the initial guess for K_1 was set to 0.32 and its minimum and maximum allowable values were 0.020 and 5.0, respectively.

Fictive Products

Imaginary products, termed fictive products herein, were included in reaction stoichiometry (Table 1). Fictive products allowed assessment of reaction pathways during simulations by acting as reaction counters. The magnitude (i.e., concentration) of the fictive product relates to the number of times a particular reaction has occurred in the reaction scheme, allowing direct comparisons of parallel reaction pathway importance.

Fictive product analysis can be employed in at least two circumstances. First, using published reaction rate constants, fictive products allow evaluation of which reactions will be important under typical conditions (e.g., drinking water conditions). Using fictive products in this manner allows selection of the minimal number of reactions required in the kinetic model. Second, fictive products can be utilized after a proposed model has been developed to evaluate whether all the reactions in the model are indeed required.

Parameter Estimation

To estimate parameters in this nonlinear system, an iterative procedure was utilized between (i) Aquasim kinetic model parameter estimates from experimental data and (ii) Brønsted relationship parameter estimates, which used Aquasim parameter estimates as inputs to estimate additional parameters for subsequent use in the Aquasim kinetic model. Iteration continued until the Aquasim parameter estimates converged.

Aquasim.—Parameter estimates were obtained in Aquasim using the parameter estimation function (secant algorithm) which was configured to minimize residual sum of squares (RSS) between measured and model simulated concentrations (Eq. 5):

$$RSS = \sum_{i=1}^n (y_{meas,i} - y_i)^2 \quad (5)$$

In Eq. 5, $y_{meas,i}$ is the i -th measurement and y_i is the model simulated concentration corresponding to the i -th measurement.

From the 65 experiments (Table S2), 11 were excluded. Six (Br-eff-1, Br-eff-2, Br-eff-3, Br-eff-4, Br-eff-5, and Br-eff-6) were excluded (as in Lei, et al.⁷) because they studied the impact of increased bromide, four (HN-1-1, HN-2-1, HN-3-1, and HN-3-2) were excluded because simulated initial NH_2Br and NHBr_2 concentrations differed substantially from the experimental data, and one (CN-1-1) was excluded because it disproportionately contributed to the RSS. The remaining 54 experiments were simultaneously fit using absorbance resolved NH_2Br and NHBr_2 concentrations ($n = 9,971$ data points).

Brønsted relationship.—The Brønsted relationship was used to estimate parameters in coordination with the Aquasim kinetic model. Typically, a Brønsted relationship is utilized as a post-analysis assessment of estimated parameters and prediction of additional parameters unable to be estimated from the experimental data. In the current research, the Brønsted relationship was used as an active part of the parameter estimation procedure in an iterative process so that the entire set of acid or base catalysts are included in Aquasim parameter estimation, assuring self-consistent rate constant estimates are obtained from experimental data and the Brønsted relationship.

Aquasim parameter estimates provided inputs to generate Brønsted relationships. Parameters unable to be obtained through Aquasim parameter estimation because of their lack of sensitivity in the Aquasim model were resolved from the Brønsted relationship, representing a full set of estimated parameters (i.e., Aquasim model and Brønsted relationship estimated parameters). The Brønsted relationship estimated parameters were then entered as fixed parameters into the Aquasim model and Aquasim parameter estimation was repeated. The entire process iterated until Aquasim model estimated parameters no longer changed.

RESULTS AND DISCUSSION

Evaluation of Published Rate Constants

Upon review of the Lei, et al.⁷ results (e.g., Figure 1), limitations became apparent. Our inability to accurately simulate the breadth of their data using their full model was attributed to two factors associated with their data analysis approach. First, Lei, et al.⁷ made assumptions regarding the importance of the two bromamine decomposition reactions (Table 1, reactions 2 and 3). For instance, when they used experiment sets NN-1 and NN-2 to determine ammonia catalysis; HN-1, HN-2, and HN-3 to determine hydrogen ion catalysis; and CN-1 and CN-2 to determine carbonate buffer catalysis, only reaction 3 for bromamine decomposition was assumed important, and reaction 2 was ignored. Importantly, Lei, et al.⁷ never verified this assumption. Second, Lei, et al.⁷ designated parameter estimates as either “measured” (determined from the kinetic model using experimental data) or “predicted” (determined from Brønsted relationships), and this terminology is used herein when describing their results. Lei, et al.⁷ only presented simulations using their measured parameters, and no simulations were presented using both their measured and predicted parameters against their experimental data to evaluate the proposed reaction scheme in its entirety as conducted herein. The impact of these limitations is subsequently discussed.

Reaction importance assumptions.—To evaluate the assumption that reaction 2 could be ignored for experiment sets NN-1, NN-2, HN-1, HN-2, HN-3, CN-1, and CN-2, a fictive product analysis was conducted using both measured and predicted parameters from Lei, et al.⁷ The fictive product analysis allowed a calculation of the percentage of bromamine decomposition associated with reaction 2 (Figures S1, S2, and S3). Overall, the analysis showed that between 53–75% of the bromamine decomposition was attributed to reaction 2 with the balance to reaction 3. Therefore, the assumption that reaction 2 could be ignored was not supported by the final model. Based on parameters estimated from their analysis, both reactions 2 and 3 were required in any data fitting, and reaction 2 was more important

for bromamine decomposition than reaction 3. Also, Lei, et al.⁷ used a step-wise analysis for rate constant estimation (Figure S4, Steps 1–4), allowing errors introduced in each estimation step to propagate throughout their analysis.

Validation of full model.—Impacts of Lei, et al.⁷ not performing validation simulations using both their measured and predicted rate constants were first accessed by calculating the relative importance of catalysts for each reaction. If predicted rate constants are shown to be important, then they should have been included in any simulations conducted. Results for this analysis with experiment sets NN-1 and CN-2 are presented in Table 3 (acid-catalysis reactions 1 and –1) and Table 4 (base-catalysis reactions 2 and 3). For reactions 1 and –1, it appears sufficient to only include the measured parameters as they are the only ones that are important to the overall reaction rates based on a 5% threshold, except experiments CN-2–3, CN-2–4, and CN-2–5 where H_2CO_3^* has minor (5.2–6.6%) importance to the overall rate constant. The same cannot be said for reactions 2 and 3. For reaction 2, only the predicted rate constants (OH^- , CO_3^{2-} , and NH_3) are important; therefore, final simulations should have been conducted to evaluate the reasonableness of their estimations. For reaction 3, the only predicted rate constant that was important was NH_3 , but it contributes 17–69% to the overall rate constant; therefore, as in the case of reaction 2, validation of its estimation from the Brønsted relationship was needed.

To further assess the implications of Lei, et al.⁷ not performing simulations including both measured and predicted parameters, simulations using both the measured and predicted rate constants for experiments sets NN-1 (Figure 1) and CN-2 (Figure 2) were conducted. It is apparent from these simulations that the implementation of the complete published model for bromamine decomposition provides a poor representation of their experimental data, and because of the previously stated concerns regarding their kinetic analysis approach, a reanalysis of the experimental data was justified. For reference, a comparison of the current analysis approach versus that conducted by Lei, et al.⁷ is summarized in Figure S4.

Model evaluation and parameter determination

Comparison of various model simulations.—An initial attempt was made to include both bromamine decomposition reactions (Table 1, reactions 2 and 3) in the reaction scheme as proposed by Lei, et al.⁷, but initial attempts were unsuccessful as the model would not converge during simultaneous parameter estimation using the 54 experiments. Therefore, the initial conclusion was that the model was overparameterized. To evaluate this initial conclusion, the individual experiments of Lei, et al.⁷ were used to estimate individual rate constants for reactions 1, –1, 2, and 3. For individual experiments where rate constants for both reactions 2 and 3 could be estimated (i.e., k_2 or k_3 not estimated as zero), k_2 and k_3 were highly, negatively correlated (–93 to –1.0), providing evidence of model overparameterization and that both reactions 2 and 3 were not needed.

To evaluate the impact of including only reaction 2 or 3, individual parameter estimates were conducted for each experiment of Lei, et al.⁷ using two schemes: (i) Scheme 1 included reactions 1, –1, and 2 and (ii) Scheme 2 included reactions 1, –1, and 3. A residual sum of squares (RSS) comparison (Figure S5) showed no apparent advantage for either scheme.

Further evidence that either reaction scheme would adequately represent the experimental data is presented in Figure 3 where simulations are presented for those experiments where selection of Scheme 1 over Scheme 2 (Figure 3, Panel A) or selection of Scheme 2 over Scheme 1 (Figure 3, Panel B) provided the greatest RSS reduction. It is evident that even for these worst-case scenarios between schemes, either scheme adequately represented the data. Overall, it was concluded that choice of either Scheme 1 or 2 would be adequate and that either, but not both, reaction 2 or 3 was required in the reaction scheme as proposed by Lei, et al.⁷

Subsequently, three lines of reasoning supported selection of Scheme 1 over 2. First, Cromer, et al.¹⁵ studied NHBr_2 decomposition and proposed two pathways. The first pathway was a tribromamine (NBr_3) and NHBr_2 reaction which is excluded because Lei, et al.⁷ found that NBr_3 was below detection limits. The second proposed pathway was a bimolecular NHBr_2 reaction consistent with current reaction 2 (Scheme 1). Second, a lower correlation was found between estimated parameters for Scheme 1 than 2. Specifically, and for the majority of experiments (Figure S6), k_{-1} was less correlated with the bromamine decomposition reaction in Scheme 1 (k_2 , $R = -0.31$ to 0.57) than Scheme 2 (k_3 , $R = -0.83$ to 0.59). Third, based on parallels with chloramine chemistry, NHBr_2 disproportionation (Scheme 1) should occur faster than a reaction of NH_2Br and NHBr_2 (Scheme 2). Based on these three reasons, Scheme 1 was selected.

Model parameter estimation summary.—As described previously, an iterative fitting procedure between the Aquasim kinetic model and the Brønsted relationships was used for parameter estimation. Through this approach, five acid-catalysis constants for reaction 1 (H_2O , HCO_3^- , NH_4^+ , H_2PO_4^- , and H^+), the equilibrium constant for reactions 1 and -1 (K_1), and four base-catalysis constants for reaction 2 (OH^- , CO_3^{2-} , HPO_4^{2-} , and H_2O) were estimated in Aquasim. The remaining three acid-catalysis constants for reaction 1 (HPO_4^{2-} , H_2CO_3 , and H_3PO_4) and four base-catalysis constants for reaction 2 (PO_4^{3-} , NH_3 , HCO_3^- , and H_2PO_4^-) were estimated from Brønsted relationships. An estimated parameter summary is provided in Table 5 (reaction 1) and Table 6 (reaction 2) with corresponding Brønsted plots in Figure 4, showing excellent R^2 values of 0.96 and 0.99 for reactions 1 and 2, respectively.

The relative catalyst importance of the individual constants for each experiment is summarized in Table S3 (reaction 1) and Table S4 (reaction 2). For reactions 1 and 2, all the important constants were directly estimated in Aquasim, except NH_3 for reaction 2. Even though the NH_3 rate constant for reaction 2 was not estimated in Aquasim, directly including the parameters from the Brønsted relationships ensures consistency between parameters estimated from the experimental data and those estimated from Brønsted relationships.

The equilibrium constant estimate for reactions 1 and -1 ($K_1 = 2.1 \pm 0.024$) compares favorably to the thermodynamic estimate ($\log K_1 = -0.5 \pm 1.2$, $K_1 = 0.020\text{--}5.0$). Because of the limitations previously stated for the Lei, et al.⁷ analysis, a direct comparison to the parameters determined in the current research must be done with caution. Regardless, parameters determined for reactions 1 and 2 (Table S5) in this research compare favorably to the previously determined parameters from Lei, et al.⁷, indicating this research offered an

improved approach for estimating the kinetic parameters but for the most part did not alter the relative significance of the catalytic species for these two reactions. Importantly however, the current reaction scheme does not include reaction 3 as in the model of Lei, et al.⁷

Simulation summary.—Final simulations with the current model and with the measured and predicted parameters from Lei, et al.⁷ were conducted (Figure S7) and RSS summarized (Figure S8) for each experiment. Based on the total RSS for each experiment (Figure S8, Panel C), the model of Lei, et al.⁷ marginally reduced the RSS for 9 (PP-1 through PP-5 and HP-1–2 through HP 1–5) of the 54 experiments compared to the current model. Whereas, the simplified, current model (3 reactions, 17 constants) represented the experimental data substantially better than that proposed by Lei, et al.⁷ (4 reactions, 28 constants) in 45 of the 54 experiments as demonstrated by an almost order of magnitude (8×10^{-7} vs. 64×10^{-7}) reduction in total RSS for the data set (Figure S8, Panel C). To highlight the improvement with the current model, Figure 5 provides simulations and experimental data for experiments selected to investigate the impact of ammonia (NN-1–3 and NN-1–5), carbonate (CN-2–3 and CN-2–5), and phosphate (NP-3 and NP- 5) concentrations. Clearly, the current model provides a better experimental data representation along with a reduced RSS. Furthermore, the holistic approach outlined in this research is general in nature and can be applied to kinetic analyses involving acid and base catalysis over a wide variety of conditions.

Practical implications

A final evaluation of the current model was conducted based on representative drinking water conditions to evaluate the minimal model applicable to drinking water. Ten conditions (Table S6) were selected, including five pHs (6, 7, 8, 9, and 10), a maximum total free ammonia concentration ($0.1 \text{ mM} = 1.4 \text{ mg N L}^{-1}$), a maximum phosphate concentration ($0.15 \text{ mM} = 4.7 \text{ mg P L}^{-1}$), and a low ($1 \text{ mM} = 12 \text{ mg C L}^{-1}$) and high ($10 \text{ mM} = 120 \text{ mg C L}^{-1}$) total carbonate concentration. Individual catalyst relative importance to the overall reaction rates is summarized in Table S7 (reaction 1) and Table S8 (reaction 2). Based on excluding species that contribute less than 5% to the overall rate constant of reactions 1 or 2, a model intended for drinking water applications could consist of only a total of eight parameters: (i) four parameters (H_2O , HCO_3^- , H_2PO_4^- , and H^+) for reaction 1, (ii) equilibrium constant for reactions 1 and –1, and (iii) three parameters (OH^- , CO_3^{2-} , and H_2O) for reaction 2. Validation of the minimal model is an avenue of future research.

ASSOCIATED CONTENT

Supporting Information Available.

Supporting information consists of 53 pages with a section describing the calculation of relative catalyst importance, 8 tables, 8 figures, and associated references. Supporting information is available free of charge at <http://pubs.acs.org/>.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Monobromamine (Panel A) and dibromamine (Panel B) simulations compared to experimental data using the measured and predicted rate constants from Lei, et al.⁷ for experiment set NN-1

Figure 2. Monobromamine (Panel A) and dibromamine (Panel B) simulations compared to experimental data using the measured and predicted rate constants from Lei, et al.⁷ for experiment set CN-2

Figure 3.

Model simulation comparisons with experimental data for parameter estimation conducted with selected individual experiments. Experiments HN-3-5 (Panel A) and NP-1 (Panel B) represent the greatest residual sum of squares (RSS) improvement for selecting reaction Scheme 1 versus 2 or reaction Scheme 2 versus 1, respectively.

Figure 4.
Brønsted plots for Reaction 1 (Panel A) and Reaction 2 (Panel B)

Figure 5. Monobromamine and dibromamine experimental data and simulations using estimated parameters from the current research compared to using the measured and predicted rate constants from Lei, et al.⁷ for experiments NN-1-3 (Panel A), NN-1-5 (Panel B), CN-2-3 (Panel C), CN-2-5 (Panel D), NP-3 (Panel E), and NP-5 (Panel F).

Table 1.

Kinetic model reactions for bromamine decomposition.

Current Reaction Number	Lei et al. ⁷ Reaction Number	Reaction Stoichiometry	Fictive Product	Rate Expression ^a
1	1	$2NH_2Br \xrightarrow{k_1} NHBr_2 + NH_3$	P ₁	$k_1[NH_2Br]^2$
-1	-1	$NHBr_2 + NH_3 \xrightarrow{k_{-1}} 2NH_2Br$	P ₋₁	$k_{-1}[NHBr_2][NH_3]$
2	10	$2NHBr_2 + H_2O \xrightarrow{k_2} HOBr + N_2 + 3Br^- + 3H^+$	P ₂	$k_2[NHBr_2]^2$
3	9	$NH_2Br + NHBr_2 \xrightarrow{k_3} N_2 + 3Br^- + 3H^+$	P ₃	$k_3[NH_2Br][NHBr_2]$

^aReactions 1 and -1 equilibrium constant, $K_1 = \frac{k_1}{k_{-1}}$

$$k_1 = k_{1,H_2O} + k_{1,H^+} + k_{1,NH_4^+} + k_{1,H_2CO_3} + k_{1,H_3PO_4} + k_{1,HCO_3^-} + k_{1,H_2PO_4^-} + k_{1,HPO_4^{2-}} + k_{1,HPO_4^{3-}}$$

$$k_{-1} = k_{-1,H_2O} + k_{-1,H^+} + k_{-1,NH_4^+} + k_{-1,H_2CO_3} + k_{-1,H_3PO_4} + k_{-1,HCO_3^-} + k_{-1,H_2PO_4^-} + k_{-1,HPO_4^{2-}} + k_{-1,HPO_4^{3-}}$$

$$k_2 = k_{2,H_2O} + k_{2,OH^-} + k_{2,NH_3} + k_{2,HCO_3^-} + k_{2,CO_3^{2-}} + k_{2,H_2PO_4^-} + k_{2,HPO_4^{2-}} + k_{2,PO_4^{3-}}$$

$$k_3 = k_{3,H_2O} + k_{3,OH^-} + k_{3,NH_3} + k_{3,HCO_3^-} + k_{3,H_2PO_4^-} + k_{3,HPO_4^{2-}} + k_{3,PO_4^{3-}}$$

Table 2.

Equilibrium constants at 25°C and ionic strength (I) = 0 M or I = 0.1 M. Ionic strength adjustments made with the Davies equation¹⁶ from I = 0 M except for the hypobromous acid (HOBr) and hypobromite ion (OBr⁻) equilibrium where adjustments were made from I = 0.5 M, pK_a = 8.80.¹⁷

Equilibrium	pKa (I = 0 M)	pKa (I = 0.1 M)	Reference
$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$	9.24	9.24	Smith, et al. ¹⁸
$\text{H}_2\text{CO}_3^* \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	6.35	6.13	Plummer and Busenberg ¹⁹
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	3.45	3.23	Adamczyk, et al. ²⁰
$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	10.33	9.88	Plummer and Busenberg ¹⁹
$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$	2.15	1.93	Smith, et al. ¹⁸
$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$	7.20	6.75	Smith, et al. ¹⁸
$\text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-} + \text{H}^+$	12.38	11.71	Smith, et al. ¹⁸
$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	7.54	7.32	Morris ²¹
$\text{HOBr} \rightleftharpoons \text{OBr}^- + \text{H}^+$	9.1	8.88	Troy and Margerum ¹⁷
$\text{Br}_{2(\text{aq})} \rightleftharpoons \text{HOCl} + \text{Br}^- + \text{H}^+$	8.46	8.24	Beckwith, et al. ²²
$\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$	14.00	13.78	Benjamin ¹⁶
$\text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{O} + \text{H}^+$	0.00	0.00	Benjamin ¹⁶

Per Adamczyk, et al.²⁰ and plummer and busenberg¹⁹, $\frac{[\text{H}_2\text{CO}_3^*]}{[\text{H}_2\text{CO}_3]} = 795$

Table 3.

Relative importance of acid catalysts for rate constants k_1 and k_{-1} from Lei, et al.⁷ for selected experiments.

Rate constants denoted as measured and predicted in Lei, et al.⁷ are designated as (M) and (P), respectively.

Red numbers indicate contributions greater than or equal to 5% of the total rate constant.

Catalyst Percent Contribution to k_1 for Given Experiment								
Experiment	H ₂ O (M)	HPO ₄ ²⁻ (P)	HCO ₃ ⁻ (M)	NH ₄ ⁺ (M)	H ₂ PO ₄ ⁻ (M)	H ⁺ (M)	H ₂ CO ₃ [*] (P)	H ₃ PO ₄ (P)
NN-1-1	23.4	0.0	0.0	44.1	0.0	32.5	0.0	0.0
NN-1-2	16.1	0.0	0.0	62.5	0.0	21.3	0.0	0.0
NN-1-3	9.5	0.0	0.0	77.0	0.0	13.5	0.0	0.0
NN-1-4	7.0	0.0	0.0	83.7	0.0	9.3	0.0	0.0
NN-1-5	5.4	0.0	0.0	87.2	0.0	7.4	0.0	0.0
CN-2-1	11.8	0.0	50.2	30.0	0.0	5.7	2.3	0.0
CN-2-2	7.7	0.0	65.7	19.8	0.0	3.8	3.0	0.0
CN-2-3	4.6	0.0	78.0	11.7	0.0	2.2	3.5	0.0
CN-2-4	3.3	0.0	83.1	8.3	0.0	1.6	3.8	0.0
CN-2-5	2.5	0.0	85.9	6.4	0.0	1.2	3.9	0.0
Catalyst Percent Contribution to k_{-1} for Given Experiment								
Experiment	H ₂ O (M)	HPO ₄ ²⁻ (P)	HCO ₃ ⁻ (M)	NH ₄ ⁺ (M)	H ₂ PO ₄ ⁻ (M)	H ⁺ (M)	H ₂ CO ₃ [*] (P)	H ₃ PO ₄ (P)
NN-1-1	33.3	0.0	0.0	20.6	0.0	46.2	0.0	0.0
NN-1-2	27.8	0.0	0.0	35.4	0.0	36.8	0.0	0.0
NN-1-3	19.7	0.0	0.0	52.3	0.0	28.0	0.0	0.0
NN-1-4	16.0	0.0	0.0	62.8	0.0	21.2	0.0	0.0
NN-1-5	13.0	0.0	0.0	69.0	0.0	18.0	0.0	0.0
CN-2-1	32.4	0.0	22.9	26.9	0.0	15.6	2.3	0.0
CN-2-2	25.7	0.0	36.4	21.6	0.0	12.6	3.7	0.0
CN-2-3	18.4	0.0	52.1	15.3	0.0	8.9	5.2	0.0
CN-2-4	14.3	0.0	60.8	11.9	0.0	6.9	6.1	0.0
CN-2-5	11.7	0.0	66.3	9.7	0.0	5.6	6.6	0.0

Table 4.

Relative importance of base catalysts for rate constants k_2 and k_3 from Lei, et al.⁷ for selected experiments. Rate constants denoted as measured and predicted in Lei, et al.⁷ are designated as (M) and (P), respectively. Red numbers indicate contributions greater than or equal to 5% of the total rate constant.

Catalyst Percent Contribution to k_2 for Given Experiment						
Experiment	OH ⁻ (P)	PO ₄ ³⁻ (P)	CO ₃ ²⁻ (P)	NH ₃ (P)	HPO ₄ ²⁻ (M)	H ₂ O(M)
NN-1-1	83.1	0.0	0.0	15.4	0.0	1.5
NN-1-2	71.5	0.0	0.0	27.3	0.0	1.2
NN-1-3	55.2	0.0	0.0	43.8	0.0	1.0
NN-1-4	45.6	0.0	0.0	53.6	0.0	0.8
NN-1-5	38.3	0.0	0.0	61.0	0.0	0.7
CN-2-1	78.6	0.0	1.3	19.6	0.0	0.5
CN-2-2	77.4	0.0	2.6	19.5	0.0	0.5
CN-2-3	75.7	0.0	5.0	18.8	0.0	0.5
CN-2-4	73.8	0.0	7.3	18.4	0.0	0.5
CN-2-5	72.1	0.0	9.5	17.9	0.0	0.4
Catalyst Percent Contribution to k_3 for Given Experiment						
Experiment	OH ⁻ (M)	PO ₄ ³⁻ (P)	CO ₃ ²⁻ (M)	NH ₃ (P)	HPO ₄ ²⁻ (P)	H ₂ O(M)
NN-1-1	11.0	0.0	0.0	20.8	0.0	68.2
NN-1-2	9.3	0.0	0.0	36.0	0.0	54.8
NN-1-3	6.5	0.0	0.0	52.4	0.0	41.1
NN-1-4	5.3	0.0	0.0	63.4	0.0	31.3
NN-1-5	4.3	0.0	0.0	69.3	0.0	26.4
CN-2-1	14.6	0.0	17.3	36.9	0.0	31.2
CN-2-2	12.3	0.0	29.3	31.5	0.0	26.9
CN-2-3	9.6	0.0	45.5	24.3	0.0	20.6
CN-2-4	7.8	0.0	55.6	19.8	0.0	16.8
CN-2-5	6.6	0.0	62.6	16.7	0.0	14.1

Table 5.

Reaction 1 summary of Brønsted plot and estimated parameters (25°C, I = 0.1 M).

Acid Catalyst	pK _a	p	q	$\log\left(\frac{K_a q}{p}\right)$	Model Implemented K ₁ ^a ± 95% CI ^d	Brønsted Plot k ₁ (M ⁻² s ⁻¹)	Model Estimated $\log\left(\frac{k_1}{p}\right)$	Brønsted Estimated $\log\left(\frac{k_1}{p}\right)$
H ₂ O	15.52	2	3	-15.34	1.1±0.095	2.0×10 ⁻² ^b	-2.0	
HPO ₄ ²⁻	11.71	1	4	-11.11	12	12		1.1
HCO ₃ ⁻	9.88	1	3	-9.40	200±6.6	200	2.3	
NH ₄ ⁺	9.24	4	1	-9.84	98±14	98	1.4	
H ₂ PO ₄ ⁻	6.75	2	3	-6.57	(3.4±0.044)×10 ⁵	3.4×10 ⁵	5.2	
H ⁺	-1.74	3	2	1.56	(6.8±0.82)×10 ⁸	6.8×10 ⁸	8.4	
H ₂ CO ₃	3.23 ^e	2	2	-3.23	2.4×10 ³	1.9×10 ⁶ ^c		6.0
H ₃ PO ₄	1.93	3	2	-2.11	1.4×10 ⁷	1.4×10 ⁷		6.7
K ₁					2.1±0.024			

^a Model k₁ values are in M⁻² s⁻¹ except H₂O which is in M⁻² s⁻¹ and k₁ which is the equilibrium constant for reactions 1 and -1^b Model k₁ divided by 55.5 M to arrive at Brønsted k₁^c Model k₁ is based on H₂CO₃ ; therefore, model k₁ value was multiplied by 795, $\frac{[H_2CO_3^*]}{[H_2CO_3]}$, to arrive at Brønsted k₁^d 95% confidence interval (CI) provided for model estimated parameters only^e pK_a is for true H₂CO₃ concentration

Table 6.

Reaction 2 Summary of Brønsted plot and estimated parameters (25°C, I = 0.1 M).

Base Catalyst	pK _a	p	q	$\log\left(\frac{K_a q}{p}\right)$	Model Implemented K ₂ ^a ± 95% CI ^c	Brønsted Plot K ₂ (M ⁻² s ⁻¹)	Model Estimated $\log\left(\frac{k_2}{q}\right)$	Brønsted Estimated $\log\left(\frac{k_2}{q}\right)$
OH ⁻	15.52	2	3	-15.34	(3.7±0.54)×10 ⁶	3.7×10 ⁶	6.1	
PO ₄ ³⁻	11.71	1	4	-11.11	1.2×10 ⁵	1.2×10 ⁵		4.5
CO ₃ ²⁻	9.88	1	3	-9.40	(2.3±0.45)×10 ⁴	2.3×10 ⁴	3.9	
NH ₃	9.24	4	1	-9.84	8.9×10 ³	8.9×10 ³		3.9
HPO ₄ ²⁻	6.75	2	3	-6.57	(1.9±0.010)×10 ³	1.9×10 ³	2.8	
H ₂ O	-1.74	3	2	1.56	9.6±0.97	1.7×10 ⁻¹ ^b	-1.1	
HCO ₃ ⁻	3.23 ^d	2	2	-3.23	28	28		1.1
H ₂ PO ₄ ⁻	1.93	3	2	-2.11	9.2	9.2		0.66

^a Model k₁ values are in M⁻² s⁻¹ except H₂O which is in M⁻² s⁻¹^b Model k₁ divided by 55.5 M to arrive at Brønsted k₁^c 95% confidence interval (CI) provided for model estimated parameters only^d pK_a is for equilibrium with true H₂CO₃ concentration