

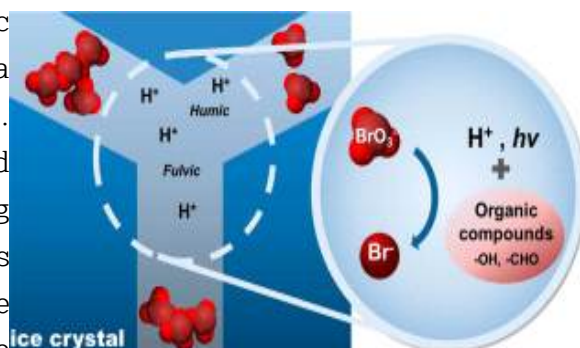
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# Accelerated Reduction of Bromate in Frozen Solution

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## ■ Introduction

Bromate ( $\text{BrO}_3^-$ ), a carcinogenic oxyhalide anion, is identified as a major disinfection byproduct (DBP). During the ozonation and chlorination treatment for drinking water, bromide in water is transformed into bromate. Bromate ( $\text{BrO}_3^-$ ), a carcinogenic oxyhalide

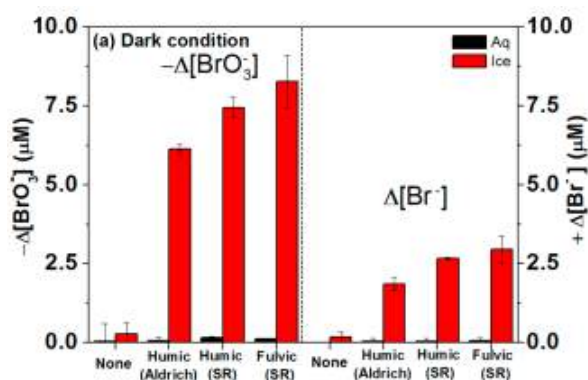


anion, is identified as a major disinfection byproduct (DBP). During the ozonation and chlorination treatment for drinking water, bromide in water is transformed into bromate. In this study, we suggest and investigate a new abiotic mechanism of bromate reduction which takes place in frozen solution. The bromate conversion in aqueous solution containing humic substances (HS), which was negligible slow, was highly accelerated when the solution was frozen and subsequently thawed.

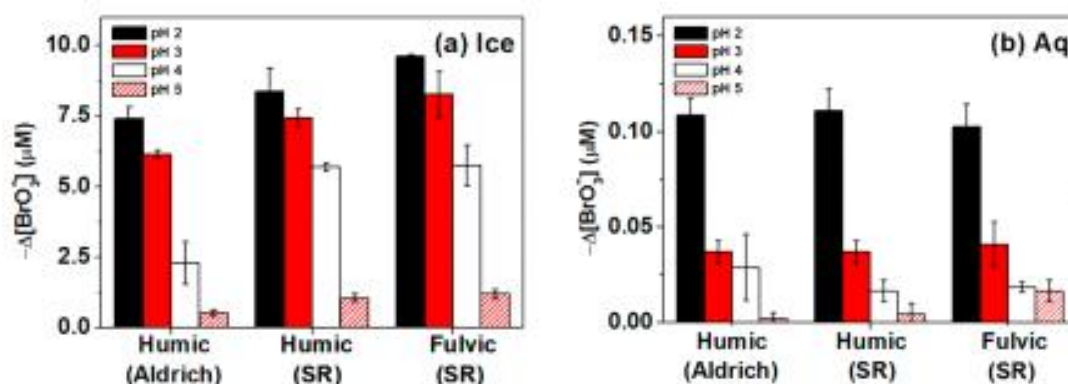
## ■ Experimental section

Stock solutions of bromate and organic compounds were prepared and those of humic/fulvic acid were made freshly every week. A sample solution with a desired concentration of substrate was prepared in a 12 × 125 mm quartz tube. Then the pH of the solution was adjusted with a standard sulfuric acid solution and sealed with a septum. The quartz tubes were put in a merry-go-around reactor in an ethanol bath maintained at  $-5\text{ }^{\circ}\text{C}$ , which was gradually cooled down to  $-20\text{ }^{\circ}\text{C}$ . Such slow freezing prevented the quartz tube from breaking due to fast cooling. The solution in the tube was completely frozen around 30 min after it was put in the ethanol bath. This moment was considered as “time zero”.

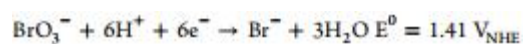
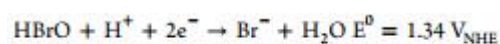
## ■ Results and Discussion



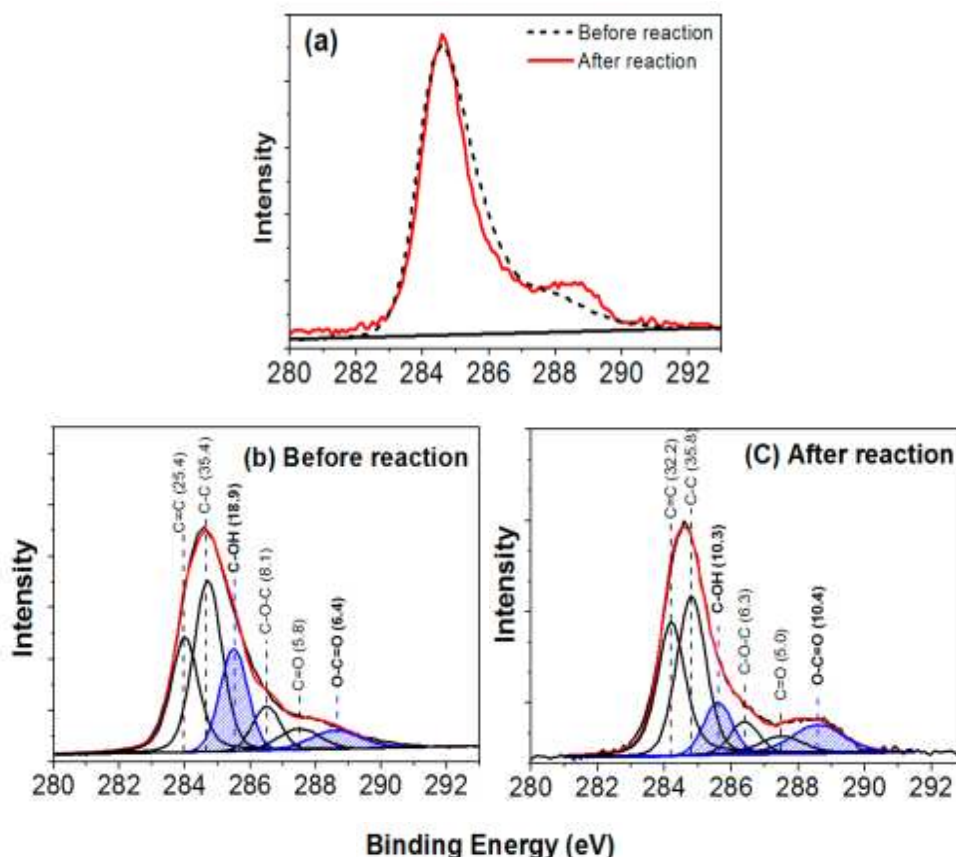
This figure shows the concentrations of removed bromate ( $\text{BrO}_3^-$ ) and produced bromide ( $\text{Br}^-$ ) under dark condition after 24 h in aqueous (25 °C) and ice (−20 °C) media in the presence of humic substances. While a negligible amount of bromate was removed in aqueous phase reactions, 30–40% of bromate was eliminated after freezing and thawing the solution.



This shows that the reduction of bromate was more favored in acidic condition in both aqueous and ice phases. The half reaction of bromate reduction indeed indicates that this reaction should be favored at an acidic condition.



Many functional groups in humic and fulvic acids may serve as a reductant for bromate. To analyze the functional group change of HS as a result of the reaction with bromate in ice, X-ray photoelectron spectroscopy (XPS) analysis was carried out.



The XPS analysis showed that the oxygen content increased in the order of humic (Aldrich) 18.6% < humic (SR) 27.8% < fulvic (SR) 30.0%, which implies that the oxygen-containing functional groups increase in this order.

The XPS analysis clearly showed that the carbons in humic acid (Aldrich) were more oxidized after the reaction with bromate in ice. The carbon content with higher oxidation state (i.e., higher C 1s binding energy) was enhanced after reaction.

## ■ Conclusion

In this work, we demonstrate a new transformation pathway that bromate can be efficiently reduced to bromide in frozen solution in the presence of organic reductants like humic substances (HS). The results showed that bromate in frozen solution could be removed by 30–40% in dark condition. The bromate reduction by HS induced a partial oxidation of HS, which was confirmed by X-ray photoelectron spectroscopic analysis of the HS sample recovered from the frozen solution. Photoluminescence analysis of HS revealed that the fluorescence quenching by bromate was observed only with very high concentration of bromate (0.1–0.2 M) in aqueous solution whereas the quenching effect in frozen solution was seen with much lower bromate concentration (5–100  $\mu\text{M}$ ). The highly enhanced removal of bromate in ice is ascribed to the freeze concentration effect that bromate and HS are concentrated by orders of magnitude to accelerate the bimolecular transformation in the ice grain boundary region.