

Enhanced Bromate Formation during Chlorination of Bromide-Containing Waters in the Presence of CuO: Catalytic Disproportionation of Hypobromous Acid

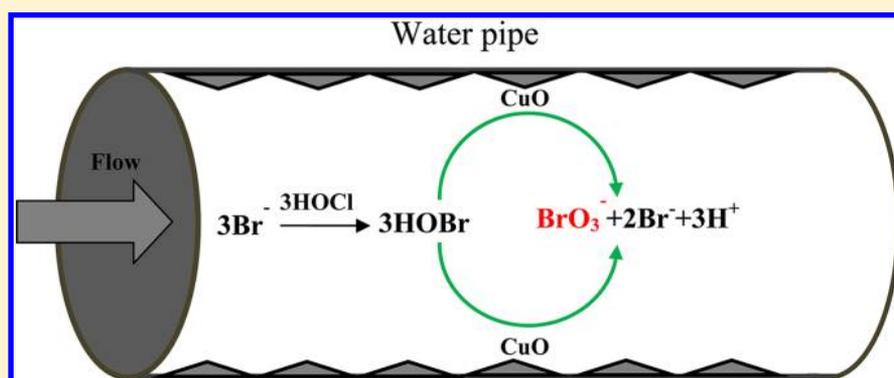
Chao Liu,[†] Urs von Gunten,^{‡,§} and Jean-Philippe Croué^{*,†}

[†]Water Desalination and Reuse Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

[‡]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, CH-8600 Dübendorf, Switzerland

[§]School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

S Supporting Information



ABSTRACT: Bromate (BrO_3^-) in drinking water is traditionally seen as an ozonation byproduct from the oxidation of bromide (Br^-), and its formation during chlorination is usually not significant. This study shows enhanced bromate formation during chlorination of bromide-containing waters in the presence of cupric oxide (CuO). CuO was effective to catalyze hypochlorous acid (HOCl) or hypobromous acid (HOBr) decay (e.g., at least 10^4 times enhancement for HOBr at pH 8.6 by 0.2 g L^{-1} CuO). Significant halate concentrations were formed from a CuO-catalyzed hypohalite disproportionation pathway. For example, the chlorate concentration was $2.7 \pm 0.2 \mu\text{M}$ ($225.5 \pm 16.7 \mu\text{g L}^{-1}$) after 90 min for HOCl ($C_0 = 37 \mu\text{M}$, $2.6 \text{ mg L}^{-1} \text{ Cl}_2$) in the presence of 0.2 g L^{-1} CuO at pH 7.6, and the bromate concentration was $6.6 \pm 0.5 \mu\text{M}$ ($844.8 \pm 64 \mu\text{g L}^{-1}$) after 180 min for HOBr ($C_0 = 35 \mu\text{M}$) in the presence of 0.2 g L^{-1} CuO at pH 8.6. The maximum halate formation was at pHs 7.6 and 8.6 for HOCl or HOBr, respectively, which are close to their corresponding pK_a values. In a HOCl– Br^- –CuO system, BrO_3^- formation increases with increasing CuO doses and initial HOCl and Br^- concentrations. A molar conversion (Br^- to BrO_3^-) of up to $(90 \pm 1)\%$ could be achieved in the HOCl– Br^- –CuO system because of recycling of Br^- to HOBr by HOCl, whereas the maximum BrO_3^- yield in HOBr–CuO is only 26%. Bromate formation is initiated by the formation of a complex between CuO and HOBr/OBr[•], which then reacts with HOBr to generate bromite. Bromite is further oxidized to BrO_3^- by a second CuO-catalyzed process. These novel findings may have implications for bromate formation during chlorination of bromide-containing drinking waters in copper pipes.

INTRODUCTION

The formation of bromate during the ozonation of bromide-containing waters has been intensively studied.^{1–5} In the presence of ozone, bromate is produced from the reactions of ozone and $\cdot\text{OH}$ radicals with bromide (Br^-), via several intermediates including hypobromite (BrO^-) and bromite (BrO_2^-).⁵ Because bromate is potentially carcinogenic, it is regulated in potable water at a maximum contaminant level (MCL) of $10 \mu\text{g L}^{-1}$ in many countries.^{6–8} Moreover, bromate is stable, and there is currently no economically feasible technology to remove it once it is formed.⁹ Therefore, the

treatment conditions have to be optimized in some cases to mitigate bromate formation while disinfection is still guaranteed (e.g., ammonia addition and lowering the pH⁹).

Due to its low cost, chlorine is globally the most used drinking water disinfectant. It is commonly used as a final treatment step to maintain a residual disinfectant in distribution

Received: May 31, 2012

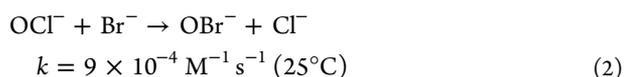
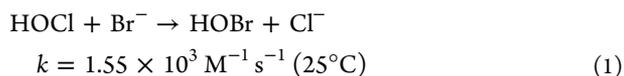
Revised: September 8, 2012

Accepted: September 10, 2012

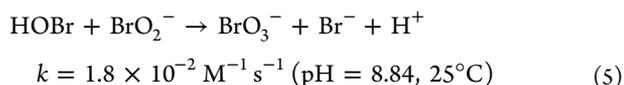
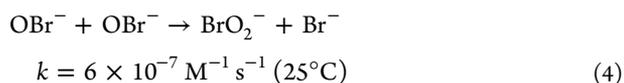
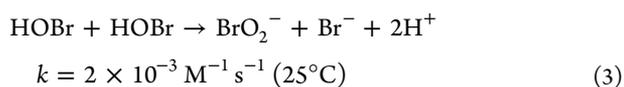
Published: September 10, 2012

systems. Bromate can be a byproduct of commercial solutions of sodium hypochlorite.¹⁰ In a survey, it has been demonstrated that a few micrograms per liter of bromate can be found in distributed waters if such products are used for final disinfection. Nevertheless, bromate formation is generally not of concern in drinking water chlorination.¹¹ Significant bromate formation in chlorinated water can be observed under some special conditions (e.g., sunlight irradiation).¹²

Bromate formation during chlorination of bromide-containing waters is a slow process. In a first step (eqs 1 and 2), bromide is oxidized by hypochlorous acid (HOCl) to form hypobromous acid (HOBr),¹³ which is in equilibrium with OBr⁻ with a pK_a of 8.8.¹



Although there is no further reaction between HOCl/OCl⁻ and HOBr/OBr⁻,¹⁴ HOBr can disproportionate to bromate and bromide (eqs 3–5).^{15,16} The disproportionation of HOBr is the reaction in which HOBr (i.e., Br(+I)) reacts with itself, leading to a reduced species (Br⁻, Br(-I)) and to oxidized species (BrO₂⁻, Br(+III), BrO₃⁻, Br(+V)).



The low rate constants for HOBr disproportionation illustrate that the formation of bromate during chlorination is a very slow process in homogeneous solution and should not lead to significant bromate levels in distribution systems.

Recently, we discovered that bromate formation can be significant in distribution systems employing chlorine as a final disinfectant. The unexpected increase of the bromate content was attributed to the presence of cupric oxide (CuO) accumulated on the surface of the pipes.¹⁷

Previous studies indicated that metal oxides (e.g., CuO),^{18–20} Cu(II) in alkaline solutions,^{21,22} and Cu(OH)₂²³ can enhance HOCl/OCl⁻ decay. A similar enhancement for HOBr/OBr⁻ decay in alkaline solution by Cu(II) was also confirmed.²¹ However, the reported products of the metal (oxides)-catalyzed decomposition of hypohalite are oxygen and the halide. Hypochlorite decay in the presence of manganese, iron, cobalt, nickel, and copper oxides did not lead to enhanced chlorate formation.¹⁹

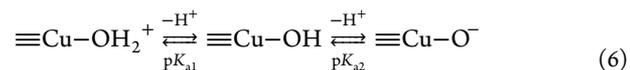
In view of our observation of enhanced bromate formation in water pipes and the potential toxicological significance of bromate production in distribution systems (e.g., in household copper pipes), the aim of this study was to elucidate the role of CuO in the enhancement of bromate formation during chlorination of bromide-containing waters. The influence of drinking water treatment parameters such as chlorine dose, bromide concentration, and pH in the presence of various

concentrations of CuO on the kinetics and extent of bromate formation was investigated.

MATERIALS AND METHODS

Reagents. All chemical solutions were prepared from reagent grade chemicals or stock solutions using deionized water (18.2 MΩ·cm, Milli-Q, Millipore). A sodium hypochlorite (NaOCl) solution was used as the source of chlorine (13% active chlorine, Acros Organics). For experiments investigating chlorate formation, chlorate-free NaOCl solution was produced by bubbling chlorine gas (99.999% pure, Abdullah Hashim Industrial Gases and Equipments Co. Ltd., Jeddah, KSA) through continuously stirred 0.1 M sodium hydroxide at 4 °C. HOBr solutions were prepared by reacting NaOCl with Br⁻ according to Lei et al.²⁴ CuO particles were prepared in our laboratory, and their surface area, i.e., 18.1 m² g⁻¹, was analyzed by a Micromeritics Tristar II surface area and porosity system. Details for the preparation of HOBr solutions and CuO particles are given in the Supporting Information (Text 1 in SI).

The pH_{pzc} (pH at which the surface has a zero charge) of the CuO particles was determined by a potentiometric titration in 0.01 M NaNO₃ solutions under a nitrogen atmosphere with 0.02 M HCl and 0.02 M NaOH.²⁵ The intrinsic surface acidity constants, i.e., pK_{a1}(int) = 7.1 and pK_{a2}(int) = 10.1 (eq 6), were determined from the titration data. The obtained pH_{pzc} is 8.6.



Analytical Methods. Residual oxidant stands for the sum of [HOCl]_T and [HOBr]_T (where [HOX]_T = [HOX] + [OX⁻]; X = Cl, Br; and [HOX]_{TO} is the initial concentration of HOX). Oxidant concentrations were analyzed spectrophotometrically by the *N,N*-diethyl-*p*-phenylenediamine (DPD) method at 515 nm.²⁶

Bromate, chlorite, and chlorate were quantified by a Dionex 1600 reagent free ion chromatograph (IC) with a KOH online eluent generator. Samples, injected via a 250 μL loop, were eluted (20 mM KOH) at a flow rate of 0.25 mL min⁻¹ through an Ionpac AS19 column. The quantification limits for bromate, chlorite, and chlorate are 1 μg L⁻¹, and relative standard deviations are below 5%. Retention times for chlorite, bromate, and chlorate are 6.5, 7.0, and 10.5 min, respectively.

The dissolved copper content was determined on an Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) with a detection limit of 0.01 μg L⁻¹.

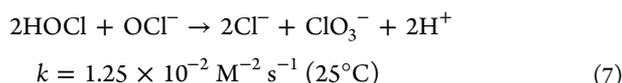
Experimental Setup. The role of several parameters in the kinetics of bromate formation was investigated (CuO dose, initial concentrations of HOCl and bromide, and pH). Table S1 (SI) gives the details of the experimental conditions. The CuO dose ranged from 0.05 to 0.5 g L⁻¹. The initial concentrations ranged from 14 to 70 μM (i.e., 1.0–5.0 mg L⁻¹ of Cl₂) for HOCl or HOBr and from 2 to 10 μM for bromide (i.e., 160–800 μg L⁻¹). The pHs were adjusted to 6.6, 7.6, 8.6, 9.6, and 10.6 with 2.5 mM tetraborate buffer and acid or base. No significant pH change was observed during the reaction for the solutions buffered at pHs 8.6, 9.6, and 10.6. The changes were less than 0.2 for the pHs 6.6 and 7.6.

All experiments were conducted in the dark and under continuous agitation using a magnetic stirrer. Reactions were initiated by the injection of a HOCl or HOBr stock solution to the tetraborate buffered solutions containing CuO at room temperature (21 ± 1 °C). Bromide was added when required.

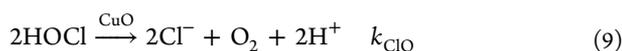
Samples were withdrawn at preselected time intervals and filtered within 15 s (insignificant considering the reaction times of several hours) through a 0.45 μm syringe filter (surfactant-free cellulose acetate membrane). The filter was pretreated with HOCl or HOBr solutions (2.5 $\text{mg L}^{-1} \text{Cl}_2$) and then rinsed with MQ water. Thus, the filtration had no significant oxidant demand. The filtered samples were analyzed for residual oxidant concentrations. For IC analyses, the samples were quenched immediately with sulfite.

RESULTS AND DISCUSSION

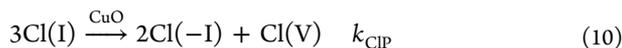
Chlorate Formation from HOCl Decay in the Presence of CuO. In the absence of metal oxides, the depletion of HOCl mainly occurs through slow disproportionation (eq 7),²⁷ and oxygen generation (eq 8) is minor (less than 10%).^{22,28}



However, in the presence of CuO, the formation of O_2 (eq 9) predominates during the HOCl decay.¹⁹



By analogy, the CuO-catalyzed disproportionation of HOCl can be described as eq 10 (where Cl(I): HOCl or OCl^- , Cl(-I): Cl^- , Cl(V): ClO_3^-)



$k_{\text{Cl}} = k_{\text{ClO}} + k_{\text{ClP}}$ is the total apparent HOCl decay rate constant if pseudo-first-order kinetics are assumed for both processes (see below).

Figure 1 shows the HOCl decay and chlorate formation in the presence of CuO for varying pH values. According to the rate constant of eq 7, the loss of chlorine in homogeneous solution would be less than 1% for a reaction time of 180 min. In agreement with previous studies, significant chlorine depletion was observed at all pH values in the presence of CuO.^{18,20} The chlorine decay rates decrease as the pH increases from 6.6 to 9.6. Applying pseudo-first-order kinetics to fit the HOCl decay, the corresponding pseudo-first-order rate constants (k_{Cl}) were $(4.0 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, $(3.5 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, $(1.0 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, and $(3.2 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ for pH 6.6, 7.6, 8.6, and 9.6, respectively (Figure S1A, Table S1, SI), which is significantly enhanced compared to homogeneous reactions. For instance, the first-order rate constant in the absence of CuO can be calculated as $1.7 \times 10^{-12} \text{ s}^{-1}$ (using $[\text{HOCl}]_{\text{TO}} = 3.7 \times 10^{-5} \text{ M}$, and a third-order rate constant of $1.25 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ at $\text{pH} = 7.3$ ²⁷). At pH 7.6, this rate constant will be even lower.²⁷ Therefore, the decay rate of HOCl was enhanced about 10^8 times at pH 7.6 in the presence of 0.2 g L^{-1} CuO.

Figure 1B shows significant chlorate formation, except at pH 9.6, indicating that chlorate can be formed via a CuO-catalyzed disproportionation reaction. Concomitant to the fast chlorine decay, chlorate concentrations at pH 6.6 and 7.6 increase quickly within the first 60 min and then reach a plateau. At pH 8.6, only a limited chlorate formation was observed up to 30 min due to the small chlorine depletion. After 30 min, the increase of chlorate is concomitant to the chlorine decay. Only traces of chlorate were detected at pH 9.6.

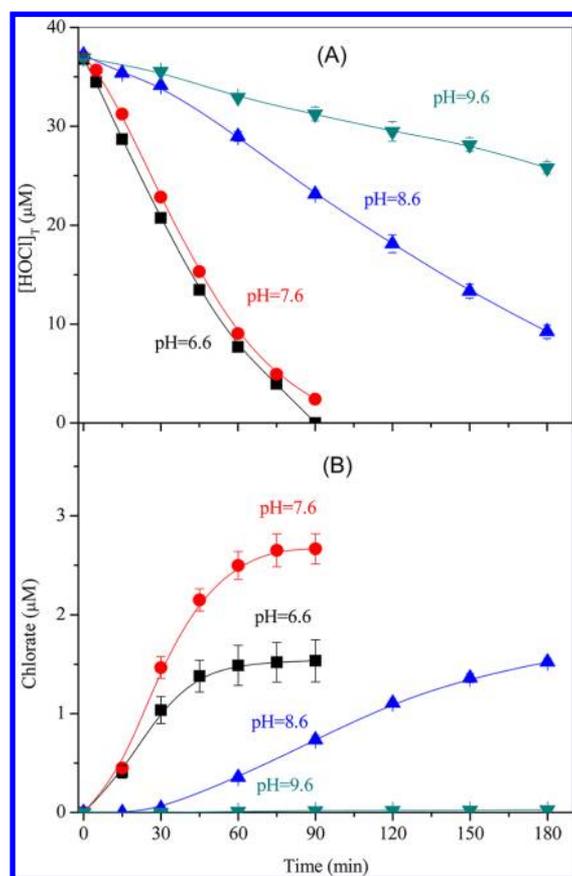


Figure 1. HOCl decay (A) and chlorate formation (B) for varying pH (2.5 mM tetraborate buffer). Experimental conditions: $T = 21^\circ\text{C}$, $[\text{CuO}] = 0.2 \text{ g L}^{-1}$, $[\text{HOCl}]_{\text{TO}} = 37 \mu\text{M}$ (2.6 $\text{mg L}^{-1} \text{Cl}_2$).

Chlorite is a possible intermediate in chlorate formation. However, chlorite concentrations were insignificant (below 0.02 μM), which is in agreement with studies performed in the absence of CuO.^{27,28} Furthermore, the adsorption of chlorate on CuO is insignificant (Figure S2, SI). A plot of $3\Delta\text{ClO}_3^-$ vs ΔHOCl (the stoichiometry for chlorate formation, eq 10) at different reaction times showed a good linear correlation (Figure S1B, SI). The fitted slopes (i.e., fractions of chlorate formation over the total HOCl decay) are $(18 \pm 1)\%$, $(27 \pm 1)\%$, $(17 \pm 1)\%$, and 1% for pHs 6.6, 7.6, 8.6, and 9.6, respectively. These fractions are significantly below 100%, demonstrating that chlorate formation (eq 10) is a minor pathway for HOCl decay. The k_{ClP} values obtained by multiplying the fractions with k_{Cl} are $(7.2 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$, $(9.5 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$, $(1.7 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$, and $4 \times 10^{-7} \text{ s}^{-1}$ for pH 6.6, 7.6, 8.6, and 9.6, respectively.

The pH effect on k_{ClP} , k_{ClO} , and the chlorate yield (ΔClO_3^- vs ΔHOCl , i.e., one-third of the slopes in Figure S1B, SI) is illustrated in Figure 2. k_{ClO} increases with decreasing pH, which agrees with observations in the absence of CuO.²⁸ This trend may indicate that the reaction to oxygen occurs between two HOCl molecules. The maximum of k_{ClP} value is observed at pH 7.6, close to the pK_a of HOCl. This may indicate that the disproportionation in the presence of CuO occurs via an interaction between HOCl and OCl^- .

Figure 2 also shows the observed chlorate yield as a function of pH. The decrease in chlorate yield from pH 7.6 to 9.6 follows the reduction of the k_{ClP} value. However, chlorate formation is not only controlled by k_{ClP} but also affected by

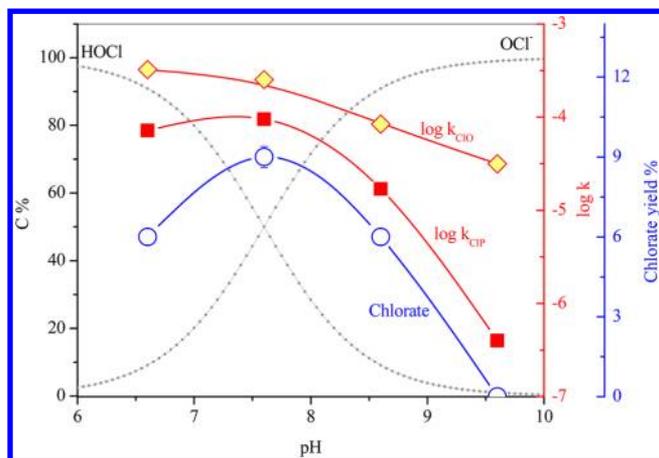
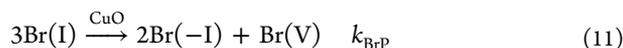


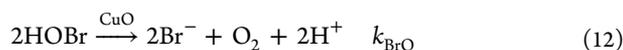
Figure 2. Influence of pH on speciation of HOCl, rate constants for oxygen formation (k_{ClO}) and disproportionation (k_{ClP}), and chlorate yield. Experimental conditions: $T = 21\text{ }^{\circ}\text{C}$, $[\text{CuO}] = 0.2\text{ g L}^{-1}$, $[\text{HOCl}]_{\text{T}_0} = 37\text{ }\mu\text{M}$ ($2.6\text{ mg L}^{-1}\text{ Cl}_2$). For pHs 6.6 and 7.6, reaction times are 90 min, while for pHs 8.6 and 9.6, reaction times are 180 min.

k_{ClO} , which contributes significantly to the HOCl decay. At pH 6.6, the highest k_{ClO} value leads to less residual HOCl available for disproportionation, which tends to decrease the chlorate yield. In contrast to our findings, chlorate was not detected during HOCl decomposition using various Cu(II) species in previous studies^{18,19,21,22} because the previous experiments were conducted under basic conditions. From our data, it remains unclear which CuO species is mainly involved in catalysis of HOCl decay and chlorate formation.

Bromate Formation from HOBr Decay in the Presence of CuO. Similarly to HOCl, the disproportionation of HOBr in the presence of CuO can be formulated by eq 11



If we consider the CuO-catalyzed decomposition of HOBr to bromide and O_2 , the reaction can be formulated as eq 12.



$k_{\text{Br}} = k_{\text{BrP}} + k_{\text{BrO}}$ is the total apparent HOBr decay rate constant if pseudo-first-order kinetics are assumed for both processes (see below).

Figure 3 shows the HOBr decay and bromate formation in the presence of CuO for various pH conditions. According to the rate constants listed in eqs 3–5, the HOBr decay in homogeneous solution is very slow for our experimental conditions ($[\text{HOBr}]_{\text{T}_0} = 35\text{ }\mu\text{M}$). For instance, at pH 8.8 in the absence of CuO, k_{Br} was reported to be $2 \times 10^{-4}\text{ M}^{-1}\text{ s}^{-1}$,¹⁶ equivalent to a first-order rate constant of $7 \times 10^{-9}\text{ s}^{-1}$. The decomposition of HOBr is enhanced in the presence of CuO at any pH ranging from 6.6 to 10.6. Figure S3A (SI) indicates that the HOBr decay follows pseudo-first-order kinetics with k_{Br} values of $(4.5 \pm 0.3) \times 10^{-5}\text{ s}^{-1}$, $(8.7 \pm 0.3) \times 10^{-5}\text{ s}^{-1}$, $(1.5 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$, $(1.7 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$, and $(1.7 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$ for pH 6.6, 7.6, 8.6, 9.6, and 10.6, respectively. Therefore, the HOBr decay rate is enhanced by more than 4–5 orders of magnitude in the presence of CuO.

Figure 3B indicates that significant concentrations of bromate were formed in the presence of CuO from the disproportionation of HOBr under various pH conditions. Bromate concentrations increase slowly within the first 15 min,

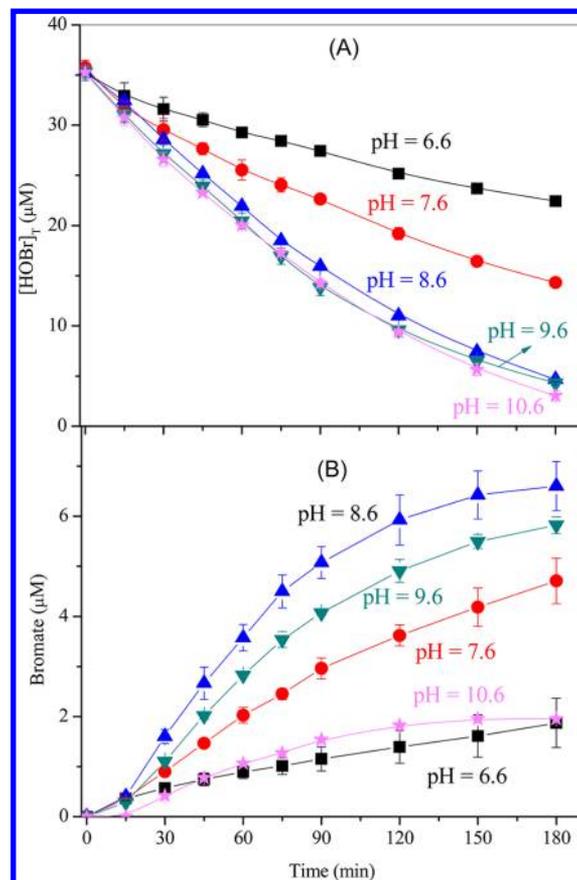


Figure 3. HOBr decay (A) and bromate formation (B) for varying pH (2.5 mM tetraborate buffer). Experimental conditions: $T = 21\text{ }^{\circ}\text{C}$, $[\text{CuO}] = 0.2\text{ g L}^{-1}$, $[\text{HOBr}]_{\text{T}_0} = 35\text{ }\mu\text{M}$.

implying that a build-up of an intermediate, probably bromite, is necessary before bromate is formed.¹⁵ After 15 min the concentration of bromate started to increase until most of the HOBr was depleted.

There is no significant adsorption of bromate on CuO, hence the formed bromate is released to the aqueous solution (Figure S2, SI). Similarly to HOCl, the slopes ($3\Delta\text{BrO}_3^-/\Delta\text{HOBr}$) did not vary significantly with reaction time, except within the initial reaction stage, probably because of the build-up of BrO_2^- (Figure S3B, SI). The fractions of decayed HOBr that lead to bromate (i.e., fitted slopes) are $(43 \pm 1)\%$, $(64 \pm 1)\%$, $(77 \pm 2)\%$, $(56 \pm 1)\%$, and $(21 \pm 1)\%$ for pH 6.6, 7.6, 8.6, 9.6, and 10.6, respectively. Again, the fractions are less than 100%, indicating that reaction 12 is important. On the basis of this, k_{BrP} values calculated by multiplying the fractions that lead to bromate with k_{Br} are $(1.9 \pm 0.1) \times 10^{-5}\text{ s}^{-1}$, $(5.6 \pm 0.2) \times 10^{-5}\text{ s}^{-1}$, $(1.2 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$, $(1.0 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$, and $(3.6 \pm 0.2) \times 10^{-5}\text{ s}^{-1}$ for pHs 6.6, 7.6, 8.6, 9.6, and 10.6, respectively.

The influence of pH on the distribution of HOBr, k_{BrP} , and bromate yield (ΔBrO_3^- vs ΔHOBr , i.e., one-third of slopes in Figure S3B, SI) is depicted in Figure 4. The rate for HOBr decay to oxygen (k_{BrO}) increases with increasing pH, suggesting that an interaction between two OBr^- might be important. The pH-dependency of k_{BrO} follows the opposite trend compared to k_{ClO} (Figures 2 and 4). The reason for this observation remains unknown currently. Similar to k_{ClP} , the maximum k_{BrP} was obtained near pH 8.6, approaching the $\text{p}K_a$ of HOBr. This may indicate that the disproportionation occurs between HOBr and OBr^- . The curve for bromate yield follows the same trend as

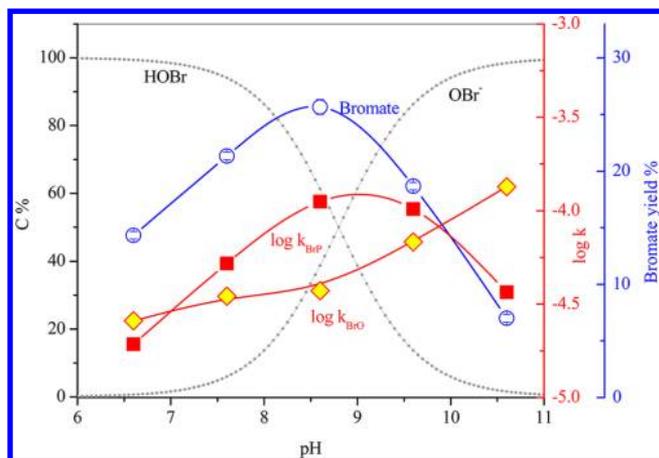


Figure 4. Influence of pH on speciation of HOBr, rate constants for oxygen formation (k_{BrO}) and disproportionation (k_{BrP}), and bromate yield. Experimental conditions: $T = 21\text{ }^{\circ}\text{C}$, $[\text{CuO}] = 0.2\text{ g L}^{-1}$, $[\text{HOBr}]_{\text{T}0} = 35\text{ }\mu\text{M}$. Reaction times are 180 min.

k_{BrP} . Maximum bromate formation is at the pH near its pK_a . Again, our data do not reveal which CuO species mainly contributes to the HOBr disproportionation.

To better understand the multiple step reactions leading to bromate formation, a conceptual kinetic model was proposed to fit the experimental data (Model 1, SI). It should be noted that in this model only CuO present in large excess is considered (i.e., the variation of the CuO species distribution with pH was not taken into account). The model simulation that agrees well with the experimental trend includes a pre-equilibrium step with the formation of a complex between HOBr/OBr⁻ and CuO. This initial phase is considered to be the rate-limiting step of the overall catalytic reaction. In the proposed model the disproportionation reaction involving a CuO–OBr⁻ complex and HOBr is the predominant reaction pathway (i.e., the reaction rate is 2 orders of magnitude higher than the one estimated for a CuO–HOBr complex). Therefore, the CuO–HOBr complex seems to play an important role only at $\text{pH} \leq 7.6$ because HOBr is the dominant species (>94%). Furthermore, this model confirms that the disproportionation reaction mainly occurs between two HOBr and one OBr⁻, whereas oxygen formation is induced by the interaction between two OBr⁻. With this model, the experimentally observed pseudo-first-order decay of HOBr and the trend of bromate formation as a function of the pH could be reproduced (Model 1, SI).

Bromate Formation during Chlorination of Bromide-Containing Waters in the Presence of CuO. Results presented above demonstrated that chlorate and bromate can be formed from the catalytic disproportionation of HOCl and HOBr, respectively. In the following section, bromate formation was investigated using more realistic drinking water treatment conditions, by chlorination of solutions containing bromide and CuO particles.

1. Effect of CuO Dose. Figure S4 (SI) depicts oxidant decay and bromate formation for various CuO doses. In the absence of CuO, only a slight oxidant decay was observed, in agreement with previous studies.^{11,14} In the presence of CuO, the oxidant decay was significantly enhanced. Applying pseudo-first-order kinetics to fit the residual oxidant decay rate, one can observe that an increase of the CuO dose from 0.05 to 0.5 g L^{-1} led to

an enhancement of pseudo-first-order rate constants (k') from $(4.4 \pm 0.3) \times 10^{-5}\text{ s}^{-1}$ to $(3.3 \pm 0.2) \times 10^{-4}\text{ s}^{-1}$ (Table S1, SI).

In the absence of CuO, no significant bromate was formed, in agreement with the data shown above (Figure S4C, SI). In the presence of CuO, a significant bromate formation was observed and enhanced with increasing CuO dose. For a CuO dose of 0.5 g L^{-1} , the production of bromate reached a plateau after 90 min, showing a bromate yield of $(90 \pm 1)\%$, while for a CuO dose of 0.2 g L^{-1} , the bromate concentration reached a plateau (a bromate yield of $(86 \pm 2)\%$) after 150 min. For a 0.05 g L^{-1} CuO dose, only $(54 \pm 6)\%$ of bromide was converted to bromate after 180 min, but no plateau was reached. Considering the higher bromate yield obtained in the presence of excess chlorine (approaching 100%), bromate becomes the major sink for bromide. Compared to the lower formation yield in the disproportionation of HOBr in the absence of HOCl, bromate formation is enhanced because when HOBr decays to Br⁻ according to eqs 11 and 12 HOCl can regenerate HOBr from Br⁻.¹⁴ This reaction occurs until Br⁻ is completely transformed to bromate. The difference between the theoretical bromate yield of 100% and the observed 90% in Figure S4C (SI) is within the experimental error.

Table S2 (SI) shows that dissolved concentrations of copper are extremely low (20–30 ng L^{-1}) and stable during the entire reaction period, indicating that there is no copper release from the CuO particles. This confirms that the production of bromate is dominated by heterogeneous reactions.

2. Effect of Initial Concentrations of Chlorine and Bromide. The effects of initial chlorine and bromide concentrations on bromate formation in the presence of CuO are shown in Figure 5. Figure S5 (SI) shows the corresponding oxidant decay for all applied initial chlorine doses. Applying pseudo-first-order kinetics to interpret the oxidant decay curves gives k' values decreasing from $(2.3 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$ to $(1.2 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$ for an increase of the initial chlorine concentration from 14 to 70 μM (Table S1, SI).

A lag phase can be observed for bromate formation, which is due to the HOCl-dependent HOBr formation. If the self-decomposition of HOCl is neglected and an initial bromide concentration of 10 μM is assumed, one can calculate the required times for 90% bromide oxidation to HOBr to be 2426, 1000, 600, and 284 s for initial chlorine concentrations of 14, 25, 37, and 70 μM , respectively. Moreover, considering the self-decomposition of HOCl in the presence of CuO, these required times will be longer and lead to a lag phase in bromate formation. Furthermore, the bromate yields reached $(3 \pm 2)\%$, $(18 \pm 6)\%$, $(64 \pm 1)\%$, and $(86 \pm 2)\%$, after 180 min with increasing initial chlorine concentrations of 14, 25, 37, and 70 μM , respectively (Figure 5A). Decreasing the initial HOCl concentrations significantly decreases the bromate yields. This is because there is not enough HOCl to oxidize Br⁻ to HOBr at a lower HOCl concentration due to the HOCl consumption through self-decay. For example, if the fast HOCl self-decay is not considered, one can calculate that at least 30 μM HOCl is needed to convert 10 μM Br⁻ to bromate. However, the HOCl self-decay is very significant, i.e., 70% consumption within 180 min (Figure 1A). Therefore, the bromate yield for an initial HOCl concentration of 37 μM is smaller than for 70 μM .

The effect of bromide concentrations on bromate formation was also investigated (Figure 5B). Figure S6 (SI) shows that the corresponding oxidant decay rate constants k' increased only slightly (i.e., $(4.5 \pm 0.3) \times 10^{-5}\text{ s}^{-1}$ to $(6.3 \pm 0.3) \times 10^{-5}\text{ s}^{-1}$) with increasing bromide concentration from 2 to 10 μM (i.e.,

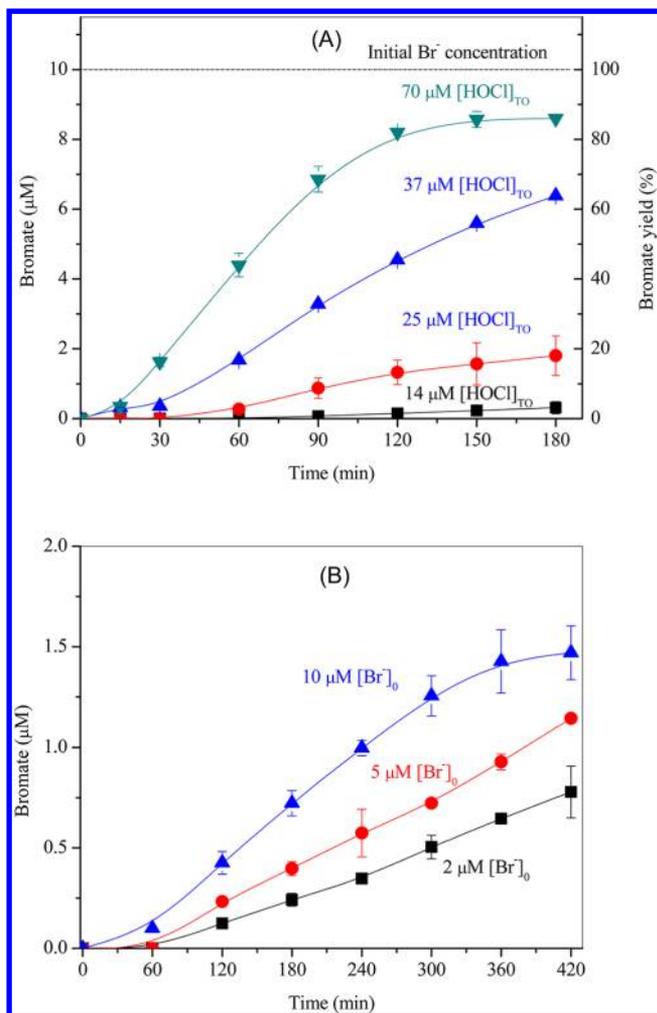


Figure 5. Effects of initial concentrations of (A) HOCl and (B) bromide on bromate formation. Experimental conditions: pH = 8.6 (2.5 mM tetraborate buffer), $T = 21\text{ }^{\circ}\text{C}$. (A) $[\text{Br}^-]_0 = 10\text{ }\mu\text{M}$, $[\text{CuO}] = 0.2\text{ g L}^{-1}$; (B) $[\text{HOCl}]_{\text{T}0} = 15\text{ }\mu\text{M}$ ($1.1\text{ mg L}^{-1}\text{ Cl}_2$), $[\text{CuO}] = 0.05\text{ g L}^{-1}$.

160–800 $\mu\text{g L}^{-1}$) (Table S1, SI). In contrast, an enhanced bromate formation was observed for an increase in the initial bromide concentration (Figure 5B). After a reaction time of 420 min, the resulting bromate concentrations were 0.8 ± 0.1 , 1.1 ± 0.1 , and $1.5 \pm 0.1\text{ }\mu\text{M}$, corresponding to bromate yields of $(40 \pm 5)\%$, $(22 \pm 2)\%$, and $(15 \pm 1)\%$ for initial bromide levels of 2, 5, and 10 μM , respectively, and a HOCl dose of 15 μM ($1.1\text{ mg L}^{-1}\text{ Cl}_2$). Increasing bromide concentration led to higher bromate concentrations because of the higher steady-state concentrations of HOBr. However, the bromate yield highly depends on the HOCl/ Br^- ratio. For high ratios (low initial Br^- concentration), the recycling of Br^- produced by eqs 11 and 12 is effective. However, when the HOCl/ Br^- ratio approaches 1, the maximum BrO_3^- concentration corresponds to the lower yield of the pure HOBr system.

3. Effect of pH. During the chlorination of bromide-containing waters in the presence of CuO, both oxidant decay and bromate formation are significantly affected by pH in the range of 6.6–9.6, overlapping with drinking water conditions (Figure 6). Oxidant decay follows pseudo-first-order kinetics (Figure S7, SI). The decay rate constants increase with decreasing pH from 9.6 to 6.6, corresponding to k' values

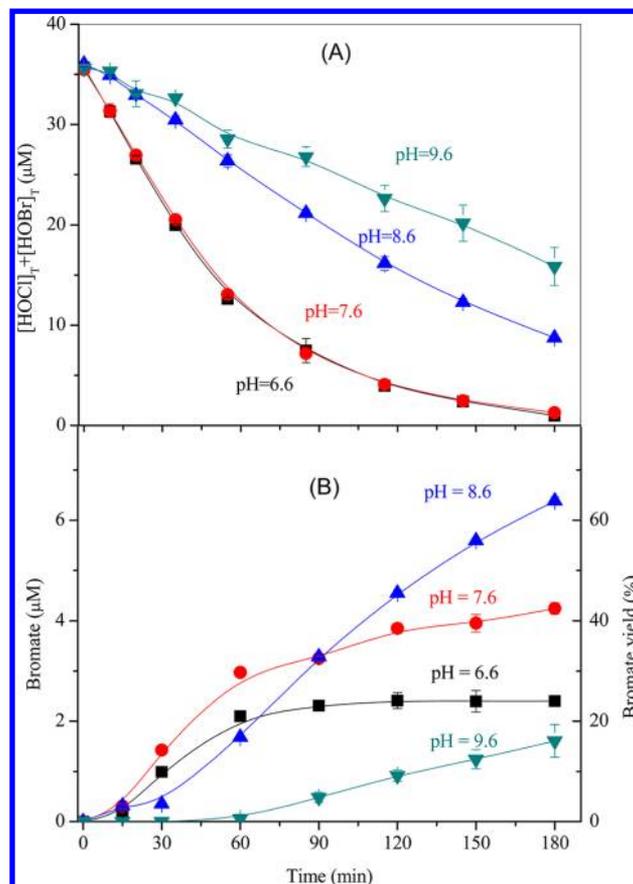


Figure 6. Effect of pH on (A) oxidant decay and (B) bromate formation. Experimental conditions: $T = 21\text{ }^{\circ}\text{C}$, $[\text{Br}^-]_0 = 10\text{ }\mu\text{M}$, $[\text{CuO}] = 0.2\text{ g L}^{-1}$, $[\text{HOCl}]_{\text{T}0} = 37\text{ }\mu\text{M}$ ($2.6\text{ mg L}^{-1}\text{ Cl}_2$).

ranging from $(6.8 \pm 0.5) \times 10^{-5}\text{ s}^{-1}$ to $(3.2 \pm 0.1) \times 10^{-4}\text{ s}^{-1}$ (Table S1, SI). This trend is similar to the HOCl–CuO system (Figure 1) but opposite to the observed trend for the HOBr–CuO system (Figure 3). This is because in the HOCl– Br^- –CuO system the reaction is initiated by HOCl, and HOCl is present in large excess of Br^- ; namely, $[\text{HOCl}]_0 = 37\text{ }\mu\text{M}$ and $[\text{Br}^-]_0 = 10\text{ }\mu\text{M}$.

Bromate formation shows a complex pattern (Figure 6B). During the first 60 min of reaction, maximum bromate formation was observed at pH 7.6, followed by pH 6.6 and 8.6. At pH 9.6 the formation of bromate is insignificant (less than $0.2\text{ }\mu\text{M}$). Using initial concentrations of 37 and 10 μM for chlorine and bromide, respectively, one can calculate the reaction times for 90% bromide oxidation to HOBr. At pHs 6.6 and 7.6, bromide is quickly converted into HOBr within 1–2 min, while at higher pH (i.e., 8.6 and 9.6), >10 min is needed to oxidize 90% of the initial bromide to HOBr. Therefore, due to the significant production of HOBr, the formation of bromate is favored at lower pH during the early stage of the reaction. The bromate concentration at pH 7.6 is higher than that at 6.6 owing to the enhanced k_{BrP} rate (Figure 4).

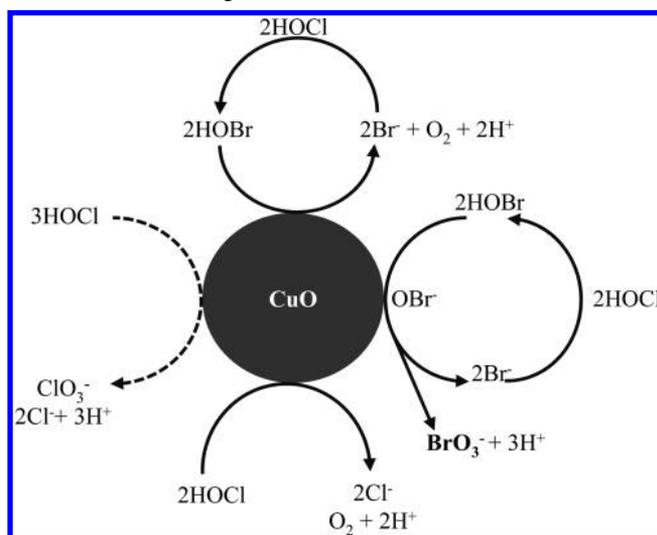
After 60 min, the remaining oxidant concentration becomes low for pH 6.6 and 7.6 (only about 33% of the initial oxidant remaining) because k_{ClO} is higher at lower pH values. Consequently, only a slow increase of bromate was observed during this phase. Due to the formation of a significant amount of HOBr, bromate further increases at pHs 8.6 and 9.6. At 180 min, about $(24 \pm 2)\%$, $(43 \pm 1)\%$, $(64 \pm 1)\%$, and $(16 \pm 3)\%$ of the initial bromide was converted to bromate for pH 6.6, 7.6,

8.6, and 9.6, respectively. The higher yield in the HOCl–Br[−] experiment compared to HOBr alone is due to the recycling of Br[−] to HOBr by HOCl.

Bromate Formation Mechanism during Chlorination of Bromide-Containing Waters in the Presence of CuO.

According to our data, a hypothetical bromate formation mechanism during chlorination of bromide-containing waters in the presence of CuO can be postulated (Scheme 1). Bromate

Scheme 1. Potential Reactions during Chlorination of Bromide-Containing Waters in the Presence of CuO^a



^aSolid lines, main pathways; dashed lines, minor pathways.

formation is initiated by the oxidation of bromide by HOCl to HOBr (eq 1). The reaction between HOCl and Br[−] dominates because the reaction rate constant between OCl[−] and Br[−] is low (eq 2).¹³

In the presence of CuO, the HOBr decay rate is significantly enhanced (e.g., 10⁴ times with 0.2 g L^{−1} CuO at pH 8.6), via two reaction pathways (eqs 11 and 12). For pH between 7.6 and 9.6, the disproportionation of HOBr to bromate is the major pathway, and the reaction rate is highest near the pK_a of HOBr. Therefore, the reaction occurs between HOBr and OBr[−].

CuO is a catalyst for HOBr disproportionation, and the catalysis has to be initiated by the adsorption of HOBr/OBr[−] on the CuO surface. Because HOBr/OBr[−] is not stable on the CuO surface, the adsorption of HOBr/OBr[−] by CuO is difficult to be confirmed. However, the presence of phosphate (1 mM) strongly inhibits bromate formation (about 80% inhibition) in a reaction system containing HOCl, Br[−], and CuO.¹⁷ Therefore, it is hypothesized that HOBr/OBr[−] can be adsorbed on the CuO surface and forms complexes.

It was reported that copper can catalyze the formation of chlorination byproducts (e.g., chloroform,²⁹ haloacetic acids³⁰). Iodine species adsorbed on δ-MnO₂ can also contribute to the formation of iodinated organic compounds.³¹ By analogy, we hypothesized that complexation of HOBr/OBr[−] by the Lewis acid CuO polarizes the bromine molecule, thus increasing its electrophilicity and as a consequence its reactivity. The CuO–bromine complex reacts with HOBr to form BrO₂[−]. According to our conceptual model (Model 1, SI), the reaction between the CuO–OBr[−] complex and HOBr is the predominant reaction pathway (i.e., the reaction rate constant is 2 orders of

magnitude higher than the one estimated for the CuO–HOBr complex). The latter reaction tends to be important only at lower pH for which HOBr is the predominant species.

The second-order rate constant for the reaction between HOCl and BrO₂[−] is 160 M^{−1} s^{−1} in homogeneous solution, and the primary product (about 85%) is ClO₃[−].³² The production of chlorite and chlorate is insignificant during HOCl–Br[−] reactions in the presence of CuO (less than 0.02 μM, Table S1, SI). This indicates that chlorate formation is a minor pathway. Therefore, it is proposed that bromate is formed by a successive oxidation of BrO₂[−] by HOBr which is catalyzed by CuO and not by the reaction between HOCl and BrO₂[−]. The consumption of HOCl is mainly via (1) oxidation of Br[−] and (2) self-decay to oxygen.

Bromide which results from these reactions is oxidized by HOCl to HOBr, which further disproportionates to BrO₃[−] and Br[−] until most of the bromide is converted to bromate as long as HOCl is present in excess.

The generation of O₂ (eqs 9 and 12) is an important side reaction for HOCl or HOBr decay. For pH values below 7.6 or above 9.6, this reaction becomes more significant. The O₂ formation is initiated by the oxidation of Cu(II) by HOCl or HOBr to form dimeric Cu(III) intermediates, and then this dimeric Cu(III) decays to give rise to Cu(II) and O₂.^{19,21} The O₂ generation does not affect the bromate yield in the HOCl–Br[−] system in excess of HOCl because of a recycling of Br[−] to HOBr.

Implications for Water Treatment. Traditionally only oxygen and halide ions were considered as the products from catalyzed hypohalite decomposition in the presence of metal oxides (e.g., CuO).^{18,19,21,22} This leads to an enhanced oxidant decay in distribution systems containing corrosion products.^{23,30} From a drinking water quality point of view, a partial loss of disinfectants is problematic, and an enhanced formation of disinfection byproduct makes this even worse. This study shows that CuO catalyzes the disproportionation of HOCl and HOBr leading to significant formation of chlorate and bromate, respectively. It is known that CuO is one of the main forms of copper corrosion.^{20,33} This may be a major concern for the drinking water quality in distribution systems containing copper pipes, which are widely used worldwide in municipal and household systems.

Drinking water regulations for bromate are stricter than those for chlorate (WHO guidelines: 10 μg L^{−1} for bromate and 700 μg L^{−1} for chlorate (provisional)⁸). Bromide levels in raw waters (e.g., groundwaters, surface waters, and desalinated waters) are highly variable in a range of 10–1000 μg L^{−1}.⁹ The average bromide concentration within natural waters in the United States is almost 100 μg L^{−1}.³⁴ Moreover, due to the high bromate yield in the HOCl–Br[−]–CuO systems, one can expect that the regulation for bromate would not be met for a 10% bromate yield (or higher yields which were found in Figure 5B) if the bromide concentration is above 80 μg L^{−1}. This hypothesis is based on laboratory experiments in clean waters without taking the water matrix of real drinking waters into consideration (mainly concentration and type of dissolved organic matter (DOM)). It is expected that the adsorption of DOM on CuO will reduce the catalytic activity of CuO for bromate formation. Moreover, HOBr may react with DOM leading to bromo-organic compounds, thereby diminishing bromate formation. However, the issue of bromate formation during chlorination should still be considered seriously when copper pipes are used.

On the basis of our results, bromate minimization for distribution systems using chlorination can be achieved by (1) replacement of copper pipes; (2) lowering the residual chlorine concentration if disinfection can still be guaranteed; and (3) pH adjustment to <7.6 if corrosion is not enhanced. Moreover, bromate could be minimized using alternative disinfectants (e.g., chlorine dioxide or chloramine which both have low rate constants for oxidation of Br^- to $\text{HOBr}^{35,36}$). Additional research should address the effects of DOM on the formation of bromate and bromo-organic byproduct during chlorination of bromide-containing waters in the presence of CuO .

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional details of the Materials and Methods, additional figures, and kinetic modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +996-2-8082984. E-mail: jp.croue@kaust.edu.sa.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank Ms. Tong Zhan for ICP-MS analyses.

■ REFERENCES

- (1) Haag, W. R.; Hoigné, J. Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. *Environ. Sci. Technol.* **1983**, *17*, 261–267.
- (2) von Gunten, U.; Hoigné, J. Bromate formation during ozonation of bromide-containing waters: Interaction of ozone and hydroxyl radical reactions. *Environ. Sci. Technol.* **1994**, *28*, 1234–1242.
- (3) Croué, J. P.; Kodjonou, B. K.; Legube, B. Parameters affecting the formation of bromate ion during ozonation. *Ozone Sci. Eng.* **1996**, *18*, 1–18.
- (4) von Gunten, U.; Oliveras, Y. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural systems. *Water Res.* **1997**, *31*, 900–906.
- (5) von Gunten, U.; Oliveras, Y. Advanced oxidation of bromide-containing waters: bromate formation mechanisms. *Environ. Sci. Technol.* **1998**, *32*, 63–70.
- (6) European Communities, European Communities (Drinking water) (No.2) Regulations. In Brussels, 2007.
- (7) U.S. Environmental Protection Agency, National Primary Drinking Water Regulations. In Washington D.C., 2001.
- (8) World Health Organization, Guidelines for Drinking-water Quality. In Geneva, 2008.
- (9) von Gunten, U. Ozonation of drinkingwater: part II. disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.* **2003**, *37*, 1469–1487.
- (10) Weinberg, H.; Delcomyn, C.; Unnam, V. Bromate in chlorinated drinking waters: Occurrence and implications for future regulation. *Environ. Sci. Technol.* **2003**, *37* (14), 3104–3110.
- (11) Huang, X.; Gao, N.; Deng, Y. Bromate ion formation in dark chlorination and ultraviolet/chlorination processes for bromide-containing water. *J. Environ. Sci.* **2008**, *20*, 246–251.
- (12) Macalady, D. L.; Carpenter, J. H.; Moore, C. A. Sunlight induced bromate formation in chlorinated seawater. *Science* **1977**, *195* (4284), 1335–1337.
- (13) Kumar, K.; Margerum, D. W. Kinetics and mechanism of general- acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. *Inorg. Chem.* **1987**, *26* (16), 2706–2711.

- (14) Margerum, D. W.; Huff Hartz, K. E. Role of halogen(I) cation-transfer mechanisms in water chlorination in the presence of bromide ion. *J. Environ. Monit.* **2002**, *4*, 20–26.

- (15) Beckwith, R. C.; Margerum, D. W. Kinetics of hypobromous acid disproportionation. *Inorg. Chem.* **1997**, *36*, 3754–3760.

- (16) Engel, P.; Oplatka, A.; Perlmutter-Hayman, B. The decomposition of hypobromite and bromite solutions. *J. Am. Chem. Soc.* **1954**, *76*, 2010–2015.

- (17) Liu, C.; Croué, J. P. Metal oxides enhanced bromate formation during chlorination of bromide-containing waters in distribution systems. In preparation.

- (18) Lewis, J. R. The catalytic decomposition of sodium hypochlorite solutions. *J. Phys. Chem.* **1928**, *32*, 1808–1819.

- (19) Lister, M. W. Decomposition of sodium hypochlorite: The catalyzed reaction. *Can. J. Chem.* **1956**, *34*, 479–488.

- (20) Li, B.; Qu, J.; Liu, H.; Hu, C. Effects of copper(II) and copper oxides on THMs formation in copper pipe. *Chemosphere* **2007**, *68*, 2153–2160.

- (21) Gray, E. T.; Taylor, R. W.; Margerum, D. W. Kinetics and mechanisms of the copper-catalyzed decomposition of hypochlorite and hypobromite. Properties of a dimeric copper (III) hydroxide intermediate. *Inorg. Chem.* **1977**, *16*, 3047–3055.

- (22) Church, J. A. Kinetics of the uncatalyzed and Cu(II) -catalyzed decomposition of sodium hypochlorite. *Ind. Eng. Chem. Res.* **1994**, *33*, 239–245.

- (23) Nguyen, C. K.; Powers, K. A.; Raetz, M. A.; Parks, J. L.; Edwards, M. A. Rapid free chlorine decay in the presence of $\text{Cu}(\text{OH})_2$: Chemistry and practical implications. *Water Res.* **2011**, *45*, 5302–5312.

- (24) Lei, H.; Marinas, B. J.; Minear, R. A. Bromamine decomposition kinetics in aqueous solutions. *Environ. Sci. Technol.* **2004**, *38* (7), 2111–2119.

- (25) Stumm, W. *Chemistry of the Solid-Water Interface*; JohnWiley and Sons: New York, 1992.

- (26) American Public Health Association (APHA). Standard Methods for the Examination of Water and Wastewater. APHA, American Water Works Association, and Water Environment Federation, Washington, D.C., 1998.

- (27) Adam, L. C.; Fabian, I.; Suzuki, K.; Gordon, G. Hypochlorous acid decomposition in the pH 5–8 region. *Inorg. Chem.* **1992**, *31*, 3534–3541.

- (28) Adam, L. C.; Gordon, G. Hypochlorite ion decomposition: Effects of temperature, ionic strength, and chloride ion. *Inorg. Chem.* **1999**, *38*, 1299–1304.

- (29) Blatchley, E. R.; Margetas, D.; Duggirala, R. Copper catalysis in chloroform formation during water chlorination. *Water Res.* **2003**, *37* (18), 4385–4394.

- (30) Zhang, H.; Andrews, S. A. Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. *Water Res.* **2012**, *46*, 2665–2673.

- (31) Gallard, H.; Allard, S.; Nicolau, R.; von Gunten, U.; Croué, J. P. Formation of iodinated organic compounds by oxidation of iodide-containing waters with manganese dioxide. *Environ. Sci. Technol.* **2009**, *43*, 7003–7009.

- (32) Nicoson, J. S.; Perrone, T. F.; Huff Hartz, K. E.; Wang, L.; Margerum, D. W. Kinetics and mechanisms of the reactions of hypochlorous acid, chlorine, and chlorine monoxide with bromite ion. *Inorg. Chem.* **2003**, *42*, 5818–5824.

- (33) Shim, J. J.; Kim, J. G. Copper corrosion in potable water distribution systems: influence of copper products on the corrosion behavior. *Mater. Lett.* **2004**, *58*, 2002–2006.

- (34) Amy, G.; Siddiqui, M.; Zhai, W.; Debroux, J. National survey of bromide in drinking waters. *Proc. of AWWA Annual Conference*. Denver, Colo: AWWA, 1993.

- (35) Hoigné, J.; Bader, H. Kinetics of reactions of chlorine dioxide (OCIO) in water - I. Rate constants for inorganic and organic compounds. *Water Res.* **1994**, *28* (1), 45–55.

- (36) Trofe, T. W.; Inman, G. W.; Johnson, J. D. Kinetics of monochloramine decomposition in the presence of bromide. *Environ. Sci. Technol.* **1980**, *14* (5), 544–549.