BROMATE PRODUCTION IN OZONE CONTACTORS

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Abstract

A pilot-scale study of the ozonation of surface waters containing moderate levels of bromide (Br^-) was conducted in order to collect kinetic parameters suitable for modeling the production of bromate. Operating in a pre-ozonation mode, the two surface waters were dosed under conditions designed to theoretically provide greater than 0.5 $\log_{10}$ inactivation levels for Giardia. Key results from the experimental study and kinetic analysis of bromate formation in these two waters are:

1) Bromate production results from rapid free radical processes. The slower, recursive reactions involving the direct oxidation of bromide and hypobromite by ozone are insignificant.

2) Ozone residual is the controlling factor in the rate and extent of bromate formation.

3) Hypobromite and hypobromous acid are formed primarily as minor byproducts of oxybromine radical decay, and do not play a significant role as precursors at pHs less than 9.0.

4) Naturally occurring organic matter plays a complex role in production and consumption of both oxygen radicals and possibly oxybromine radicals.

5) Gas-liquid contactor hydrodynamics play a critical role in bromate formation, influencing mass transfer rates, peak ozone residuals, spatial-temporal concentration gradients, and liquid backmixing phenomena.

INTRODUCTION

Bromate Toxicity

Oral feeding studies involving rodents have shown that the ingestion of bromate (BrO_3^-) via drinking water can promote the formation of renal tumors (Kurokawa et al., 1987). Given this data, the United States Environmental Protection Agency (USEPA) has classified BrO_3^- as a possible human carcinogen, and is likely to propose a maximum contaminant level in the range of 5 - 10 μg/L .

Initial mechanistic studies on the toxicity of BrO_3^- have focused on the formation of 8-hydroxy-deoxyguanosine (8-OHdG), an oxidation byproduct of the DNA base guanosine, as a possible cause for the production of renal tumors (Kasai, 1987). As guanosine has the lowest oxidation potential, E° = 0.71 V, of the DNA bases, guanosine acts preferentially as an electron source for the reduction of radical adducts of other DNA bases, as well as most other organic and inorganic radicals (Jovanovic and Simic, 1986).

At acidic pHs, as may occur under physiologic conditions, BrO_3^- is a moderately strong oxidant, $E^\circ = 1.15$ V, with reaction rates generally proportional to $[H^+]^2$ (Figure 1) (Noyes, 1980; Jwo and Chang, 1989). Under these conditions, BrO_3^- is known to react directly with a number of aromatic compounds, particularly hydroxy-aromatic and amino-aromatic compounds, generating aromatic radicals (Orbán and Körös, 1978; Herbine and Field, 1980). Furthermore, the decay of BrO_3 under strongly acidic conditions exhibits complex autocatalytic behavior (Field et al., 1972). As a result, a number of other oxidants, such as bromine dioxide (BrO_2), bromite (BrO_2^-), and bromine (Br_2), which are capable of generating organic radicals and brominated organic species, may be cyclically regenerated during the reduction of BrO_3^- (Noyes, 1980). In particular, BrO_2 ($E^\circ = 1.33$ V) is known to rapidly oxidize a variety of organic compounds, and is likely to play a key role in the formation of organic radicals under physiologic conditions (Neta et al. 1988).

Based on the lack of reaction during <u>in vitro</u> studies of the interaction of BrO_3^- with guanosine, Kasai et al. (1987) concluded that the oxidation of the guanosine base resulted from indirect radical reactions, possibly involving the hydrogen peroxide (H_2O_2) induced formation of oxygen radicals. However, the details of this study were not noted, particularly the pH ranges over which this reaction was studied, and whether any substances were added to induce the decomposition of BrO_3^-. Based on the previous discussion, it would appear that it is not the simple presence of BrO_3^-, but the rate and extent of BrO_3^- decay which control the formation of organic radicals.

A number of kinetic models are available for modeling the decay of BrO_3^- at acidic pHs in the presence of aliphatic and aromatic compounds (Edelson et al., 1979; Field and Boyd, 1985; Györgyi et al., 1985; Györgyi and Field, 1991; Turányi et al., 1993). While these models may prove to be simplistic in comparison to human physiology, they may be of some use in modeling the decay of BrO_3^- within the human gut.

Previous Studies

Recent studies of the formation of bromate during the ozonation of bromide-containing surface waters have focused primarily on the direct oxidation pathway, as described in the extensive study of the oxidation of Br^- to BrO_3^- in distilled water by Haag and Hoigné (1983).

$$O_3 + Br^- \rightarrow BrO^- + O_2 \qquad k_1 = 160\ M^{-1}\ s^{-1} \tag{1}$$

$$O_3 + BrO^- \rightarrow Br^- + 2O_2 \qquad k_2 = 330\ M^{-1}\ s^{-1} \tag{2}$$

$$O_3 + BrO^- \rightarrow BrO_2^- + O_2 \qquad k_3 = 100\ M^{-1}\ s^{-1} \tag{3}$$

$$O_3 + BrO_2^- \rightarrow BrO_3^- + O_2 \qquad k_4 = > 1 \times 10^5\ M^{-1}\ s^{-1} \tag{4}$$

In this model, the oxidation of hypobromite (BrO^-) to bromite (BrO_2^-) is the rate controlling step in the formation of BrO_3^-. As a result, control strategies for minimizing BrO_3^- formation have been based primarily on minimizing hypobromite (BrO^-) concentrations, either through pH reduction

$$HOBr \rightleftarrows H^+ + BrO^- \qquad pK_a = 8.8 \tag{5,6}$$

or reactions with ammonia (NH_3) (Haag and Hoigné, 1983; Wajon and Morris, 1982; Pastina Christina, et al., 1984).

$$HOBr + NH_3 \rightleftarrows NH_2Br + H_2O \qquad k_7 = 7.4 \times 10^7\ M^{-1}\ s^{-1} \quad k_8 = 0.3\ s^{-1} \tag{7,8}$$

In a previous pilot-scale study, the formation of bromate (BrO_3^-) was found to increase under conditions designed to optimize the production of hydroxyl radicals (OH) (Metropolitan Water District of Southern California and James M. Montgomery, Consulting Engineers, Inc., 1991) The PEROXONE process, which involves the optimized pre-addition of H_2O_2 to the O_3 contactor influent, was found to significantly increase BrO_3^- formation.

The fact that BrO_3^- formation increased under these treatment conditions is particularly interesting in that H_2O_2 has long been known to rapidly reduce HOBr and BrO^- to Br^- (Young, 1950; Buxton and Dainton, 1968).

$$HOBr + H_2O_2 \rightarrow Br^- + H^+ + H_2O + O_2 \qquad k_9 = 5.8 \times 10^4\ M^{-1}\ s^{-1} \tag{9}$$

$$BrO^- + H_2O_2 \rightarrow Br^- + H_2O + O_2 \qquad k_{10} = 5 \times 10^5\ M^{-1}\ s^{-1}\ \text{(assumed rate)} \tag{10}$$

Given that the rate of HOBr reduction by H_2O_2 is much greater than the rate of oxidation of BrO^- by O_3, particularly at a pH of 8.0, the high levels of BrO_3^- formed during these experiments could not have fbeen a result of the oxidation of BrO^- or HOBr by O_3, OH, or other oxidizing radicals. Furthermore, it would appear that the oxidation of Br^- by OH, not O_3

$$OH + Br^- \rightleftarrows BrOH^- \qquad (11,12)$$

$$k_{11} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$$

$$k_{12} = 3.3 \times 10^{7}\ s^{-1}$$

is the initial reaction in the formation of BrO_3^- under these conditions (Zehavi and Rabani, 1972).

These conclusions are supported by the results of testing involving the pre-addition of NH_3 to O_3 contactor influent. At concentrations up to 0.5 mg-N/L, NH_3 was found to have little impact on the formation of BrO_3^- (Krasner et al., 1993). As the rate of reaction of NH_3 with HOBr is extremely rapid, even at low pHs, the lack of any significant impact on BrO_3^- production indicates that BrO_3^- formation results from reactions not involving the HOBr and BrO^- species.

Based on this analysis, further pilot scale tests were conducted to examine the impact of contactor operations on the kinetics of BrO_3^- formation by a presumed free radical mechanism.

METHODS

O_3 residuals

O_3 residuals were measured by a gravimetric adaptation of the standard volumetric indigo technique. The volume of ozonated water added to a flask containing indigo was determined by weighing the flask prior to sampling and after sampling, with the difference being equal to the sample volume. O_3 residual were calculated from the formula

$$O_3\,(mg/L) = \frac{(ABS * TV)\ Blank - (ABS * TV)\ Sample}{0.42 * SV * l}$$

where
ABS = sample absorbance at 600 nm
TV = total volume = SV + indigo aliquot (mL)
SV = sample volume (mL)
l = absorbance pathlength (cm)
0.42 = ϵ / MW $\approx$ (20,000 M^{-1} cm^{-1}/48,000 mg/mole)

From this formula it can be seen that the standard formula is a specific case of this more general equation.

In a comparison of the gravimetric method and the standard volumetric method using ozonated surface water, the gravimetric method samples were found to have higher O_3 residuals, 0.453 vs. 0.392, with equal precision for both methods (n=20). The apparent difference between the two methods appears to be due to a negative bias of the volumetric method with O_3 losses resulting from offgassing during turbulent thin layer flow down the neck of the volumetric glassware, as well as O_3 decay prior to bulk mixing during the neck filling portion of sampling.

Hydrogen Peroxide

Hydrogen peroxide was analyzed by the enzymatic fluorescence method with modifications as suggested by Zika and Saltzman (1982) and Zepp et al. (1988). O_3 was stripped from solution using a oil-free compressor with the gas passing through a one-inch diameter spherical diffuser at the bottom of the graduated cylinder. The stripping procedure was followed to eliminate O_3 residuals and the consequent artifact formation of H_2O_2 resulting from the reaction between O_3 and p-hydroxyphenylacetic acid during sample addition. The fluorescence reagent was prepared as described by Kok et al. (1986) with the exception that 50 mg/L of horseradish peroxidase was used in the preparation of 100 mL of fluorescence reagent (Zepp et al., 1988).

Bromate

Bromate was analyzed by ion chromatography using bicarbonate-carbonate eluent and a 200 μL injection loop (Krasner et al., 1993). During the period over which these experiments were conducted, the minimum reporting level for BrO_3^- concentration was lowered from 5 μg/L to 3 μg/L. Unless otherwise noted, O_3 residuals were allowed to decay within the sample bottles. Sample quenching was accomplished by the addition of sufficient diethylamine to produce a 100 ppm solution upon bottle filling.

Bromide, Total Organic Carbon, and UV Absorbance

Bromide, and total organic carbon were measured in accordance to method description in Standard Methods. UV absorbance was measured in a 1 cm cell at 260 nm.

Surface Waters

Two surface which are imported to the Southern California region were studied. State Project Water (SPW), taken from the East Branch aqueduct, was used in the majority of the experiments. SPW is impacted by saline water prior to transport to Southern California reservoirs. As a result, Br^- levels have varied over the past several in the range of 0.15-0.45 mg/L.

Colorado River Water (CRW) was used in a number of experiments to compare BrO_3^- formation in different source waters. CRW typically contains less than 0.08 mg/L of Br^-. For the experiments with CRW, Br^- was added as the NaBr salt. Further descriptions of the two surface waters can be found the report by MWDSC and JMM (1991)

Contactors

Two contactors, 50 L and 100 L, were constructed of PVC, with portions near the diffusers constructed of clear PVC. Both were constructed and operated intermittently for a year prior to the onset of this study. Both were equipped with approximately 25 sample taps with the majority placed near the diffusers. The sample taps were 1/4" O.D. teflon tubing with the flow controlled during sampling by a 1/4" stainless steel ball valve.

The 50 L contactor was constructed with 3" O.D. pipe and was approximately 1050 cm in total length. The downflow, gas-liquid contacting portion of the contactor was 525 cm in length, with the 1" diameter spherical diffuser placed 20 cm above the bottom. The horizontal flow portion, 75 cm in length, was the intermediate portion between the downflow leg and the 475 cm upflow portion. The 100 L contactor, constructed of 6.4" O.D pipe, was 550 cm in length, with the diffuser placed at the mid-portion of the contactor. Both contactors were operated at water flow rates ranging from 5 to 20 gpm.

O_3 was generated from hospital-grade oxygen using laboratory scale O_3 generators. Gas concentrations in most experiments were typically 2.0% (w/w), as measured by UV absorbance.

Kinetic Models

BRDOM Model

The radical reactions were modeled using the RISØ model to account for oxyradical behavior; the various bromine and oxybromine species were modeled using the NDRC-NIST inorganic radical database as the primary reference source and guide (Bjergbakke et al., 1984; Bjergbakke et al., 1989; Neta et al., 1988). Organic radicals were modeled primarily on reaction sets described in the database compiled by Neta et al., (1990). Reaction sets describing key reactions of HCO_3^--CO_3^{2-} system as well as impact of NH_3 were included in the BRDOM model as well.

The stiff, coupled, nonlinear differential equations, comprised of 65 species and 190 reactions, were integrated using a reaction kinetics modeling program utilizing a variable-step adaption of Gear's method and a sparse Jacobian matrix (Braun et al., 1988).

Direct Oxidation Model

The direct oxidation model, as proposed by Haag and Hoigné (1983), was altered so that the oxidation of BrO_2^- by O_3 would be analogous to the reversible oxidation reaction of chlorite (Haag and Hoigné, 1983; Kläning et al, 1985; Kläning et al., 1984).

$$O_3 + BrO_2^- \rightleftarrows O_3^- + BrO_2 \qquad (22,23)$$
$$k_{22} = 1 \text{ x } 10^5 \text{ M}^{-1} \text{ s}^{-1}$$
$$k_{23} = 5 \text{ x } 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Furthermore, the acid dissociation constant for bromous acid ($HBrO_2$) was

$$HBrO_2 \rightleftarrows H^+ + BrO_2^- \qquad (24,25)$$
$$pK_a = 4.9$$

was assume to be equal to 4.9, rather than the value of 2 expected using the Pauling relationship for oxoacids. This value is based on recent reevaluations of the kinetics and thermodynamics for the decay of BrO_2^- (Massagali et al, 1970; Field and Fösterling, 1986).

These decay initiating reactions, along with the following reaction,

$$O_3 + Br_2^- \rightarrow O_3 + Br_2 \qquad (26)$$
$$k_{26} = 5 \text{ x } 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (assumed rate)}$$

which is analogous to the oxidation of Br_2^- by HO_2, would also explain the results of Sayato et al. (1990) that in solutions with very high Br^- levels, OH radicals were responsible for the conversion of Br^- to HOBr (Sutton and Downes, 1972). A similar reaction involving the oxidation of Cl_2^- by O_3 has recently been reported (Bielski, 1993).

INITIAL RESULTS

Observed Rate of BrO_3^- Formation

The formation of BrO_3^- in the two waters is a rapid process (Table 1). Furthermore, it is scaled to the rate and extent which the O_3 residual decays, and not to the lifetime of O_3 as would be expected from the direct reaction model. A comparison of the actual BrO_3^- formation to the predicted BrO_3^- formation, based on the direct reaction model is included to further highlight the deficiencies of the direct reaction model. The concept that BrO_3^- formation is dependent on O_3 residual decay and not O_3 residual lifetime is further illustrated in Table 2 which compares the production of BrO_3^- in two different waters. As shown, the two water had similar levels of BrO_3^- formation despite pronounced differences in O_3 decay rates.

OH Radical Scavenging

Radical scavenging experiments, using isopropyl alcohol (IPA) as the primary OH scavenger, show that the rapid oxidation of Br^- by OH to be the key reaction in initiating the formation of BrO_3^- (Table 3). The minimal scavenging effect found at the lowest IPA concentration, 0.3 mg/L, again suggests that the oxidation of HOBr and BrO^-, in this case by

$$OH + HOBr \rightarrow BrO + H_2O \quad (13)$$
$$k_{13} = 2.0 \times 10^9\ M^{-1} s^{-1}$$

$$OH + BrO^- \rightarrow BrO + OH^- \quad (14)$$
$$k_{14} = 4.2 \times 10^9\ M^{-1} s^{-1}$$

OH radicals, plays little, if any, role in BrO_3^- production in these waters (Kläning and Wolff, 1985; Buxton and Dainton, 1968). Had these reactions played a significant part in the formation of BrO_3^-, a 50% reduction should have resulted.

Further analysis of the impact of IPA addition on BrO_3^- formation shows that actual reductions are less than the theoretical reductions based on competition kinetics between IPA and Br^- for OH radicals. This is due to the scavenging of OH radicals primarily by naturally occurring dissolved organic matter (DOM) (Hoigné et al., 1987; Haag and Yao, 1991).

$$OH + DOM \rightarrow {}^{\bullet}DOM + OH^- \quad (15)$$
$$k_{15} \approx 2 \times 10^4\ L/mg\ s^{-1},\ [DOM] = TOC\ (mg/L)$$

At higher O_3 doses, similar results are found, with BrO_3^- formation reduced below the detection limit, when sufficient IPA was added (Table 3). At the higher O_3 doses, the actual reductions in BrO_3^- formation agreed fairly well with the predicted reductions, based on the kinetic competition for OH between Br^- and IPA (Wolfenden et al., 1982).

$$OH + CHOH(CH_3)_2 \rightarrow {}^{\bullet}COH(CH_3)_2 + H_2O \quad (16)$$
$$k_{16} = 1.9 \times 10^9\ M^{-1} s^{-1}$$

In similar experiments using ethanol as a radical scavenger, somewhat different results were found. While ethanol reacts with OH at the same rate as IPA, ethanol was much more effective in lowering BrO_3^- production, even when compared on a molar basis (Table 4) (Wolfenden et al., 1982). This appears to be due primarily to the enhanced decay rate of O_3 in the presence of ethanol (Staehelin and Hoigné, 1985). Alternately, this phenomena may be explained by the fact that the primary oxidation byproduct of ethanol, the hydrated form of acetaldehyde, reacts more quickly with OH than does ethanol (Schuchmann and von Sonntag, 1988; Wolfenden et al., 1982). In contrast, acetone reacts much more slowly with OH than does IPA (Wolfenden et al., 1982).

O_3 Contactors - Dose and Residual

To further explore the relationship between O_3 dose, O_3 residual, and BrO_3^- formation, a number of experiments were conducted with the contactor operated in a recycle mode. In these experiments, O_3 was applied in small sequential increments over an extended period of time. Table 5 compares the BrO_3^- formation in these experiments to the results of the experiments where O_3 was applied in a single dose. As shown, BrO_3^- formation shows little dependence on accumulated O_3 dose, but is highly dependent on O_3 residual.

The results of these recycle experiments are similar to the results of bench-scale experiments conducted where extended O_3 doses are required to produce measurable quantities of BrO_3^- in surface waters containing moderate levels of Br^- (Krasner et al., 1991; Siddiqui and Amy, 1993; Glaze et al., 1993). To better mimic both BrO_3^- formation and the mass transfer and decay of O_3 residuals within pilot-scale and full-scale O_3 contactors, future bench-scale experiments should revert back to using concentrated aliquots of aqueous O_3 for dosing experiments. Alternately, to lower BrO_3^- production in full-scale facilities, future O_3 contactors should be designed to maintain low O_3 residuals throughout the contactor.

In a number of experiments, the impact of the gas-liquid mixing zone above the O_3 diffuser on BrO_3^- formation was studied. In the first experiment, the possibility that the formation of BrO_3^- is influenced by gas-liquid interfacial reactions was investigated. This was checked by comparing the production of BrO_3^- in a low Br^- (0.08 mg/L) surface water where additional Br^- (0.25 mg/L) was added to the water flow at two different locations. In the first run, Br^- was added to the contactor influent. In the second run, Br^- was added just downstream of the O_3 diffuser in the gas free reaction zone. Both runs were found to have similar BrO_3^- levels, with the second run having a slightly higher level of BrO_3^- formation. These two runs confirm that BrO_3^- forms primarily as the result of the decay of O_3.

In the second experiment, the impact of gas-liquid hydrodynamics on BrO_3^- formation was investigated. In a number of runs, the formation of BrO_3^- in the 3" (7.7 cm) diameter - 50 L contactor used in the majority of experiments was compared to a 6.4" (16.2 cm) diameter - 100 L contactor. The primary difference between the two contactors was the impact of different superficial water velocities on the mass transfer zone when operated at similar volumetric flow rates. In the 3" - 50 L contactor, the high superficial water velocities led to well defined hydrodynamics, with the water flow dominating the hydrodynamics of the gas-liquid mixing zone, resulting in a compressed O_3 mass transfer zone. As a result, O_3 residuals measured just downstream of the O_3 diffuser were similar to the applied dose. Furthermore, little BrO_3^- formation occurred within the gas-liquid mixing zone.

In contrast, the operation of the 6.4" - 100 L at superficial velocities similar to those likely to be found in full scale contactors resulted in poorly defined hydrodynamics within the gas-liquid mixing zone immediately above the diffuser. In general, the hydrodynamics were governed by the rise and coalescence of gas bubbles, resulting in the formation of convection cells directly above the diffuser. The reaction zone within this region could be furthered defined by extensive backmixing within this relatively high O_3 residual zone. As a result, the effluent from the 6.4" - 100 L contactor was found to have higher levels of BrO_3^- than the 3" - 50 L even when operated at similar O_3 doses and volumetric flow rates (Table 6). Furthermore, the initial downstream O_3 residual measurements were far less than the applied O_3 dose. This indicates that a significant portion of the O_3 dosed into the 6.4"- 100 L contactor decays within the gas-liquid mixing zone. As a result, the majority of BrO_3^- formation in the 6.4" - 100 L contactor occurred within the gas-liquid mixing zone, and not downstream of the diffuser. Furthermore, the disparity between initial O_3 residuals in the two contactors, even when treating the same water, indicates that the concept of "O_3 demand", when applied to full-scale contactors is an unwitting ad hoc description of the impact of contactor hydrodynamics on dispersion and subsequent decay, not an indicator of general water quality, nor a measure of easily oxidized constituents.

pH Variations

A decrease in the influent pH from the initial value of 8.0 to 7.0 prior to ozonation resulted in decreases in BrO_3^- formation of 45% - 60% when sulfuric acid was used to lower the pH. Alternately, when the coagulant $FeCl_3$ was added to the contactor influent and the pH reduced from 8.0 to 7.0, essentially no change in BrO_3^- formation was found. While the decrease in BrO_3^- formation on the addition of acid is often assumed to result from a equilibrium-based reduction in BrO^- available for reaction, the decrease in BrO_3^- formation appears to be due to the reductions in the efficiency of OH radical generation at lower pHs. This conclusion is supported by the lack of change in BrO_3^- formation in the Fe^{3+} - O_3 system.

The oxidation of DOM results in the formation of peroxyorganic radicals. The rate of peroxyorganic radical decay is pH dependent, typically increasing as the pH of the water is raised (Bothe et al., 1977). However at low pHs, the rate of peroxyorganic radical decay may be slow enough to allow for the direct reaction of O_3 with some of the slower decaying radicals. As a result, O_3 is consumed without generating OH radicals. At the high doses of $FeCl_3$ (~100 μM) used in this run, Fe^{3+} may impinge on these reactions by either complexing with DOM, prior to oxidation or possibly, by outcompeting O_3 for the oxidation of peroxyorganic radicals (Brault and Neta, 1984). Either case would allow for the radical decay of O_3 resulting in the formation of OH radicals.

An attempt was made to reduce BrO_3^- formation by raising the pH so that

$$\mathrm{OH} + \mathrm{Br}^- \rightleftarrows \mathrm{BrOH}^- \rightleftarrows \mathrm{Br} + \mathrm{OH}^- \qquad (11,12,17,18)$$

$$k_{17} = 3.3 \times 10^6\ \mathrm{s}^{-1}$$

$$k_{18} = 1.3 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

the OH^- induced decay of the bromide radical (Br) back to OH and Br^- would be the dominant reaction. The pH of the water was raised from 7.8 to 9.0 and then to 9.7. As shown in Table 7, the pH increase resulted in a reduction of BrO_3^- of only 30% - 41%. Further kinetic modeling with the BRDOM model showed that while reaction (18) would control the fate of the Br radical, the conversion of bicarbonate (HCO_3^-) to carbonate (CO_3^{2-}) at these pHs resulted in the significant production of BrO_3^-.

At the pHs typically found in this study, 7.0 - 8.0, the slow oxidation of bicarbonate (HCO_3^-)

$$\mathrm{OH} + \mathrm{HCO_3^-} \rightarrow \mathrm{CO_3^-} + \mathrm{H_2O} \qquad (19)$$

$$k_{19} = 4 - 8 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

played a minor role (Buxton et al., 1988; Holcman et al, 1987). However at higher pHs, where carbonate (CO_3^{2-}) concentrations become appreciable, the faster reaction OH with CO_3^{2-} plays a critical role in forming an alternate reaction involving the carbonate radical (CO_3^-) (Buxton et al., 1988).

$$\mathrm{OH} + \mathrm{CO_3^{2-}} \rightarrow \mathrm{CO_3^-} + \mathrm{OH}^- \qquad (20)$$

$$k_{20} = 4 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

At these higher pHs, the main reaction pathway for BrO^- shifted from reduction by H_2O_2, reaction (10), to oxidation by CO_3^- (Buxton and Dainton, 1968).

$$\mathrm{CO_3^-} + \mathrm{BrO}^- \rightarrow \mathrm{CO_3^{2-}} + \mathrm{BrO} \qquad (21)$$

$$k_{21} = 4.3 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

Given these modeling results, there would appear to be at least two key pH dependent pathways for the formation of BrO_3^-. Furthermore, this high pH pathway in which BrO^- is now the key precursor maybe minimized through the addition of NH_3 and formation of bromamine.

Bromide Levels

Increasing the initial Br^- levels from 0.22 mg/L to 0.39 mg/L and 0.79 mg/L was found to increase BrO_3^- formation. The increases result from increased probabilites of reaction between OH and Br^-. Furthermore, increased Br^- levels will act to stabilize the Br radicals which through the reactions

$$\mathrm{Br} + \mathrm{Br}^- \rightleftarrows \mathrm{Br_2^-} \qquad (22,23)$$

$$k_{22} = 1.1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

$$k_{23} = 5 \times 10^4\ \mathrm{s}^{-1}$$

which may allow for more reactions with other oxidants (Mamou et al. 1977).

DISCUSSION

From these experiments it can be shown that BrO_3^- formation is a fairly rapid process. Furthermore, the formation of BrO_3 was shown to be initiated by the OH radical oxidation of of Br^-, and is highly sensitive to residual O_3 concentrations and relatively insensitive to total O_3 doses.

A skeleton model describing the key reactions (FIgure 2) in the BRDOM model can be described by the following reactions.

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \quad (24)$$
$$O_3^- \rightleftarrows O^- + O_2 \quad (25)$$
$$O^- + H_2O \rightleftarrows OH + OH^- \quad (26)$$

$$OH + Br^- \rightleftarrows BrOH^- \rightleftarrows Br + OH^- \quad (11,12,18,19)$$
$$Br + O_3 \rightarrow BrO + O_2 \quad (27)$$
$$2BrO + H_2O \rightarrow BrO_2^- + HOBr + H^+ \quad (28)$$
$$O_3 + BrO_2^- \rightarrow O_3^- + BrO_2 \quad (29)$$
$$2BrO_2 + H_2O \rightarrow BrO_3^- + BrO_2^- + 2H^+ \quad (30)$$

With the exception of reaction (27), all the reactions in this skeleton model are generally accepted reactions. Without reaction (27), the BRDOM defaults to being an extended version ofthe Richardson model, which like the direct oxidation model, underpredicts BrO_3^- formation, but to a lesser degree than the direct oxidation model.

In the gas phase, O_3 is known to react with Br radicals, resulting in the formation of bromine monoxide (BrO) (Michael et al., 1978).

$$Br + O_3 \rightarrow BrO + O_2 \quad (27)$$

A similar aqueous phase reaction was postulated by Haruta and Takeyama (1981).

In an attempt to further elucidate Br radical chemistry an excess of H_2O_2 was added to the contactor influent in one experiment in an attempt to scavenge Br radicals through the reaction

$$Br + H_2O_2 \rightarrow Br^- + H^+ + HO_2 \quad (31)$$
$$k_{22} = 5 \times 10^9\ M^{-1}\ s^{-1}$$

(Sutton et al., 1965). Assuming an aqueous phase reaction between Br and O_3, with rate constant similar to that found in the gas phase, $6 \times 10^8\ M^{-1}\ s^{-1}$, the excess of H_2O_2 would still have quenched Br and eliminated BrO_3. However, BrO_3^- production was reduced only 47%. Given the reaction conditions, it is apparent that the reaction rate between Br and O_3 is extremely fast, $k_{30} \sim 1 \times 10^{10}\ M^{-1}\ s^{-1}$. However, given the methods used to determine this rate constant, this rate estimate can hardly be considered to be a reliable value.

CONCLUSIONS

In surface waters containing moderate levels of Br^- and DOM it can be expected that the formation of OH will lead to the oxidation of Br^- and the possible formation of BrO_3^-. A number of conditions can be imposed on the operation of a full scale contactor in order to minimize BrO_3^- formation. These operating conditions may include contactor operation at low O_3 concentrations, and with minimal backmixing. However, as O_3 serves may purposes, the impact of low O_3 concentration operation on other process criteria is uncertain, particularly with respect to disinfection.

Further work in this area should be conducted with filtered water, operating in a post-ozonation mode. It is likely that the removal of some of the more easily oxidized constituents during the sedimentation and filtration process may improve process predictability and stability.

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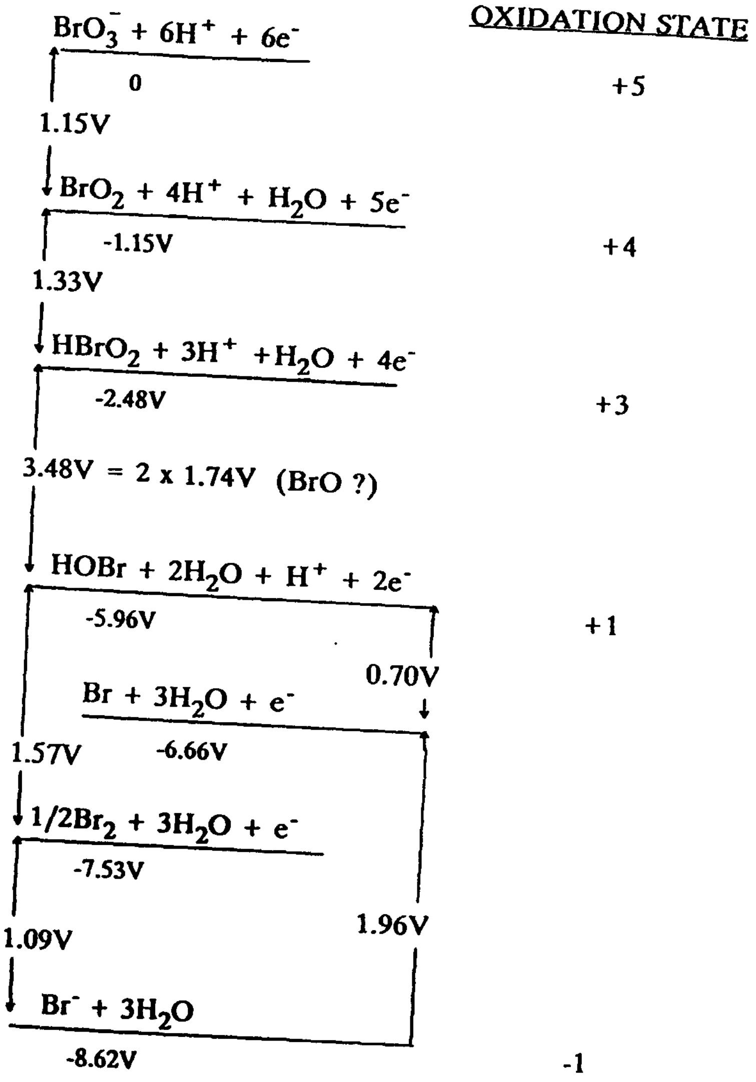

FIG. 1

TABLE 1. OBSERVED RATE OF BrO3 FORMATION IN SPW

O3 Dose (mg/l)	Br- (mg/l)	Initial O3 Residual (mg/l)	O3 Residual Half-life (s)	O3 Decay Period (s)	BrO3 (µg/l)	Predicted BrO3 Dir Rxns (µg/l)	Reaction Quenching Agent
1.0	0.28	0.85	21	42	8	0.1	DEAM
1.0	0.28	0.85	21	> 1000	9	0.1	---
2.0	0.28	1.86	34	42	22	1	DEAM
2.0	0.28	1.86	34	42	26	1	Air Strip
2.0	0.28	1.86	34	> 1000	33	2	---
4.0	0.17	3.79	122	1	8	0.006	DEAM
4.0	0.17	3.79	122	16	18	0.4	DEAM
4.0	0.17	3.79	122	29	23	1	DEAM
4.0	0.17	3.79	122	70	43	5	DEAM
4.0	0.17	3.79	122	> 1000	180	23	---

TABLE 2. COMPARISON OF BrO3 FORMATION IN TWO DIFFERENT SURFACE WATERS

WATER	O3 Dose (mg/l)	Br- (mg/l)	Initial O3 Residual (mg/l)	O3 Residual Half-life (s)	BrO3 (µg/l)	Predicted BrO3 Dir Rxns (µg/l)
SPW	1.0	0.28	0.85	21	9	0.1
CRW	1.0	0.34	0.75	50	13	0.9

TABLE 3. THE IMPACT OF OH RADICAL SCAVENGING ON THE PRODUCTION OF BrO3

O3 Dose (mg/l)	IPA Dose (mg/l)	Br- (mg/l)	Initial O3 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)	Predicted BrO3 Dir Rxns (µg/l)
1.0	0	0.28	0.91	19	15	0.1
1.0	0.3	0.28	0.88	17	13	0.1
1.0	3.0	0.28	0.80	10	8	0.02
1.0	6.0	0.28	0.71	9	< 5	0.01
2.0	0	0.28	1.86	34	33	2
2.0	18	0.28	1.07	24	< 5	0.3
4.0	0	0.29	3.31	80	122	17
4.0	24	0.29	3.00	29	12	3
4.0	0	0.17	3.79	122	180	23
4.0	150	0.17	6.28*	20	< 3	3
7.0	0	0.29	6.26	118	303	69
7.0	12	0.29	5.82	78	61	38
7.0	24	0.28	6.64	40	50	33

* Gas Entrainment

TABLE 4. THE IMPACT OF DIFFERENT ALCOHOLS ON BrO3 FORMATION

O3 Dose (mg/l)	Alcohol Dose (mg/l)	Alcohol Dose (µM)	Initial O3 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)
	Ethanol	Ethanol			
1.0	0	0	0.85	18	15
1.0	1	22	0.78	11	3
1.0	2	43	0.62	10	< 3
1.0	4	87	0.59	7	< 3
1.0	6	130	0.56	6	< 3
1.0	8	174	0.52	5	< 3
	IPA	IPA			
1.0	0	0	0.91	19	15
1.0	0.3	5	0.88	17	13
1.0	3	50	0.80	10	8
1.0	6	100	0.71	9	< 5
1.0	12	200	0.80	8	< 5

TABLE 5. IMPACT OF O3 RESIDUAL & O3 DOSE ON BrO3 FORMATION

SINGLE DOSE				
O3 Dose (mg/l)	Initial O3 Residual (mg/l)	Initial H2O2 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)
1.0	0.91	---	19	15
2.0	1.86	0.087	34	33
4.0	3.31	0.070	80	122
7.0	6.26	---	117	303

RECYCLE OPERATION (0.4 mg/l per pass)				
Accumul. O3 Dose (mg/l)	Initial O3 Residual (mg/l)	Initial H2O2 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)
0.4	0.13	---	0.4	< 5
1.4	0.23	---	2	< 5
2.4	0.33	---	6	6
3.3	0.37	---	10	12
4.4	0.36	---	18	16
5.4	0.34	---	23	19
6.4	0.35	---	24	25

RECYCLE OPERATION (0.2 mg/l per pass)				
Accumul. O3 Dose (mg/l)	Initial O3 Residual (mg/l)	Initial H2O2 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)
0.20	---	0.033	---	< 3
0.67	0.04	0.038	2	< 3
1.34	0.13	---	2	< 3
2.00	0.17	0.061	2	< 3
2.67	0.22	0.060	6	< 3
4.00	0.19	0.035	7	8

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* SPW, pH 8.0, 24-26 deg C, Br- from 0.28 to 0.29 mg/l, velocities from 7.5 to 17.5 cm/s

TABLE 6. IMPACT OF CONTACTOR HYDRODYNAMICS ON BrO3 FORMATION *

O3 Dose (mg/l)	Contactor Diameter (inches)	Superficial Velocity (cm/s)	Initial O3 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)
1.0	3	15	0.91	19	15
1.0	6.4	4.6	0.41	17	24
2.0	3	12.5	1.86	34	33
2.0	6.4	3.4	1.12	39	45

---

* Br- = 0.28 mg/l

TABLE 7. pH EFFECTS ON BrO3 FORMATION *

O3 Dose (mg/l)	pH	Additive	Initial O3 Residual (mg/l)	O3 Residual Half-Life (s)	BrO3 (µg/l)
1.0	8.0	--	0.91	19	15
1.0	7.0	H2SO4	0.87	25	6
1.0	7.0	FeCl3	1.04	33	14
2.0	8.0	--	1.49	49	71
2.0	7.0	H2SO4	1.63	81	38
2.0	7.8	--	1.63	47	17
2.0	9.0	NaOH	1.23	21	10
2.0	9.7	NaOH	1.07	14	12

* Br- ranges from 0.22 to 0.29 mg/l

TABLE 8. IMPACT OF Br- LEVELS ON BROMATE FORMATION

O3 Dose (mg/l)	Br- mg/l	Initial O3 Residual mg/l	O3 Residual Half-Life s	BrO3 µg/l
1.0	0.22	0.83	22	5
1.0	0.39	0.86	23	12
1.0	0.79	0.88	25	28

FIG 2