Decay Kinetics of Hypobromous Acid From HBr-Activated Solutions

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Background

When hydrogen bromide (HBr) is activated with sodium hypochlorite the resultant hypobromous acid solution is inherently metastable. This study reports the decay constants and the half-life for two concentrations of activated HBr solutions and also tracks the decay of ready to use HBr solution. The purpose of this study is to provide meat and poultry users of HBr an indication of the persistency of hypobromous acid in the activated solution (reported as bromine). It will also guide users of the time frame through which the activated solutions should be used. An additional objective of this study was to observe the change in pH of the activated hypobromous acid solutions over time.

Methodology

A low and a high concentration of activated hypobromous acid solutions were employed in this study. The solutions were made by introducing sodium hypochlorite (bleach) to the HBr solutions until the endpoint was reached, (color turned pale yellow). Once the HBr solutions were activated, an initial pH and temperature were recorded and activity of hypobromous acid was measured using the iodometric titration and reported as bromine. The solutions were stored in the dark to prevent additional degradation of hypobromous acid due to UV light exposure. The activities of the solutions were tested periodically for 7-8 hours, along with recording the pH and temperature of each solution. The temperature ranged from 74-80^{o} Fahrenheit for all three studies.

The volumes used in the high and low concentration hypobromous acid solutions are displayed in Table 1 below. Throughout this report the low concentrated hypobromous acid solution will be referred to as Solution 1 and the high concentration solution hypobromous acid will be referred to as Solution 2.

Table 1

Low Concentration HBr (Solution 1)	High concentration HBr (Solution 2)
896.6 mL Hard Water	844.4 mL Hard Water
6.9 mL HBr solution	11.2 mL HBr solution

Hard city water was accurately measured out with a graduated cylinder. The HBr solution was measured using a graduated pipette and added to the water. The solution was gently agitated before continuing. With gentle mixing, sodium hypochlorite was added to the HBr solution to activate it. The resultant hypobromous acid solution was initially colorless. As the sodium hypochlorite was added, the color changed from

colorless to bright yellow to a dark orange/red then to a pale yellow. The pale yellow indicated the endpoint of the activation. At the endpoint, the pH of the activated solution should theoretically be around neutral. The color of the solutions slowly regressed back to dark orange as time elapsed. The color regression occurred because of the instability of hypobromous acid. After the solution was activated, the time was recorded as zero minutes (T_0) and samples and readings were started.

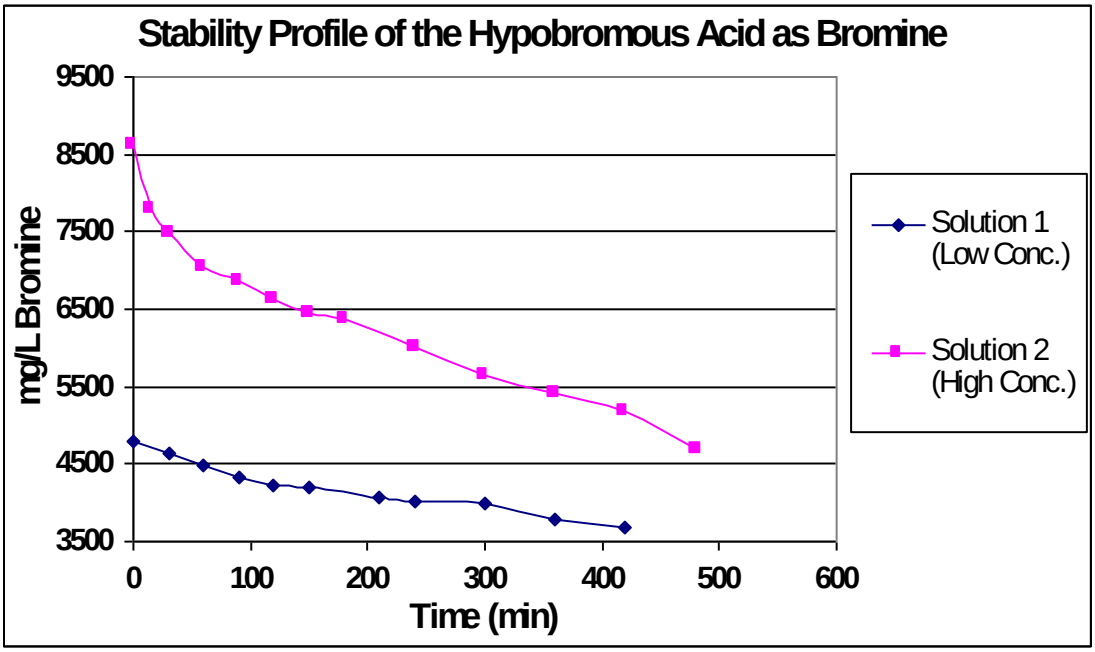
Results and Discussion

High and Low Concentration Solutions of Hypobromous Acid

Graph 1 illustrates the persistency of the hypobromous acid (reported as bromine) for the low and high concentration activated HBr solutions. Solution 1 (low concentration hypobromous acid solution) utilized 6.9 mL of HBr solution in 896.6 mL of hard water. After the solution was activated, the activity tested at 4,670 ppm as bromine, but due to the unstable nature of the activated solution, after seven hours the activity decayed to 3,692 ppm as bromine. Solution 2 (high concentration hypobromous acid solution) utilized 11.2 mL of HBr solution in 844.4 mL of hard water. Initially the solution generated 8620 ppm as bromine, but due to the unstable nature of the solution, after eight hours the activity declined to 4,694 ppm as bromine.

The overview of the decay of hypobromous acid over time provides users with a tentative means to determine the activity of the activated solutions over time if the solution is not exposed to light. Ideally, the hypobromous acid solutions should be used relatively quickly to reduce decay side reactions. The half-life of each solution is reported in Table 2.

Graph 1

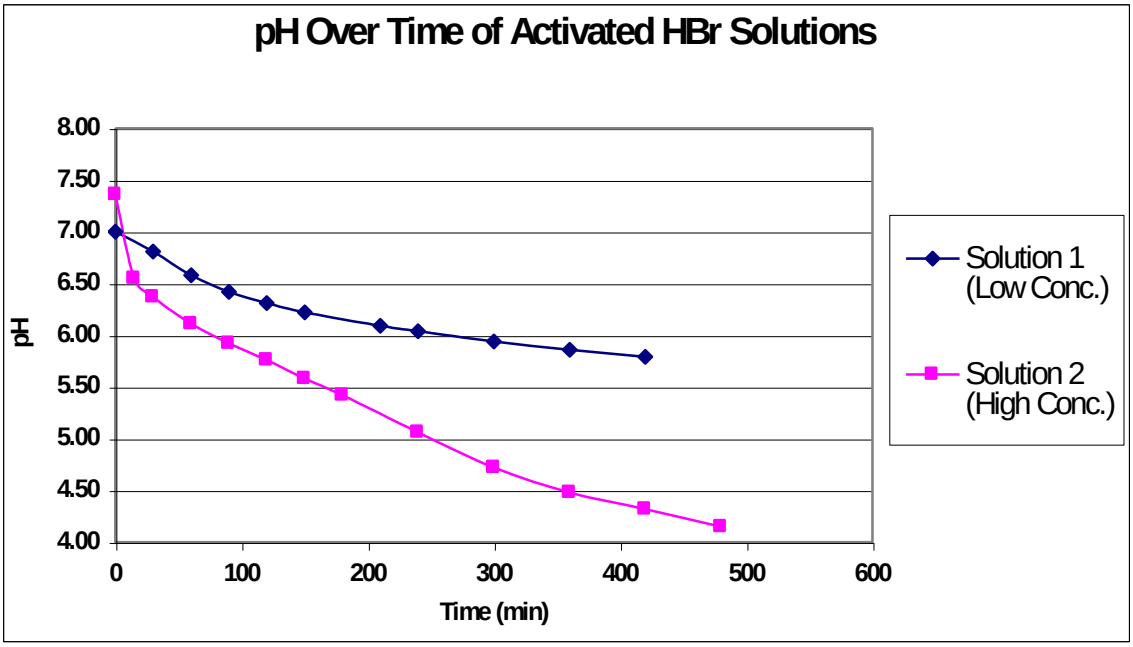


The pH of the HBr activated solutions is driven by the decay of hypobromous acid. Therefore, the pH was observed while the hypobromous acid solutions decayed. Once a solution of HBr is activated with sodium hypochlorite, the pH increases to 7-7.8. As the hypobromous acid decays, the pH also drifts lower as hypobromous acid decays according to the following equation:

$$2\ HOBr = O_2 + 2\ HBr \quad \text{.....(Eq. 1)}$$

In Graph 2, the pH was tracked over the time span of the study for both hypobromous acid solutions. The initial pH of Solution 1 after activation was 7.00, and after seven hours the pH dropped to 5.79. The initial pH of Solution 2 after activation with sodium hypochlorite was 7.36, and after eight hours the pH dropped to 4.15.

Graph 2

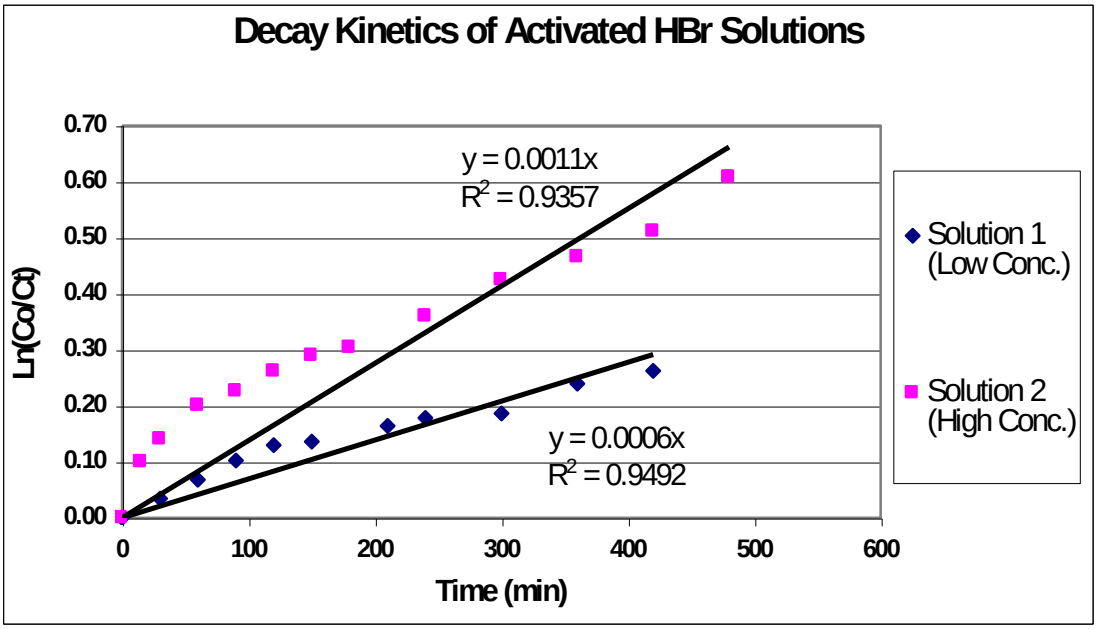


Although equation (1) would indicate that the reaction proceeds by a second order mechanism, due to the fact that the solutions were monitored for less than one complete half life, the decay kinetics were modeled according to a pseudo first-order response. Graph 3 represents the pseudo first-order decay kinetics of hypobromous acid Solutions #1 and #2. A linear regression line was imposed on the data for Solutions 1 and 2. On the graph, both the equation of the line and the R^2 value (correlation coefficient) are represented. The slope of the line represents the rate constant for the decay reaction. The R^2 value represents how precisely the linear regression line fits the data. An R^2 value of 1 indicates that the linear regression line fits the data perfectly.

The slope for the linear regression line for Solution 1 was 0.0006. This indicates that the low concentration HBr activated solution decayed with a rate constant of $0.0006 min^{-1}$. The R^2 value calculated for Solution 1 was 0.9492. This indicates the decay of hypobromous acid in Solution 1 corresponded very closely to a mechanism of pseudo

first-order decay. The slope for the linear regression line for Solution 2 was 0.0011. This indicates that the high concentration HBr activated solution decayed with a rate constant of 0.0011min^{1}. The R^2 value calculated for Solution 2 was 0.9357. This indicates the decay of hypobromous acid in Solution 2 also corresponded very closely to a mechanism of pseudo first-order decay.

Graph 3



The half-lives for the decay of hypobromous acid in Solutions 1 and 2 (calculated by dividing the slopes of the respective regression lines by 0.692 – (the natural logarithm of 2) are displayed in Table 2 below. The half-lives are reported in minutes and hours. Solution 1 has approximately twice as long a half-life than Solution 2.

Table 2

	Half-Life of Hypobromous Acid
Solution 1 (low concentration HBr activated solution)	1206 min (20hrs)
Solution 2 (high concentration HBr activated solution)	656 min (11hrs)

It is predicted that carcass washing with hypobromous acid solution may require a maximum of 300 ppm as bromine. There are two different methods for generating Ready-To Use (RTU) carcass wash. One method is through dilution of a more concentrated solution and the other is by direct in-line generation of the 300 ppm as bromine solution. For the first method, the hypobromous acid solution is activated and only needs to be diluted accordingly, depending on the concentration of hypobromous acid solution utilized, high or low concentration. The dilutions to obtain a 300 ppm as bromine solution are displayed below in Table 3.

Table 3

Original Concentration	
Solution 1 (Low concentration HBr activated solution)	Must dilute down 15.6 times
Solution 2 (High concentration HBr activated solution)	Must dilute down 28.7 times

Hence proportioning equipment must be used in order to dilute the activated hypobromous acid solutions. The Dositron proportioning pump or similar device would be a suitable to accomplish the dilution. It is a water-powered injector and uses volumes to accurately inject chemicals directly into the water flow. It also helps regulate the chemical injection to fewer inconsistencies should water pressure or flow change. It is recommended that cycle times be kept short for generating hypobromous acid at higher ranges, in order to avoid excessive pH drops of the activated hypobromous acid, which will require additional bleach adjustments.

Direct Generation of 300 ppm as Bromine From HBr

Some carcass washing facilities will undoubtedly wish to eliminate the cost of a proportioning device and directly generate a 300 ppm as bromine solution using HBr. Therefore, a further study was undertaken in which stoichiometric amounts of HBr and NaOCl bleach were introduced to water in order to prepare a Ready-to-Use solution. A further objective of this study was to examine the rate at which the NaOCl was converted to HOBr by performing free and total DPD measurements in the presence of glycine. (Glycine complexes with unreacted chlorine so that all the halogen that responds to the free DPD indicator is HOBr). It was found that within one minute of activating the HBr solution with NaOCl bleach that all the halogen had converted to HOBr, evidenced by the fact that a few KI crystals added to the DPD free chlorine test vial did not increase the absorbance of the RTU solution.

The RTU carcass wash was prepared using the recipe listed in Table 4.

Table 4

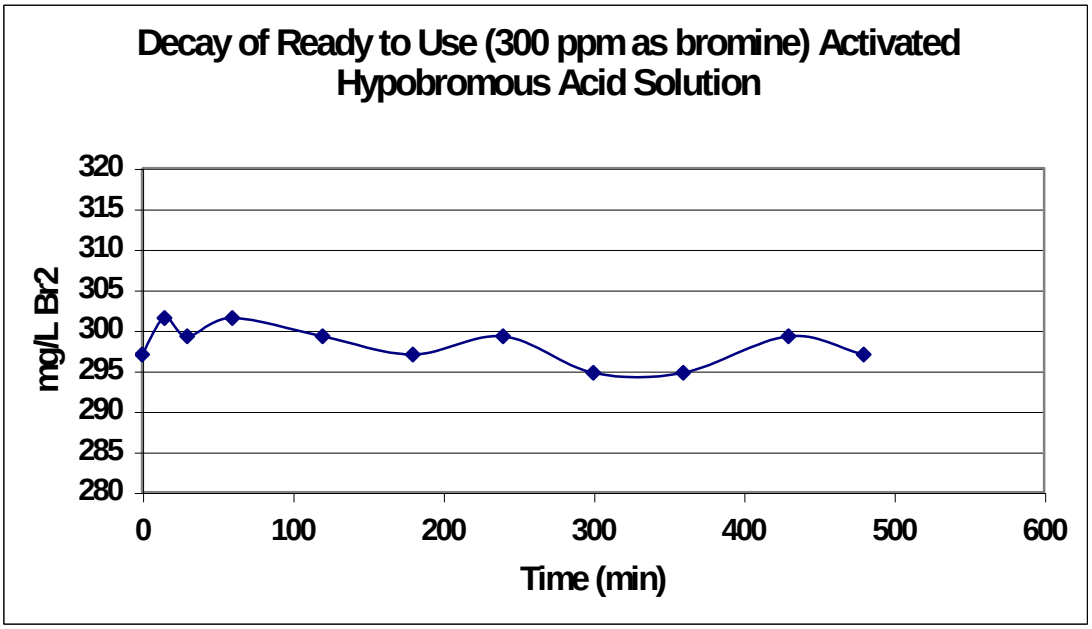
Component	**Volumes**
Hard Water	900 mL
HBr Solution	0.40 mL
Sodium Hypochlorite 12.5%	0.71 mL*

*Note this volume is based on 12.5% sodium hypochlorite. If the activity is different then the volume must be adjusted accordingly.

Graph 4 illustrates the decay of directly-generated RTU hypobromous acid solution. Upon activation, this solution was stored in the dark and tested for activity over an eight-hour period of time.

The RTU 300 ppm as bromine hypobromous acid solution is relatively stable. The activity did not degrade after eight hours. The temperature during the eight hours ranged from 74-77^{o} Fahrenheit. After the solution was activated, the activity was 297 ppm as bromine and after eight hours the activity remained 297 ppm as bromine. Due to the stability of the solution, the decay rate constant and half-life could not be determined.

Graph 4

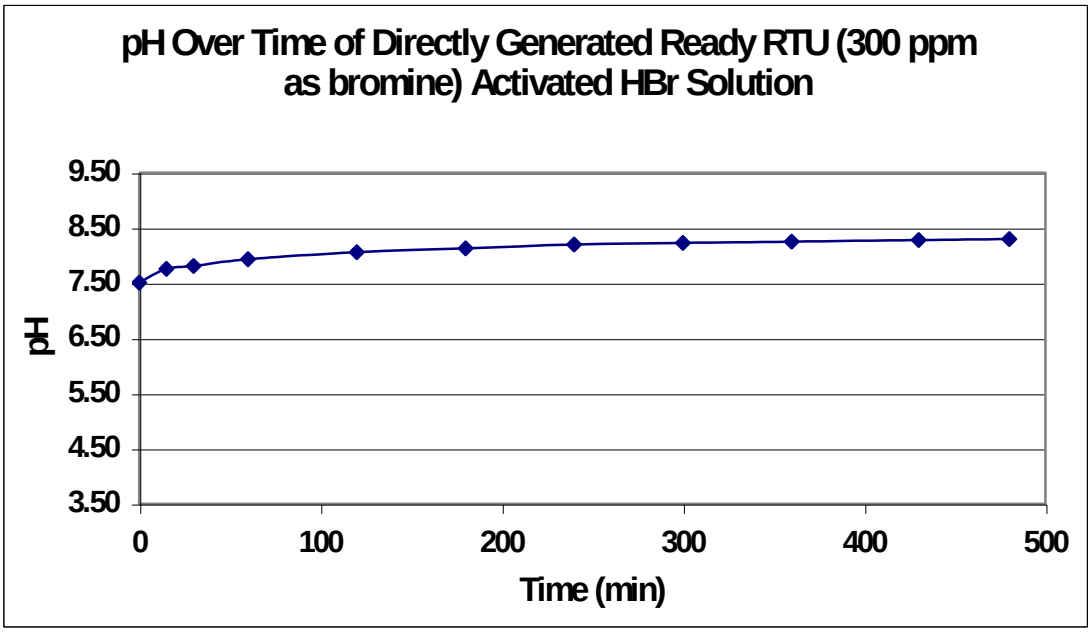


Graph 5 illustrates the pH progression of the ready to use activated solution (300 ppm as bromine). After the HBr solution was activated, the pH was 7.51. The pH gradually increased to 8.30 by the end of the study, after eight hours. In the previous studies, for both the high and low concentration activated HBr solutions, the pH gradually decreased over time. The difference in pH drift between the previous solutions and the ready to use HBr solution is the due to the stability of the respective solutions. The pH of the HBr activated solution is driven by the decay of hypobromous acid. As the hypobromous acid decays, the pH also drifts lower as hypobromous acid decays according to the following equation:

$$2\ HOBr = O_2 + 2\ HBr \text{……..(Eq. 2)}$$

But, in the RTU activated solution, there is no apparent decay of hypobromous acid over the eight hour time span; therefore the reaction above does not occur within eight hours after the solution has been activated.

Graph 5



Conclusions

- Low and high concentrations of hypobromous acid solutions were prepared in this study. The decay of hypobromous acid and pH was monitored over time. The purpose of this study was to provide meat and poultry carcass wash users of HBr an indication of the persistency of hypobromous acid and a time frame through which the HBr activated solutions must be used.

- Solution 1 (low concentration) utilized 6.9 mL HBr solution and 896.6 mL hard water. Solution 2 (high concentration) utilized 11.2 mL HBr solution and 844.4 mL hard water. Both were activated with the addition of sodium hypochlorite bleach with proportional amounts.

- Solution 1 initially tested at 4,800 ppm as bromine at pH 7.00. After seven hours, the activity dropped to 3,692 ppm as bromine and ended with a pH 5.79. Solution 2 initially tested at 8,620 ppm as bromine at pH 7.36. After eight hours the activity dropped to 4,694 ppm as bromine with a final pH of 4.15. As the hypobromous acid decays, the pH declined consistently.

- The rate constant and R^2 value were calculated for each decay profile. The low concentration, Solution 1, decayed with a rate constant of $0.0006min^{-1}$. This was approximately half that of the high concentration, Solution 2. Solution 2 decayed with a rate constant of $0.0011min^{-1}$. The R^2 values were similar for both solutions, indicating that the decay was pseudo first-order at both the high and the low concentrations.

- The half-life was calculated for both the high and low concentration hypobromous acid solutions. Solution 1 (low concentration) had a half-life of 1206 min (20hrs). The half-life for Solution 2 (high concentration) was only 656 min (11hrs). When comparing the two half-lives, it is apparent that the low concentration of hypobromous acid solution (Solution 1) has a half-life approximately twice as long as the high concentration of Solution 2. It must be taken into consideration that the temperature that these studies were conducted at was between 74-80^{o} Fahrenheit. The water used in carcass washing may be much colder than this. The colder the water, the slower the hypobromous acid decays leading to longer half-lives once the solution is in the water.

- 200-300 ppm as bromine is the desired dose for carcass washing plants utilizing hypobromous acid. Two methods can be used to dose water to the desired bromine levels; through dilution with a proportioning device; or by direct generation of the RTU 300 ppm as bromine solution.

- As evidenced by the free DPD indicator measurement in the presence of glycine, direct generation of the 300 ppm as bromine RTU solution immediately results in quantitative generation of HOBr. No halogen is present as unreacted NaOCl.

- For users employing proportioning equipment to dilute the activated hypobromous acid solutions, it is recommended that the high concentrated solutions of activated solution should be used (or at least diluted) within reasonably quick timeframes to avoid loss in activity due to decay caused by lowered pH. An activated solution can be reconstituted. This can be accomplished by simply adding more sodium hypochlorite to the decayed solution. As the hypobromous acid decays, the pH of the solution drops and the color becomes a more intensely orange as the speciation of hypobromous acid reverts to elemental bromine instead of the pale yellow (after activation). When more sodium hypochlorite is added to the solution the color of the solution returns to the pale yellow indicating the regeneration of hypobromous acid and the pH increases to around >7.