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EFFECTS OF PH AND ALKALINITY ON OZONATION OF BROMIDE AND CHLORIDE IN SEAWATER

A series of laboratory experiments were performed in which unbuffered and buffered solutions of NaBr and NaCl were exhaustively ozonated. The production patterns and relative abundances of the products were compared in order to quantify the roles of pH, carbonate system and borate system in ozone reactions with these two halides in seawater. Concentrations of hypohalites in solutions where pH was buffered in the range 8.6-8.8 were consistently lower than those in the equivalent unbuffered solutions. Bromate production rates in unbuffered NaBr solution, NaBr solution buffered with 3 meq/L carbonate alkalinity, and that buffered with 3 meq/L borate alkalinity were, respectively, 1.30 $\mu\text{M}/\text{min}$, 1.58 $\mu\text{M}/\text{min}$ and 0.83 $\mu\text{M}/\text{min}$. Our finding that, relative to carbonate alkalinity, borate alkalinity enhances the production of hypobromite while simultaneously depressing bromate formation, may have important consequences for seawater facilities such as aquaria and mariculture that use borate buffers. Hypobromite produced during ozonation in such systems is a desired secondary disinfectant, due to the very short half-life of dissolved ozone in seawater. The use of borate buffers may thus serve to enhance the potential for disinfection while simultaneously diminishing the unwanted bromate accumulation in these environments.

Key Words: Ozone; Seawater; pH Buffers; Hypobromite; Hypochlorite; Bromate.

1. INTRODUCTION

Ozonation is used more and more as a method of disinfection in seawater facilities such as mariculture and aquaria. Research done in fresh water has shown that a variety of reduced chemical species may be oxidized during ozonation (Hoigne and Bader, 1978; Hoigne et al., 1985; Olson and Barbier, 1994). The most abundant inorganic species present in seawater in reduced form are chloride and bromide ions.

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Oxidation of bromide to produce hypobromite and bromate is a particularly important pathway of ozone consumption in seawater, due to the fast reaction kinetics (Haag and Hoigne, 1983a; Steslow, 1991). Even in artificial seawater where no bromide salts are added, the trace impurity present in technical grade NaCl can be the dominant inorganic species consuming ozone (Grguric et al., 1994).

While the kinetics of chloride oxidation by ozone are several orders of magnitude slower than those of bromide (Haag and Hoigne, 1983b), high chloride concentration in seawater (up to several hundred mM) means that in this medium, there is a possibility for hypochlorite formation. One importance of pH in these reactions lies in its effect on the speciation of hypohalous acids. Hoigne et al. (1985) have shown that hypobromite and hypochlorite ions exhibit great preference in reactivity towards ozone relative to the protonated forms. The pK_a 's of hypobromous and hypochlorous acids at 25°C are 8.68 (Mills and Meadows, 1995) and 7.54 (Bousher et al., 1986), respectively. This means that in ambient seawater at pH 8.3, 29% of the total hypobromous acid and 85% of the total hypochlorous acid is potentially reactive towards ozone. Because hypobromite ion is a precursor to bromate, the pH may control the production of this potentially toxic species through the speciation of hypobromous acid.

In ocean water, pH is buffered by 2-3 meq/L alkalinity. Bicarbonate and carbonate ions account for about 90% of total alkalinity, while most of the rest is due to borate ions (Skirrow, 1975). Bicarbonate and carbonate are known to be hydroxyl radical scavengers (Hoigne et al., 1985) and as such, they affect decomposition pattern of ozone. Therefore, both the pH and the presence of buffering species influence ozonation reactions in seawater. To examine the impact of these parameters on oxidation of bromide and chloride by ozone, we performed a series of laboratory experiments ozonating unbuffered and buffered solutions of NaBr and NaCl. The production patterns and relative abundances of the products were compared in order to quantify the roles of pH, carbonate system and borate system in ozone reactions with these two halides in seawater.

2. EXPERIMENTAL METHODS

Ozonation by-products were systematically studied during a series of long-term experiments in which unbuffered and buffered solutions of distilled water, pure NaBr and pure NaCl were ozonated. Exhaustive ozonation was performed for up to 3 hours in batch mode under dark conditions. Sodium bromide used was GR grade and was obtained from E. M. Science. To avoid bromide contamination of sodium chloride solutions, ultra-pure NaCl containing less than 0.6 ppm Br by weight (or less than 0.2 μ M Br in a 30 g/L NaCl solution) was obtained from Aldrich. Analytical grade sodium bicarbonate, sodium carbonate, boric acid and sodium borate were used. All the buffers were checked for hypohalite and bromate impurities and only sodium borate was found to have bromate present at the detection level.

Ozone was produced by ozonating dry oxygen in a Henkel SS300 ozone generator and delivered into solution through a fritted-glass diffuser. The applied ozone delivery rate was determined in a separate experiment by ozonating an acidic solution of potassium iodide and titrating the liberated iodine. The maximum ozonation rate used was 1.3 g O_3 /h.

During ozonation of solutions, pH was monitored to the nearest 0.01 unit using a Corning 150 Ion Analyzer with a Broadley James combination pH electrode. The redox potential was measured to the nearest 10 mV using an Orion Digital Ionalyzer 501 with an Orion platinum redox combination electrode (model 96-78). The electrode was standardized using solutions of potassium ferrocyanide/potassium ferricyanide and potassium fluoride. The ozonated solution was sampled every 10-30 min and concentrations of dissolved ozone, hypobromite plus hypochlorite, and bromate were determined.

The concentration of dissolved ozone in each aliquot was measured on a Perkin-Elmer Lambda 3B UV-Visible spectrophotometer with the wavelength set at 253.7 nm. The first absorbance reading of the solution was taken within 2 min after sampling. The interfering absorbance of HOBr, which is significant at this wavelength (Galal-Gorchev and Morris, 1965) was determined by purging the ozone in the sample with air for 2 min and then taking a second absorbance reading. Ozone concentrations were calculated from the difference between the two absorbance readings in combination with the extinction coefficient of Hart et al. (1983). A detection limit of 10 μM was calculated from 3 standard deviations of the minimum reproducible absorbance reading.

Concentrations of hypohalites and bromate were determined by two successive iodometric titrations, modified from Haag (1981). The first titration, carried out at pH 3.8, measured the sum of hypochlorite and hypobromite concentrations. After the end point was reached, the second titration of the same sample at pH 1 was performed to determine the concentration of bromate. The titrant was prepared from standard 0.1 N sodium thiosulfate solution obtained from J.T. Baker Inc. The analyses were validated by titrating standard potassium bromate solution prepared from dried analytical grade potassium bromate. Dissolved ozone interference with the method was eliminated by outgassing of samples prior to analysis. Interference of hydrogen peroxide was tested by performing titrations with and without the bromate reduction catalyst. The results showed that in all solutions containing hypohalites, concentration of hydrogen peroxide was negligible by comparison ($<2 \mu\text{M}$). Thus, detection limits for the two methods were $5 \mu\text{M}$ for the hypohalite titration and $2 \mu\text{M}$ for the bromate titration.

Alkalinity was determined on several samples before and after ozonation. The method of Strickland and Parsons (1972) for total alkalinity was used. The difference between the calculated and the empirically determined alkalinity values was at most 10%, in solutions of low alkalinity.

3. RESULTS AND DISCUSSION

EFFECTS OF pH AND CARBONATE ALKALINITY ON OZONATION OF NaBr AND NaCl SOLUTIONS

Figures 1 and 2 show dissolved ozone concentrations as a function of time during ozonation of NaBr and NaCl solutions. Steady state of dissolved ozone was reached much faster in unbuffered NaCl solution (Figure 2) than in unbuffered NaBr solution (Figure 1). The difference shows high initial ozone consumption by the NaBr solution relative to the NaCl solution. Concentrations of dissolved ozone in carbonate-buffered media were lower than those in unbuffered media and steady state was not attained (Figures 1 and 2). The initial pH values of the

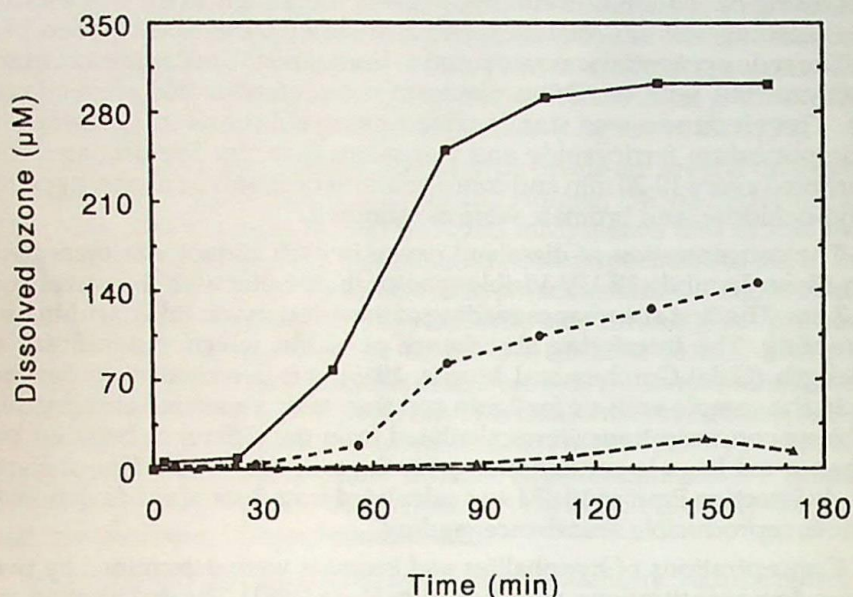


Figure 1. Dissolved ozone concentrations as a function of time during ozonation of 120 μM NaBr: (squares) unbuffered; (circles) buffered with 3 meq/L carbonate alkalinity; (triangles) buffered with 3 meq/L borate alkalinity.

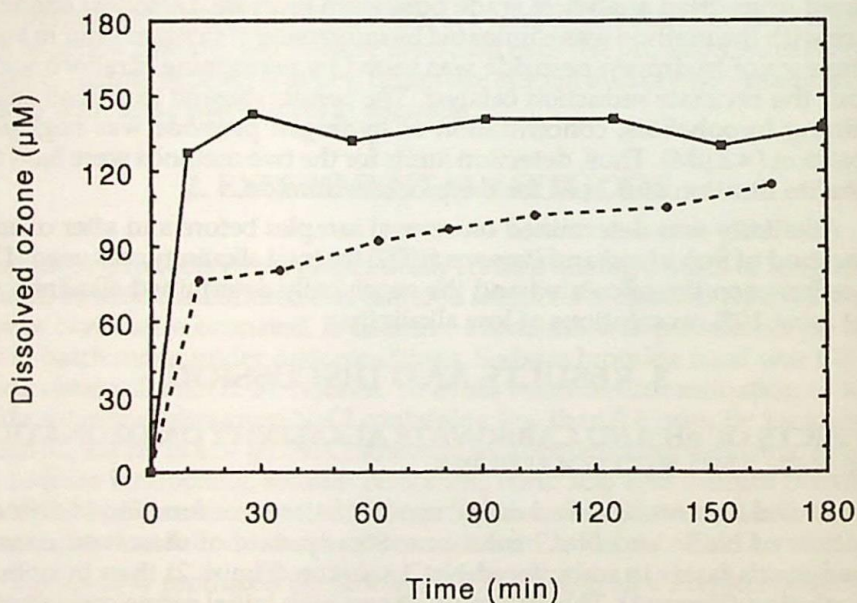


Figure 2. Dissolved ozone concentrations as a function of time during ozonation of 78 mM NaCl: (squares) unbuffered; (circles) buffered with 3 meq/L carbonate alkalinity.

unbuffered NaBr and NaCl solutions were 5.3 and 5.0, respectively. The pH of the buffered solutions was in the range 8.6-8.8. Previous research has shown (Peleg, 1976; Staehelin and Hoigne, 1982) that hydroxide ions initiate decomposition of ozone in fresh water. Our results demonstrate that this process takes place in halide media as well, where stability of ozone decreases with increasing pH. Lower concentrations of dissolved ozone in carbonate-buffered solutions of NaBr and NaCl were also responsible for a decrease in redox potential of 150-200 mV in those media, relative to the redox potential in unbuffered solutions.

Production of hypohalites in buffered vs. unbuffered solutions exhibited pronounced differences. In solutions of NaBr, buffering the pH resulted in decreased concentrations of hypobromite, particularly later in the ozonation process (Figure 3). Only in buffered solutions of NaBr did the concentration of hypobromite ever decrease below detection limit of 5 μM before the end of ozonation (Figure 3). In NaCl solutions, there was a dramatic effect of alkalinity on the production of hypochlorite (Figure 4). This production in unbuffered NaCl solution followed a linear pattern where:

$$[\text{HOCl}] = 0.572 \cdot t + 4.180 \quad (r^2 = 0.994).$$

Ozonation of the same solution buffered with 3 meq/L carbonate alkalinity produced less than 5 μM hypochlorite (Figure 4). The presence of carbonate and bicarbonate ions in concentrations similar to those found in seawater thus effectively blocks the formation of hypochlorite during ozonation of NaCl media.

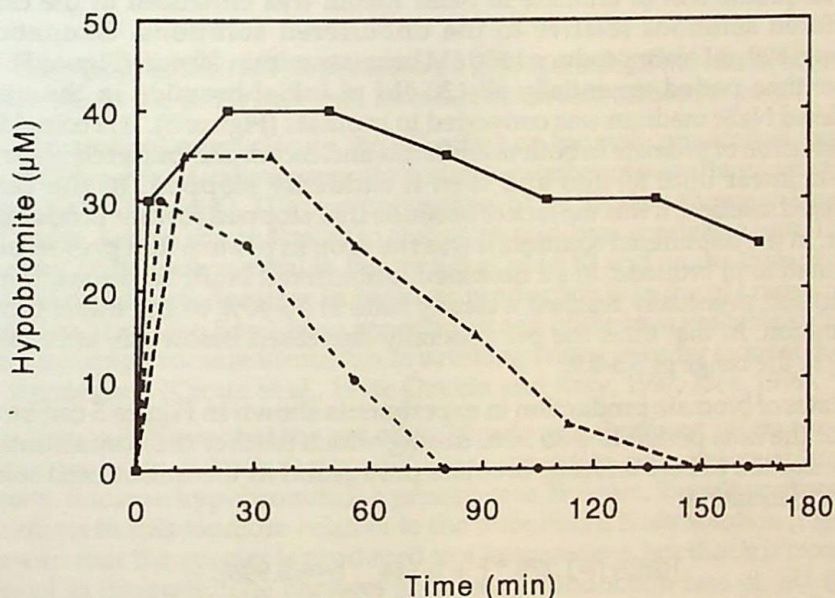


Figure 3. Concentrations of hypobromite as a function of time during ozonation of 120 μM NaBr: (squares) unbuffered; (circles) buffered with 3 meq/L carbonate alkalinity; (triangles) buffered with 3 meq/L borate alkalinity.

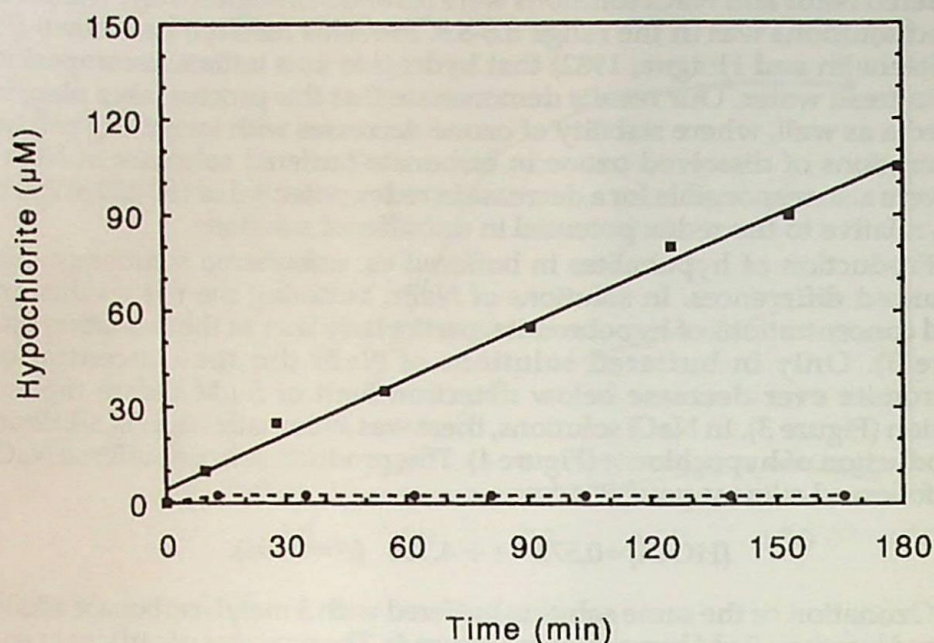


Figure 4. Concentrations of hypochlorite as a function of time during ozonation of 78 mM NaCl: (squares) unbuffered; (circles) buffered with 3 meq/L carbonate alkalinity.

The production of bromate in NaBr media was enhanced in the carbonate-buffered solutions relative to the unbuffered solutions. Ozonation of unbuffered 120 µM NaBr produced 100 µM bromate within 80 min (Figure 5). Over the same time period, essentially all 120 µM of initial bromide in the carbonate-buffered NaBr medium was converted to bromate (Figure 5). It is coincidental that production of bromate in both unbuffered and carbonate-buffered NaBr solutions was linear until 80 min and then it suddenly stopped. In the carbonate-buffered solution, it was the lack of bromide that stopped further production of bromate. In the unbuffered solution, it was the drop in pH to 6 that prevented further formation of bromate. In all ozonated, unbuffered NaBr solutions, bromate concentration eventually reached a steady state at 80-90% of the initial bromide concentration. At that time, the pH generally decreased below 6.5, after initially peaking in the range of 8.3-8.9.

Rates of bromate production in experiments shown in Figure 5 can be compared for the time period of 0-80 min, during which neither the concentration of bromide nor the pH are limiting. Bromate production in the unbuffered solution follows the equation:

$$[\text{BrO}_3^-] = 1.279 * t + 0.344 \quad (r^2 = 0.996),$$

while in the presence of 3 meq/L carbonate alkalinity, the equation is:

$$[\text{BrO}_3^-] = 1.579 * t - 1.337 \quad (r^2 = 0.995).$$

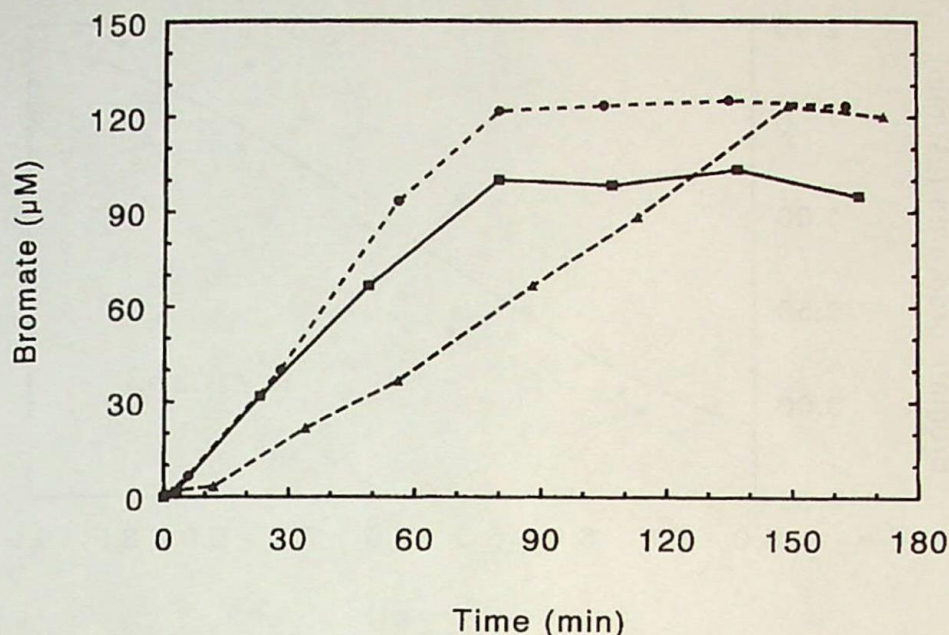


Figure 5. Concentrations of bromate as a function of time during ozonation of 120 μM NaBr: (squares) unbuffered; (circles) buffered with 3 meq/L carbonate alkalinity; (triangles) buffered with 3 meq/L borate alkalinity.

The ratio of the two slopes shows a 23% increase in the rate of bromate production when the pH is buffered by bicarbonate and carbonate ions.

To analyze more closely the pH effect on bromate production, production rates at different pH values were plotted for a number of unbuffered solutions containing NaBr (Figure 6). The best polynomial fit for the data shown in Figure 6 was third order, with a shape similar to that of an acid-base speciation plot. The inflection point of the polynomial in Figure 6 is at pH 6.87 and on the basis of our data, the most significant decrease in bromate production is in the pH range of 7.5-6.5. Ozonation at pH 6-6.5 has been reported as one of the best available technologies for minimizing bromate formation in drinking water, in order to meet the current EPA regulations (Croue et al., 1996; Ozekin and Amy, 1997; Rice, 1999).

Figure 5 shows that the net effect of carbonate-buffered pH on ozonation of sodium bromide is both faster and more complete conversion of bromide to bromate. Because hypobromite is a precursor to bromate, lower hypobromite concentrations in this medium relative to the unbuffered NaBr solution (Figure 1) do not mean that the species is produced to a lesser extent, but that it is more rapidly oxidized to bromate. The changes in bromate production rate vs. pH (Figure 6) show that at a given bromide concentration and ozonation rate, it is the speciation of hypobromous acid that is controlling the rate of bromate production. The large observed pH effect is due to the reaction rate of OBr with ozone, which is at least 3.3×10^4 times greater than that of HOBr (Hoigne et al., 1985).

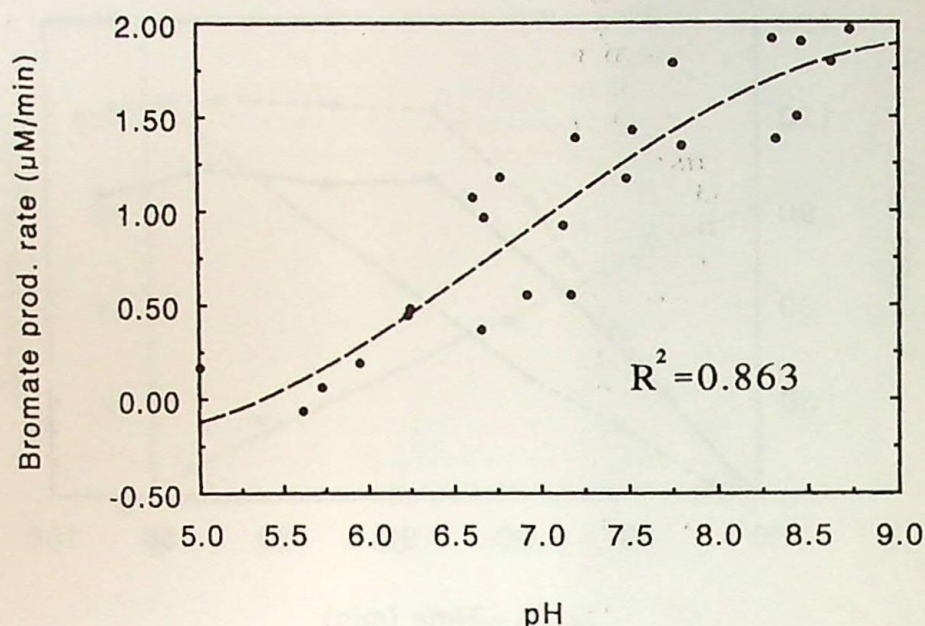


Figure 6. Bromate production rates versus pH during ozonation of unbuffered NaBr solutions. Dashed line and correlation coefficient represent the best fit through the data.

Our conclusions are different from those of Sayato et al. (1990) who measured concentrations of hypobromite, but not bromate, in unbuffered and carbonate-buffered solutions of NaBr. Their observation that bicarbonate and carbonate inhibit formation of hypobromite lead them to the conclusion that oxidation of bromide by ozone is controlled primarily by hydroxyl radicals, which would have been effectively scavenged in carbonate-buffered solutions. Measurements of bromate in this study show the dominant effect of hypobromous acid speciation and thus the importance of the molecular ozone mechanism. This is in agreement with the more recently reported findings (Von Gunten and Hoigne, 1994).

4. OZONATION OF NaBr SOLUTIONS BUFFERED WITH BORIC ACID/SODIUM BORATE

To examine whether the type of buffer exerts any influence on the production of hypobromite and bromate, experiments were performed in which the pH was buffered with a mixture of boric acid and sodium borate. The concentration of dissolved ozone during ozonation of 120 µM NaBr solution buffered with 3 meq/L borate alkalinity did not rise above 30 µM (Figure 1), even after all the bromide was converted to bromate. This is in contrast to the 3 meq/L carbonate-buffered NaBr solution where the concentration of dissolved ozone reached 140 µM once all the bromide was converted to bromate (Figure 1). The difference in pH between the carbonate-buffered and borate-buffered solutions was at most 0.5 pH units, reached at the end of ozonation. A similar difference (0.4 pH units) between distilled water media buffered with 2 meq/L vs. 3 meq/L carbonate alkalinity resulted

in dissolved ozone differences of less than $20 \mu\text{M}$. Thus, the pH cannot account for the observed differences of up to $110 \mu\text{M}$ in dissolved ozone concentration between carbonate and borate-buffered media. This is a strong indication that decomposition of ozone is accelerated in the presence of borate relative to carbonate.

Concentrations of hypobromite during ozonation of borate-buffered NaBr solution (Figure 3) were lower than in the unbuffered NaBr solution, but higher than in the carbonate-buffered NaBr solution. In contrast, production of bromate in borate-buffered NaBr solution was slower for the first 80 min than that in either unbuffered or carbonate-buffered NaBr solution (Figure 5). The comparison of slopes in this time interval shows that bromate production in the borate-buffered medium is only 53% of that in the carbonate-buffered medium. All the initial bromide is eventually converted to bromate in both buffered media (Figure 5), which again emphasizes the importance of pH in the bromate formation process.

Bromate production in NaBr solutions buffered with 1 meq/L and 3 meq/L borate alkalinity is shown in Figure 7. In the solution containing 1 meq/L borate, all the initial bromide was converted to bromate in 100 min. The same conversion took 145 min in the solution buffered with 3 meq/L borate. Bromate production was linear in both cases, with a rate of $1.12 \mu\text{M}/\text{min}$ in 1 meq/L borate solution and $0.83 \mu\text{M}/\text{min}$ in 3 meq/L borate solution. Variations in pH between the two solutions were at most 0.1 pH units, not large enough to explain the observed difference in bromate production rates. The presence of borate species thus serves to slow down significantly the rate of bromate formation in NaBr solutions. This trend is in contrast with that in carbonate-buffered NaBr solutions, where higher alkalinity either did not have an impact on bromate production or made it slightly faster by buffering the pH better.

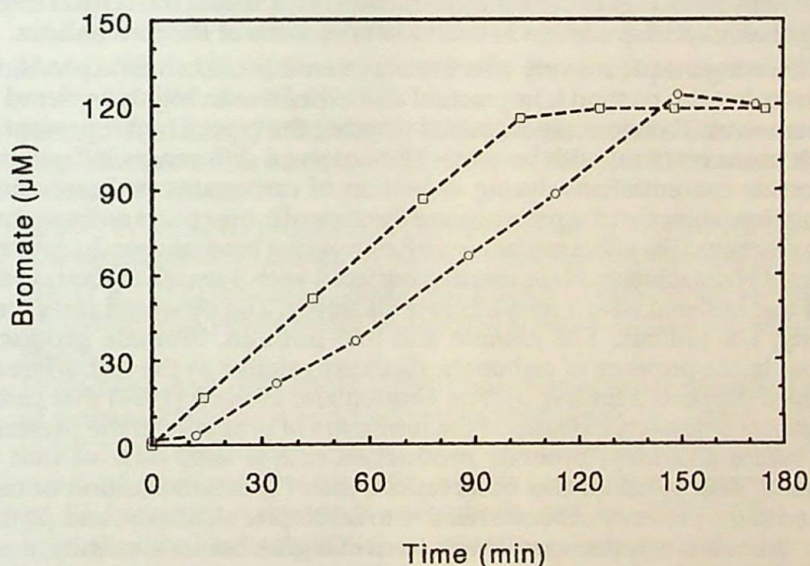


Figure 7. Bromate concentrations as a function of time during ozonation of $120 \mu\text{M}$ NaBr buffered with: (squares) 1 meq/L borate alkalinity; (circles) 3 meq/L borate alkalinity.

The conclusions reached above mean that the very low dissolved ozone concentrations in borate-buffered NaBr solutions cannot be explained by bromate production. Hoigne et al. (1985) report that boric acid does not react with ozone with any appreciable rate constant, in either protonated or unprotonated form. Therefore, ozone consumption by oxidation of borate can be ruled out. The low ozone concentrations in borate- vs. carbonate-containing media may be the result of an enhancing effect of borate on radical chain ozone decomposition. At a constant ozone delivery rate, the chain initiation reaction is dependent only on pH (Stahelin and Hoigne, 1982), so its rate should be the same in solutions containing different buffers. The difference between carbonate and borate buffers could be in their impact on chain propagation reactions. Some oxyanions (e.g. phosphate) have been reported to act as radical chain promoters (AWWA, 1991). The observed parameters in this study are consistent with the behavior of borate as a radical chain promoter, in contrast to the behavior of bicarbonate and carbonate ions which act as radical chain inhibitors.

5. CONCLUSIONS

Ozonation experiments performed in this study show that of the parameters studied, pH has the most important effect on the formation of hypochlorite, hypobromite and bromate during ozonation of NaCl and NaBr solutions. Concentrations of hypohalites in solutions where pH was buffered in the range 8.6-8.8 were consistently lower than those in the equivalent unbuffered solutions. Under the buffered pH conditions, conversion of bromide to bromate by the end of ozonation was essentially 100%. In the equivalent unbuffered solutions, this conversion did not exceed 80-90% despite long ozonation times. These observations, together with the change in bromate production rates, reveal the central role of pH and hypohalous acid speciation in ozonation reactions of the two halides.

Lowering the pH is a very effective way to minimize bromate production in fresh water, but this method is impractical and expensive in highly buffered media such as seawater. Therefore, we examined whether the type of buffer present has an effect on ozone reactions with bromine. The observed differences in hypobromite and bromate concentrations during ozonation of carbonate- vs. borate-buffered NaBr solutions show that the presence and the type of buffer plays an important role in these reactions. The effect can be seen by comparing bromate production rates in unbuffered NaBr solution, NaBr solution buffered with 3 meq/L carbonate alkalinity, and that buffered with 3 meq/L borate alkalinity. The observed rates were, respectively, 1.30 $\mu\text{M}/\text{min}$, 1.58 $\mu\text{M}/\text{min}$ and 0.83 $\mu\text{M}/\text{min}$. Bromate production is enhanced in the presence of carbonate alkalinity relative to the unbuffered solution, which supports a finding by Von Gunten and Hoigne (1994) that carbonate radicals act as secondary oxidants in the formation of bromate. In the presence of 3 meq/L borate alkalinity, bromate production rate is only 64% of that in the unbuffered NaBr solution. Our observations that: (1) decomposition of ozone is enhanced in the presence of borate relative to carbonate alkalinity, and (2) the production rate of bromate decreases in solutions of higher borate alkalinity, lead us to the conclusion that borate acts as a radical chain promoter in this medium.

Borate salts are used to help buffer the pH in some seawater aquaria and mariculture facilities, where carbonate species are lost through outgassing or pre-

cipitate formation. Our findings that borate alkalinity enhances the production of hypobromite while simultaneously depressing bromate formation may have important consequences for these facilities. Hypobromite produced during ozonation in such systems is a desired secondary disinfectant, due to the very short half-life of dissolved ozone in seawater. Thus, the use of borate buffers may serve to enhance the potential for disinfection while simultaneously diminishing bromate accumulation in these environments.

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Figure Captions

Sažetak

UČINAK PH I ALKALITETA NA OZONIZACIJU BROMIDA I KLORIDA U MORU

Napravljena je serija laboratorijskih analiza u kojima su nepuferirane i puferirane otopine NaBr i NaCl bile temeljito ozonizirane. Postupci i dobiveni relevantni uzorci su se usporedili kako bi se kvantificirala uloga pH, karbonatni i boratni sustavi u ozonskim reakcijama s dvoje soli u moru. Koncentracije hipohalita u otopinama u kojima je pH puferiran u omjeru od 8,6 do 8,8, bile su niže nego one u istovjetnim nepuferiranim otopinama. Omjeri dobivanja bromata u nepuferiranoj NaBr otopini, NaBr otopini puferiranoj s 3 meq/L karbonatnog alkaliteta i oni puferirani s 3 meq/L boratnog alkaliteta, iznosile su 1,30 $\mu\text{M}/\text{min}$, 1,58 $\mu\text{M}/\text{min}$ i 0,83 $\mu\text{M}/\text{min}$. Naše otkriće da, s obzirom na karbonatni alkalitet, boratni alkalitet pojačava stvaranje hipobromita, a istodobno smanjuje stvaranje bromata, mogla bi imati značajne posljedice kod objekata koji koriste more, kao što su akvarij ili u marikulturi, gdje se upotrebljavaju boratni puferi. Hipobromit koji je nastao tijekom ozonizacije tih sustava poželjno je sekundarno sredstvo za dezinfekciju zbog vrlo kratka poluvremena života otopljenog ozona u moru. Upotreba boratnih pufera može na taj način poslužiti kako bi se povećala mogućnost dezinfekcije, a da bi se istodobno smanjilo neželjeno taloženje bromata u tim okruženjima.

Ključne riječi: pH puferi, hipobromiti, hipoklorit, bromat 1