

## Introduction

- HOCl and HOBr are important oxidants in a variety of aqueous solutions, including drinking water, wastewater, and sites of inflammation in mammals.<sup>1</sup>
- HOCl and HOBr can react with nucleophilic organic compounds to generate halogenated disinfection by-products (DBPs).
- Salicylic acid (SA) is significant in that it has been detected in drinking water influent and is present in human blood following dietary consumption (e.g., selected fruits, vegetables, and nuts).<sup>2</sup>
- SA can react with free chlorine and free bromine at the unsubstituted positions *para* ( $k_5$ ) and *ortho* ( $k_3$ ) to the hydroxyl group (Figure 1).

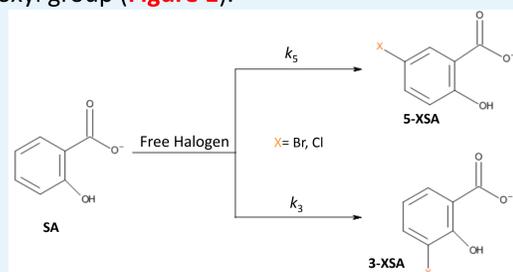


Figure 1. Halogenation of SA ( $pK_{a1} = 2.97$ ,  $pK_{a2} = 13.7$ ) by free chlorine or free bromine.

- In aqueous solutions containing free chlorine and/or free bromine, HOCl and HOBr are widely assumed to be the only active halogenating agents.
- Recent research has demonstrated that additional free halogen species (including  $Cl_2$ ,  $Cl_2O$ ,  $BrCl$ ,  $BrOCl$ ,  $Br_2$ , and  $Br_2O$ ) can contribute to the halogenation rates of aromatic compounds.<sup>3,4</sup>

### PURPOSE:

To examine the effects of solution conditions likely to influence halogen speciation (e.g., pH and  $[Cl^-]$ ) on rates and regioselectivity of SA bromination and chlorination.

## Methods

- Chlorination reactors typically contained 20 mM phosphate buffer, 10 mM NaCl, 500  $\mu M$   $HOCl_T$ , and 90 mM  $NaNO_3$ .
- Bromination experiments typically contained 20 mM phosphate buffer, 5 mM NaCl, 30  $\mu M$   $HOCl_T$ , 20  $\mu M$  NaBr, and 95 mM  $NaNO_3$ .
- All reactions were performed at 20.0 °C.
- Pseudo-first-order and second-order conditions were employed for chlorine ( $[HOCl_T]/[SA]_0 > 10$ ) and bromine ( $[HOBr_T]_0 = [SA]_0$ ) reactors, respectively.
- Solution conditions were varied to test the effects of pH and  $[Cl^-]$ .
- Reactors were periodically sampled and quenched with sodium thiosulfate.
- SA and bromination/chlorination products of SA were analyzed via HPLC-DAD.

## Chlorination

- Example time course for the reaction of SA with free chlorine (Figure 2).

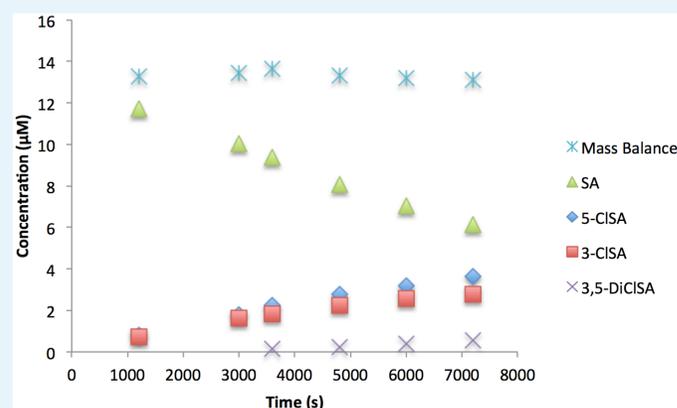


Figure 2. Loss of SA and formation of 5-CISA and 3-CISA at pH = 6.97,  $[HOCl_T] = 500 \mu M$ ,  $[NaCl] = 20 \text{ mM}$ ,  $[NaNO_3] = 79 \text{ mM}$ , and  $T = 20.0 \text{ }^\circ C$ .

- At all examined pH values, SA preferentially reacts with free chlorine at the *ortho* position, yielding 3-CISA (Figure 3).
- Regioselectivity did not change appreciably for the examined pH range (Figure 4).

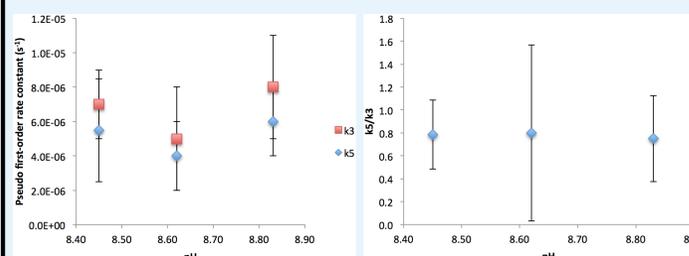


Figure 3. Chlorine experiments with pH as an independent variable; all error estimates herein denote 95% confidence intervals.

Figure 4. Ratio of  $k_5/k_3$  vs. pH as an independent variable.

- Rate constants for SA chlorination increases with increasing chloride concentration at constant ionic strength ( $[NaCl] + [NaNO_3] = 0.1 \text{ M}$ , Figure 5).

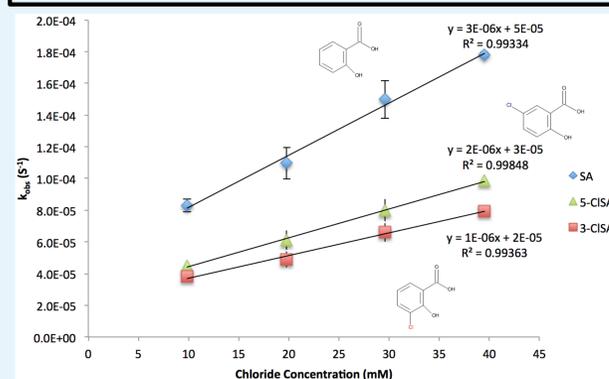


Figure 5. Regiospecific rate constants for SA chlorination as a function of chloride concentration at pH 6.98.

## Bromination

- Example time course for the reaction of SA with free bromine (Figure 6).

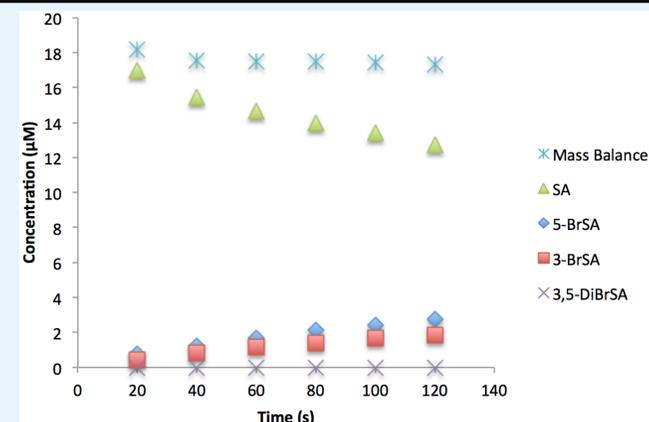


Figure 6. Loss of SA and formation of 5-BrSA and 3-BrSA at pH = 6.92,  $[NaBr]_0 = 20 \mu M$ ,  $[HOCl_T] = 30 \mu M$ ,  $[NaCl] = 5 \text{ mM}$ ,  $[NaNO_3] = 94 \text{ mM}$ , and  $T = 20.0 \text{ }^\circ C$ .

- At all examined pH values, SA preferentially reacts with free bromine at the *para* position, yielding 5-BrSA (Figure 7).
- As pH increases, selectivity toward bromination at the *para* position appears to decrease (Figure 8).

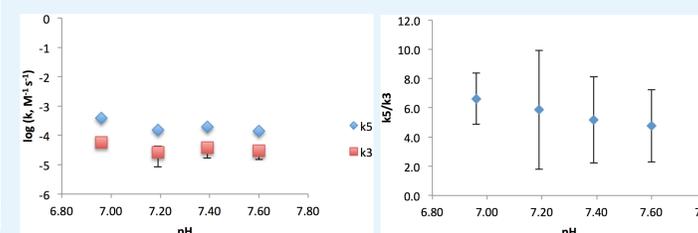


Figure 7. Regiospecific rate constants for SA bromination as a function of pH.

Figure 8. Ratio of rate constants for formation of 5-BrSA and 3-BrSA as a function of pH.

- Rate constants for SA bromination increases with increasing chloride concentration at constant ionic strength ( $[NaCl] + [NaNO_3] = 0.1 \text{ M}$ , Figure 9).

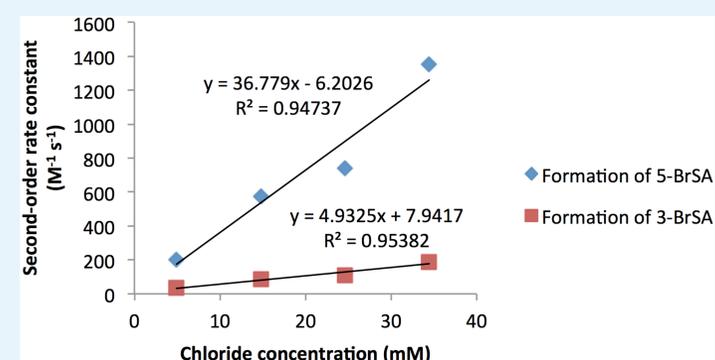


Figure 9. Regiospecific rate constants for SA bromination as a function of chloride concentration at pH 6.96.

## Discussion and Conclusions

- Chlorination reactions of SA are substantially slower than are bromination reactions of SA.
- As  $[Cl^-]$  increased, rates of SA chlorination and bromination also increased, likely due to increases in  $[Cl_2]$  and  $[BrCl]$  (Figures 10 and 11).

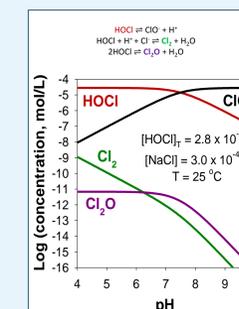


Figure 10. Speciation diagram of aqueous free chlorine.

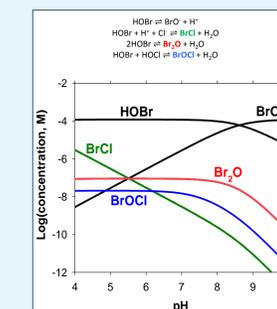


Figure 11. Speciation diagram of aqueous free bromine in the presence of excess free chlorine.

- Chloride can serve as a catalyst of SA chlorination and bromination by promoting the formation of  $Cl_2$  and  $BrCl$ .
- Prior studies demonstrated that  $Cl_2$  is several orders of magnitude more inherently reactive (relative to HOCl) toward modestly nucleophilic organic compounds (e.g., aromatic ethers and a substituted thiophene).<sup>5-7</sup>
- Previous work has also shown that  $BrCl$  is  $\sim 7$  orders of magnitude more inherently reactive than is HOBr in reactions with anisole.<sup>8</sup>
- Our work indicates that  $BrCl$  and  $Cl_2$  can influence the rate and regioselectivity of SA bromination and chlorination, respectively.

## Acknowledgements

We extend our thanks to the American Chemical Society Petroleum Research Fund (Grant #54560-UNI4), Towson University's Office of Undergraduate Research, Fisher College of Science and Mathematics, and the Department of Chemistry for their financial support.

## References

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