

Two New Methods of Synthesis for the Perbromate Ion: Chemistry and Determination by LC-MS/MS

Aleksey N. Pisarenko,^{*,†} Robert Young,^{†,‡} Oscar Quiñones,[†] Brett J. Vanderford,[†] and Douglas B. Mawhinney[†]

[†]Southern Nevada Water Authority, Applied Research & Development Center, P.O. Box 99954, Las Vegas, Nevada 89193, United States

[‡]Department of Soil & Crop Sciences, Colorado State University, Fort Collins, Colorado 80523-1170, United States

 Supporting Information

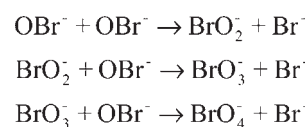
ABSTRACT: Historically, the synthesis of perbromate ion through conventional oxidation routes has proven elusive. Herein, we report perbromate ion formation through the reaction of hypobromite and bromate ions in an alkaline sodium hypobromite solution. Formation was established via LC-MS/MS analysis of the bromate and perbromate ions in the reaction solutions over a 13-day period. Furthermore, it was discovered that the perbromate ion was also formed as a result of the electrospray ionization process. Selective reduction of the bromate ion prior to analysis was used to confirm the two formation pathways.

Perbromate has captivated inorganic chemists attempting its synthesis since the 19th century.¹ It was not until 1968 that substantial amounts of perbromate ions were synthesized using fluorine gas and xenon difluoride to oxidize bromate ions.^{2,3} The development of these methods of synthesis allowed investigation of the properties of perbromate, including reactions, stability, and thermodynamic properties.^{3–7} In brief, it was found that once perbromate is formed, it is stable in aqueous solutions, which allowed the development of various characterization methods.^{2,8–12} Unfortunately, the difficulties associated with these methods of synthesis have prevented the widespread study of perbromate chemistry.

It has been hypothesized that the main difficulties in synthesizing perbromate (oxidation potential, $E^\circ = 1.763$ V) are due to unfavorable reaction rates and a relatively high energy barrier between Br(V) and Br(VII), which limit the choice of a suitable oxidation agent.^{4,6,13} While other studies reported the unsuccessful oxidation of a bromate ion to perbromate using ozone and other strong oxidants, oxidation was recently reported by researchers employing boron-doped conductive diamond electrodes.¹⁴ Hydroxyl radicals generated during electrolysis of water converted small quantities of bromate to perbromate, which was characterized using cyclic voltammetry and thermogravimetric analysis.

Until the early 2000s, there were no known reports of perchlorate ions (ClO_4^-) in sodium hypochlorite solutions. Since then, several studies have established the presence of perchlorate in sodium hypochlorite solutions, as well as increases in perchlorate concentration in these solutions over time.^{15–17} The potential regulation of perchlorate in drinking water and the

Scheme 1. Decomposition of Hypobromite and Formation of Perbromate



widespread use of sodium hypochlorite in drinking water treatment prompted a specific study to evaluate the factors impacting its rate of formation in sodium hypochlorite solutions.¹⁸ Sensitive analytical methodologies suited for quantitation of perchlorate in sodium hypochlorite¹⁹ were developed and employed to determine the thermodynamic properties for perchlorate formation. It was found that hypochlorite (OCl^-) and chlorate (ClO_3^-) concentrations, as well as ionic strength, are all important factors in perchlorate formation.^{18,20} Comparatively, hypobromite is a weaker oxidant ($E^\circ = 0.760$ V) than OCl^- ($E^\circ = 0.890$ V), although it is more reactive than hypochlorite.²¹ However, hypobromite has also been shown to decompose to bromate in a similar fashion to hypochlorite.²² Given the similarities in chemistries, it was hypothesized that perbromate (BrO_4^-) could form through a similar pathway involving reactions of hypobromite and bromate, as shown by Scheme 1.

The primary objective was to monitor the formation of bromate and perbromate via LC-MS/MS. Changes in bromate were also monitored using a modified ion chromatography (IC) method for cross-validation.²³ A previously described liquid chromatography tandem mass spectrometric (LC-MS/MS) method for bromate¹⁹ was modified to include perbromate-specific multiple reaction monitoring (MRM) transitions of $^{81}\text{BrO}_4^-$ (m/z 145) to $^{81}\text{BrO}_3^-$ (m/z 129) and $^{79}\text{BrO}_4^-$ (m/z 143) to $^{79}\text{BrO}_3^-$ (m/z 127).

An alkaline solution of sodium hypobromite was prepared over the course of ~ 2.0 h by slowly adding 25 mL of liquid bromine (Br_2) to a chilled 500 mL aqueous solution containing 8.25% sodium hydroxide (NaOH) by weight. The reaction vessel was maintained at 10–15 °C, while the oxidation reduction potential (ORP, mV) was continuously monitored to ensure that a rapid depletion of hydroxide ions did not occur. The prepared solution was standardized by iodometric titration, resulting in $[\text{OBr}^-] = 0.953$ M. This solution was also found to contain $[\text{BrO}_3^-] = 2.27$ mM, determined by the described LC-MS/MS

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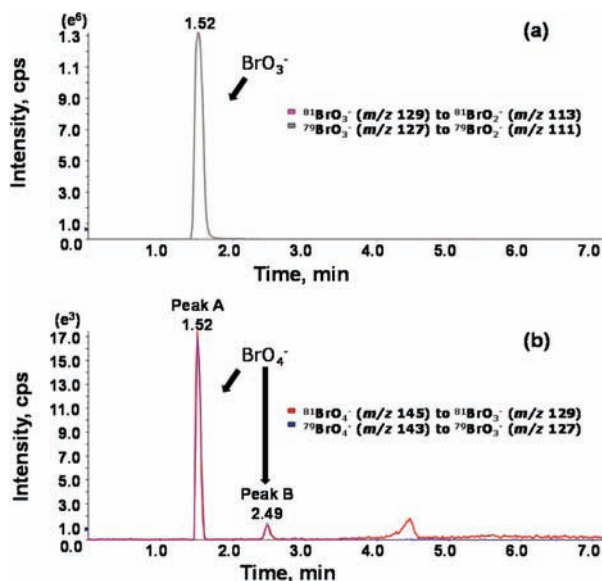


Figure 1. Extracted ion chromatograms of (a) bromate and (b) perbromate in the sodium hypobromite sample (diluted by a factor of 1000) after 13 days of incubation at 40 °C (note, cps = counts per second).

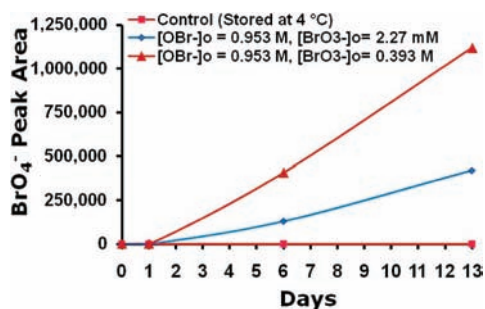


Figure 2. Formation of perbromate in sodium hypobromite solutions stored at 40 °C (control: $[\text{OBr}^-]_0 = 0.953\text{M}$, $[\text{BrO}_3^-]_0 = 2.27\text{ mM}$).

method. The stock solution of sodium hypobromite (pH 12.5) was split into three aliquots. The first was incubated at 40 °C in a water bath to increase the rate of decomposition of hypobromite. NaBrO_3 was added to the second aliquot to achieve a BrO_3^- concentration of 0.393 M (in duplicate) and incubated at 40 °C. The third aliquot was kept at 4 °C for the duration of the study, as a control sample. Changes in BrO_3^- and BrO_4^- were monitored over an incubation period of 13 days.

Figure 1 shows overlaid extracted ion chromatograms for bromate and perbromate in the sodium hypobromite sample (diluted by a factor of 1000) after 13 days at 40 °C. Two perbromate peaks, one coeluting with bromate at 1.5 min (peak A) and a second peak at 2.5 (peak B) min, were observed. The two peaks displayed both MRM transitions in the correct ratio for the naturally occurring isotopic abundance of Br. Peak B was determined to be due to perbromate formed during the reaction and was used to monitor the evolution of perbromate in incubated sodium hypobromite samples.

Figure 2 shows the formation of perbromate over incubation time at 40 °C in sodium hypobromite solutions at various initial bromate concentrations. As shown by Figure 2, perbromate

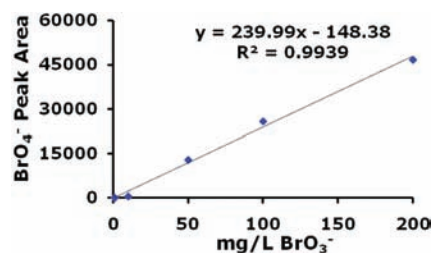


Figure 3. Change in perbromate peak A as a function of bromate concentration in aqueous bromate solutions at pH 11.2.

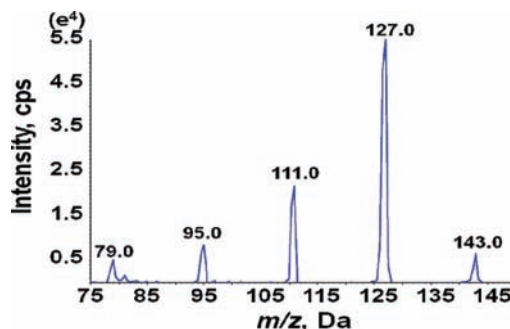


Figure 4. Product ion mass spectrum of $^{79}\text{BrO}_4^-$ (m/z 143).

formation is strongly dependent on the initial concentration of bromate. As hypobromite decomposes, the bromate concentration increases (shown in the Supporting Information, Figure SI-1), allowing the formation of perbromate. In the sample spiked with bromate at the start of incubation, perbromate formed at a faster rate. These findings support the hypothesis that perbromate formation is dependent on reaction of the hypobromite and bromate.

The perbromate that coeluted with the bromate peak (peak A, 1.5 min, Figure 1) was found to be directly dependent on the presence of bromate. To investigate this phenomenon, various bromate standard solutions were prepared at a pH matching that of the diluted hypobromite samples. Bromate standard solutions of 1, 10, 50, 100, and 200 mg/L were adjusted to pH 11.2 using sodium hydroxide and analyzed by the described LC-MS/MS method. Figure 3 shows the increase in perbromate peak A area as a function of bromate concentration. Note that perbromate peak B was not detected in these solutions. These results confirm that perbromate peak A is due to perbromate formed solely from reactions involving bromate in the electrospray ionization process and represent a second viable synthesis route. Figure 4 shows the product ion spectrum for $^{79}\text{BrO}_4^-$ (m/z 143), from infusion of a 1000 mg/L BrO_3^- standard solution, and reveals BrO_3^- , BrO_2^- , BrO^- , and Br^- product ions. The product ion spectrum for $^{81}\text{BrO}_4^-$ (m/z 145) (Figure SI-2) and analytical details (Table SI-1) are provided in the Supporting Information.

Attempts were made to collect product ion spectra of perbromate peak B in the samples with LC-MS/MS. However, perbromate peak B lacked sufficient intensity to generate such spectra of acceptable quality.

To further confirm the two formation pathways for perbromate, the selective reduction of bromate was conducted in hypobromite samples. Earlier studies have shown that both bromate and perbromate are reduced by sulfite. However, at acidic pH, the reaction of perbromate is slow,⁵ while the reaction

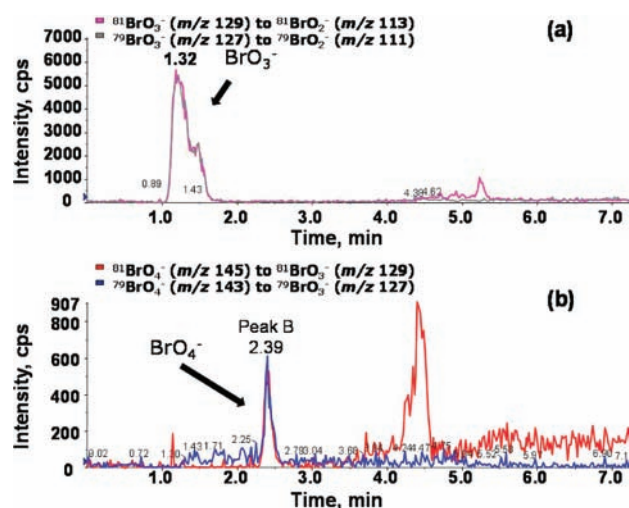


Figure 5. Extracted ion chromatograms of (a) bromate and (b) perbromate in sodium hypobromite sample spiked with 0.1 M HCl and 0.001 M SO_3^{2-} .

of bromate proceeds readily.^{24,25} Given that sample solutions needed to be diluted by a factor of 1000 for LC-MS/MS analysis, it was possible to spike other chemicals in the process of dilution. Thus, hypobromite solutions were prepared, in duplicate, containing 0.1 M HCl and 0.001 M SO_3^{2-} (Figure 5).

Figure 5 illustrates that, when bromate is mostly reduced by sulfite, perbromate peak A is not present due to the decreased concentration of bromate. However, the later eluting perbromate peak B is still present and not significantly reduced by the sulfite. Therefore, the presence of perbromate peak B must be attributed to the oxidation of bromate by the hypobromite, further supporting the conclusions drawn from Figure 2.

This work shows that perbromate can form in concentrated sodium hypobromite solutions, likely via a pathway similar to perchlorate formation, although more work is needed to determine the rate law. The results also demonstrate that small amounts of perbromate are produced during electrospray ionization, and bromate can be selectively reduced without significantly affecting perbromate concentrations. The two methods of synthesis discussed in this study merit investigation beyond the scope of this work; however, the synthesis and analytical methods employed will likely be of interest to those involved in inorganic, analytical, and environmental chemistry.

■ ASSOCIATED CONTENT

S Supporting Information. Formation of bromate over time during decomposition of hypobromite and product ion mass spectrum of $^{81}\text{BrO}_4^-$ (m/z 145). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: aleks.pisarenko@snwa.com or aleks.pisarenko@gmail.com.

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