

Introduction

- HOCl and HOBr are important oxidants in a variety of aqueous solutions, including drinking water, wastewater, and sites of inflammation in mammals.¹
- 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).²
- 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).

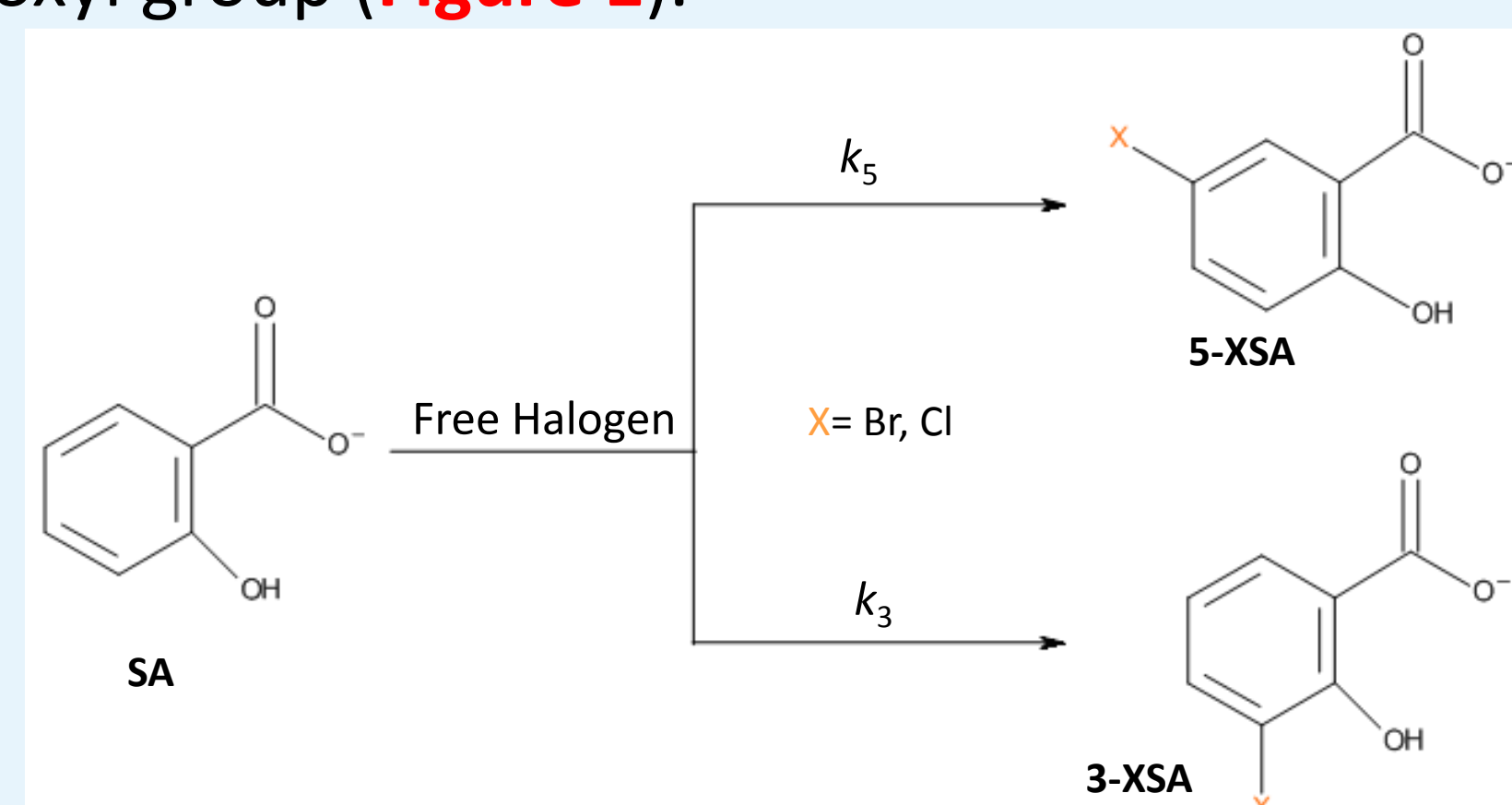


Figure 1. Halogenation of SA ($pK_{a1} = 2.97$, $pK_{a2} = 13.7$) by free chlorine or free bromine.

- 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.^{3,4}

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 μM $HOCl_T$, and 90 mM $NaNO_3$.
- Bromination experiments typically contained 20 mM phosphate buffer, 5 mM NaCl, 30 μM $HOCl_T$, 20 μM 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).

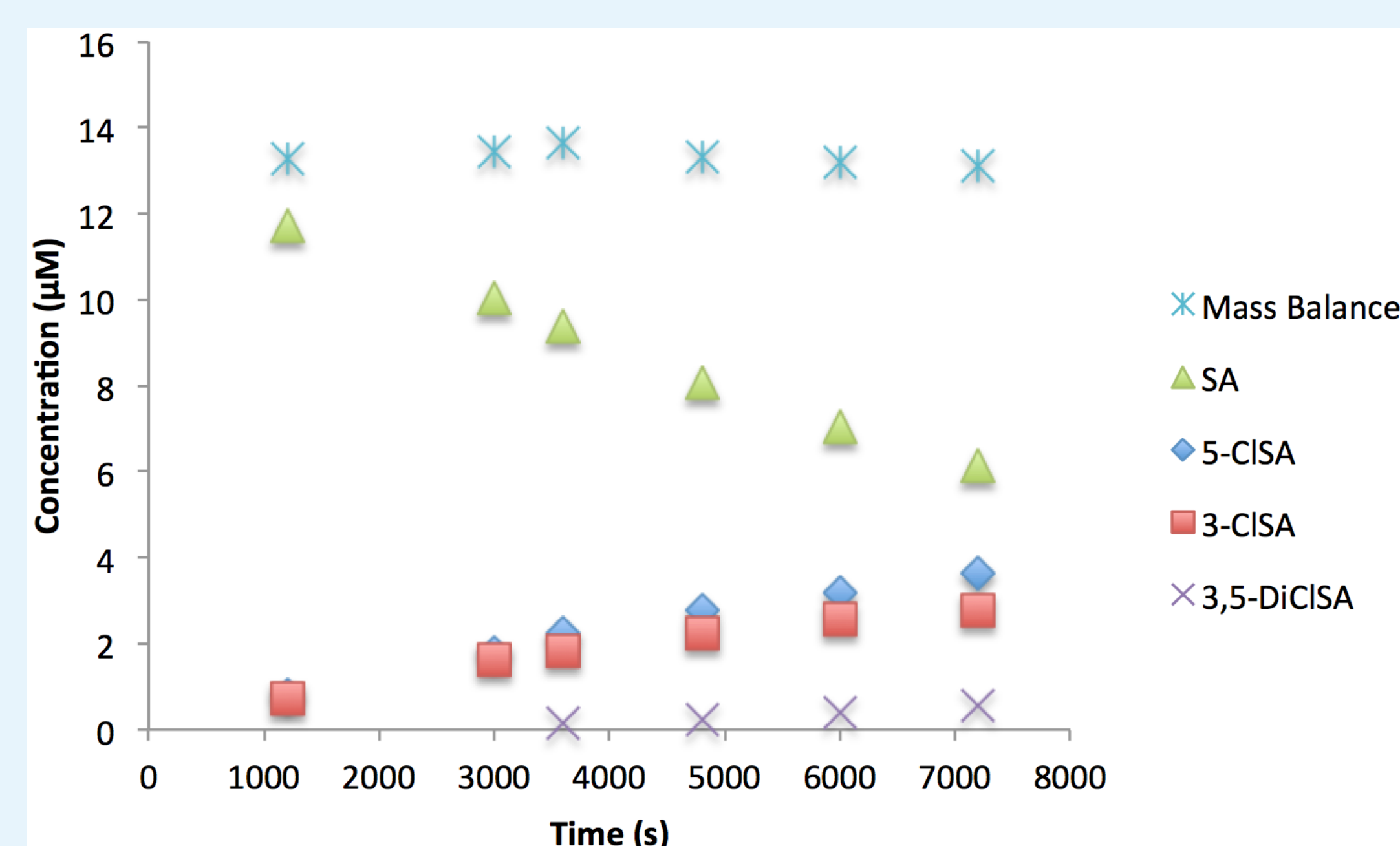


Figure 2. Loss of SA and formation of 5-CISA and 3-CISA at pH = 6.97, $[HOCl_T] = 500 \mu M$, $[NaCl] = 20 \text{ mM}$, $[NaNO_3] = 79 \text{ mM}$, and $T = 20.0 \text{ }^\circ C$.

- 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).

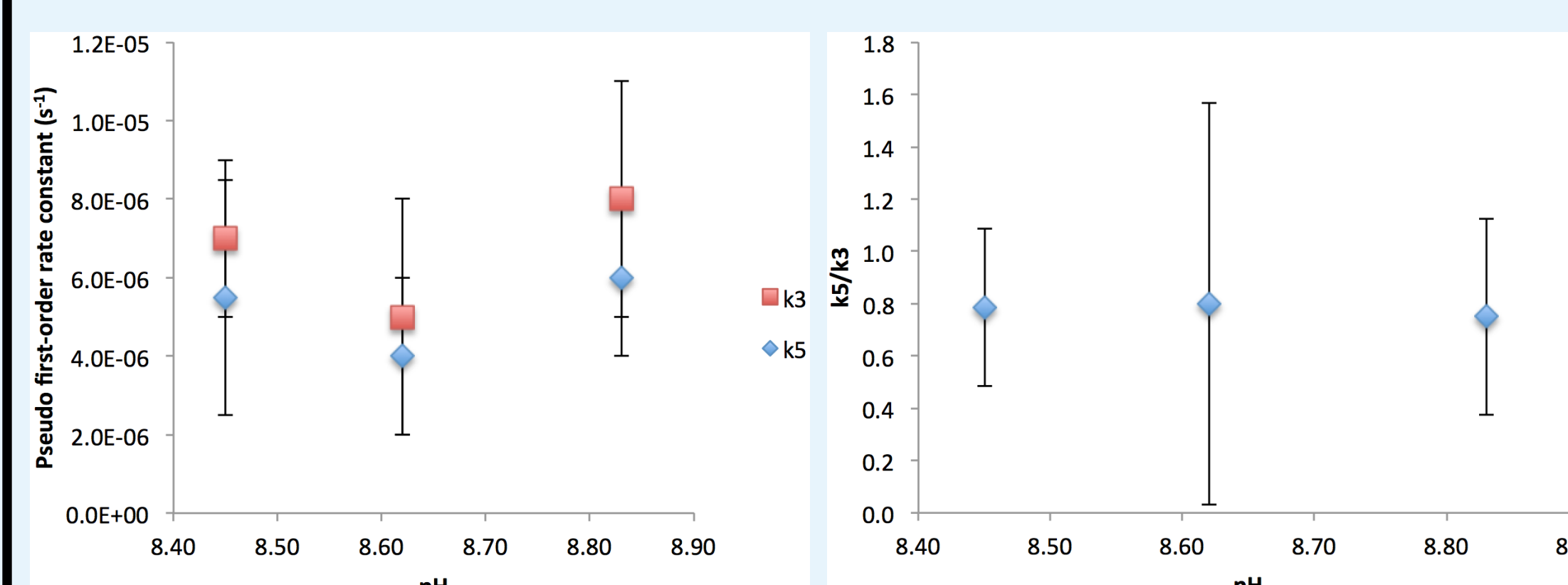


Figure 3. Chlorine experiments with pH as an independent variable; all error estimates herein denote 95% confidence intervals.

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).

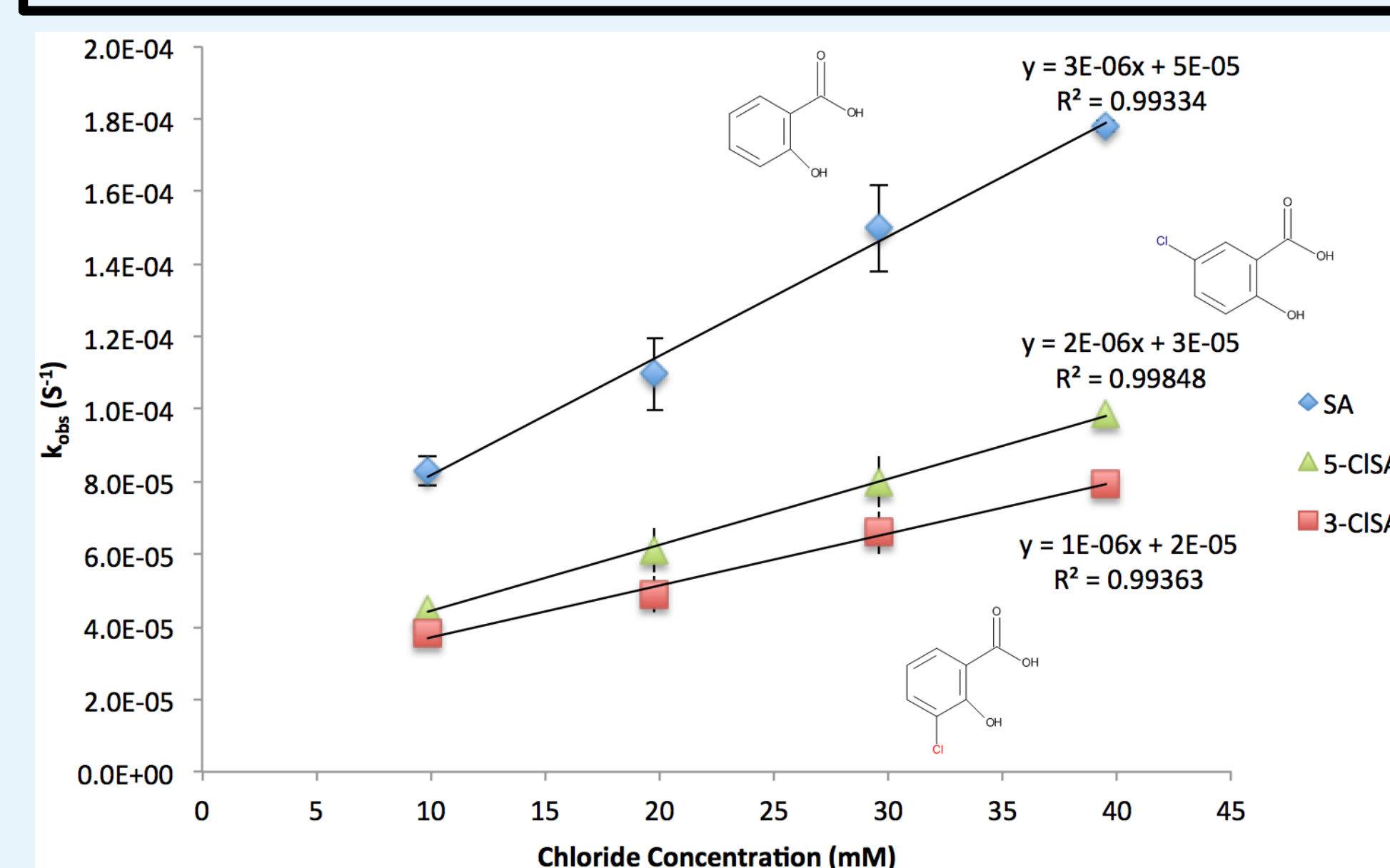


Figure 5. Regiospecific rate constants for SA chlorination as a function of chloride concentration at pH 6.98.

Bromination

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

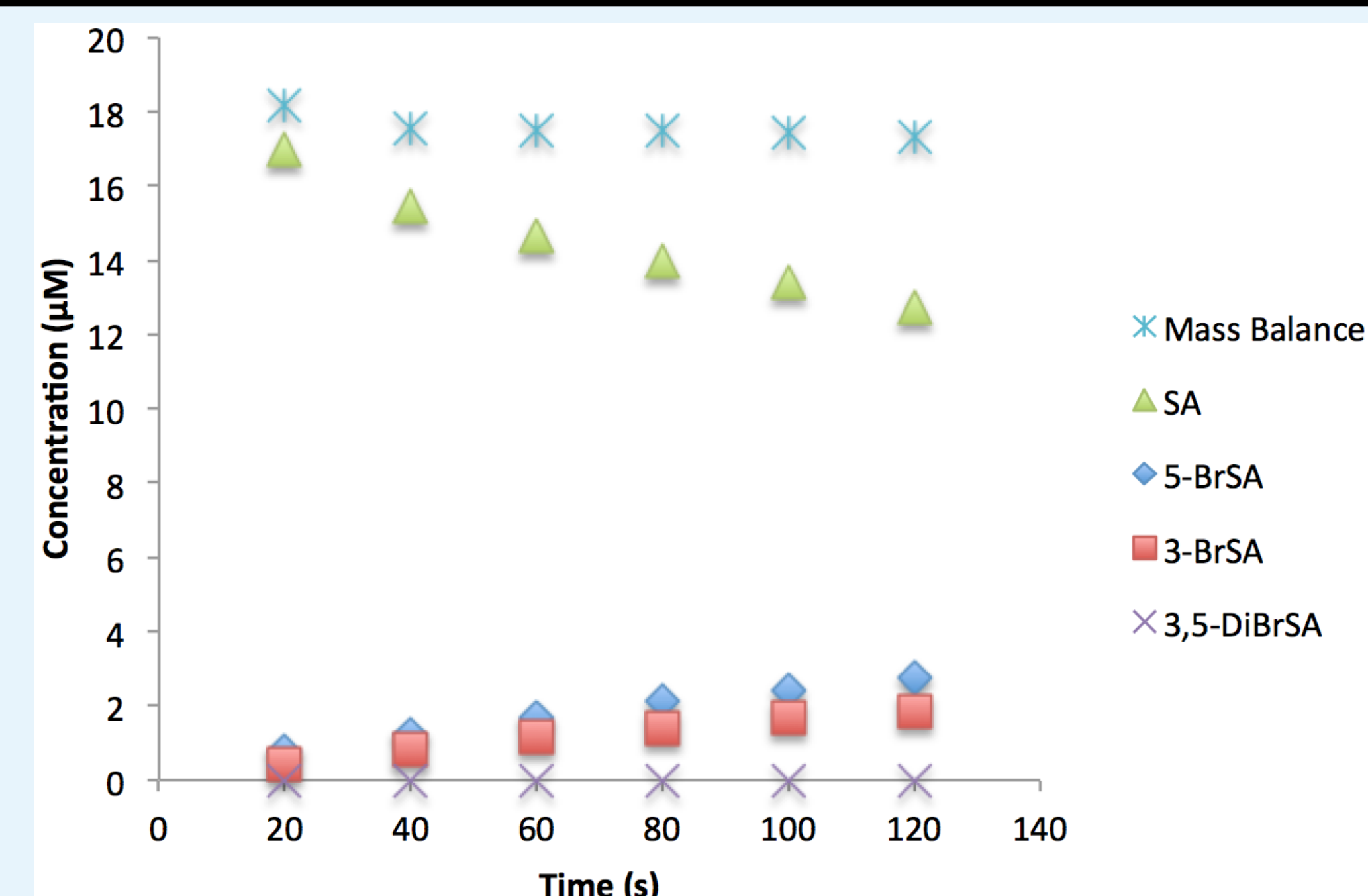


Figure 6. Loss of SA and formation of 5-BrSA and 3-BrSA at pH = 6.92, $[NaBr]_0 = 20 \mu M$, $[HOCl_T] = 30 \mu M$, $[NaCl] = 5 \text{ mM}$, $[NaNO_3] = 94 \text{ mM}$, and $T = 20.0 \text{ }^\circ C$.

- 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).

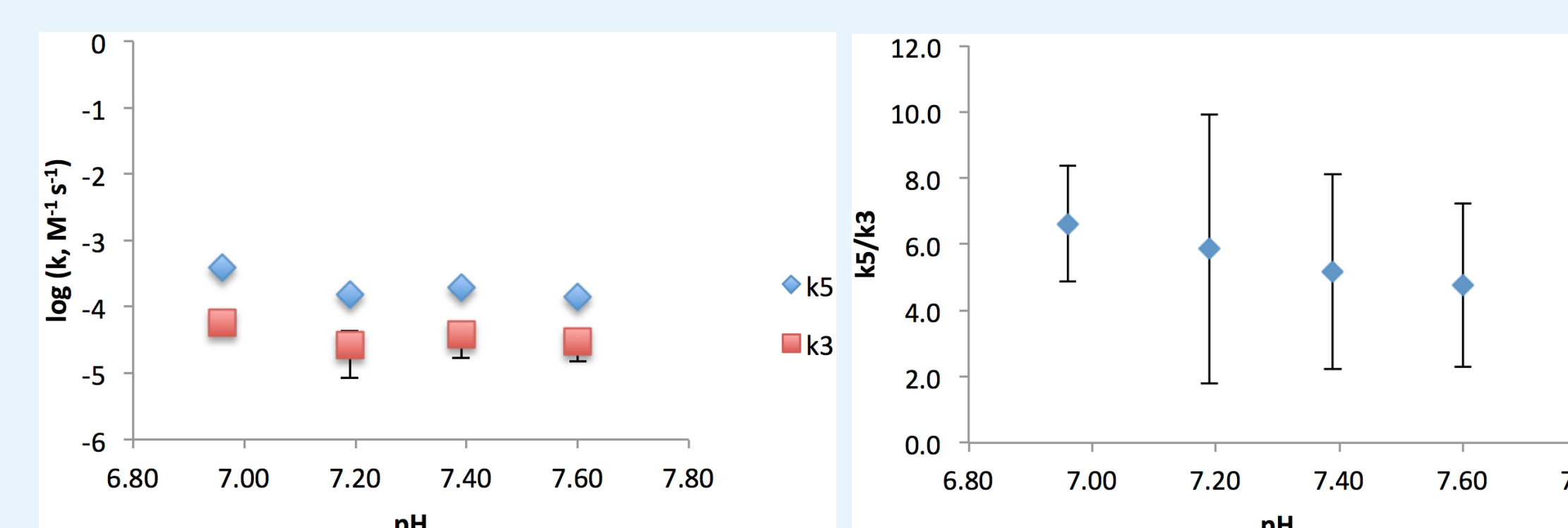


Figure 7. Regiospecific rate constants for SA bromination as a function of pH.

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).

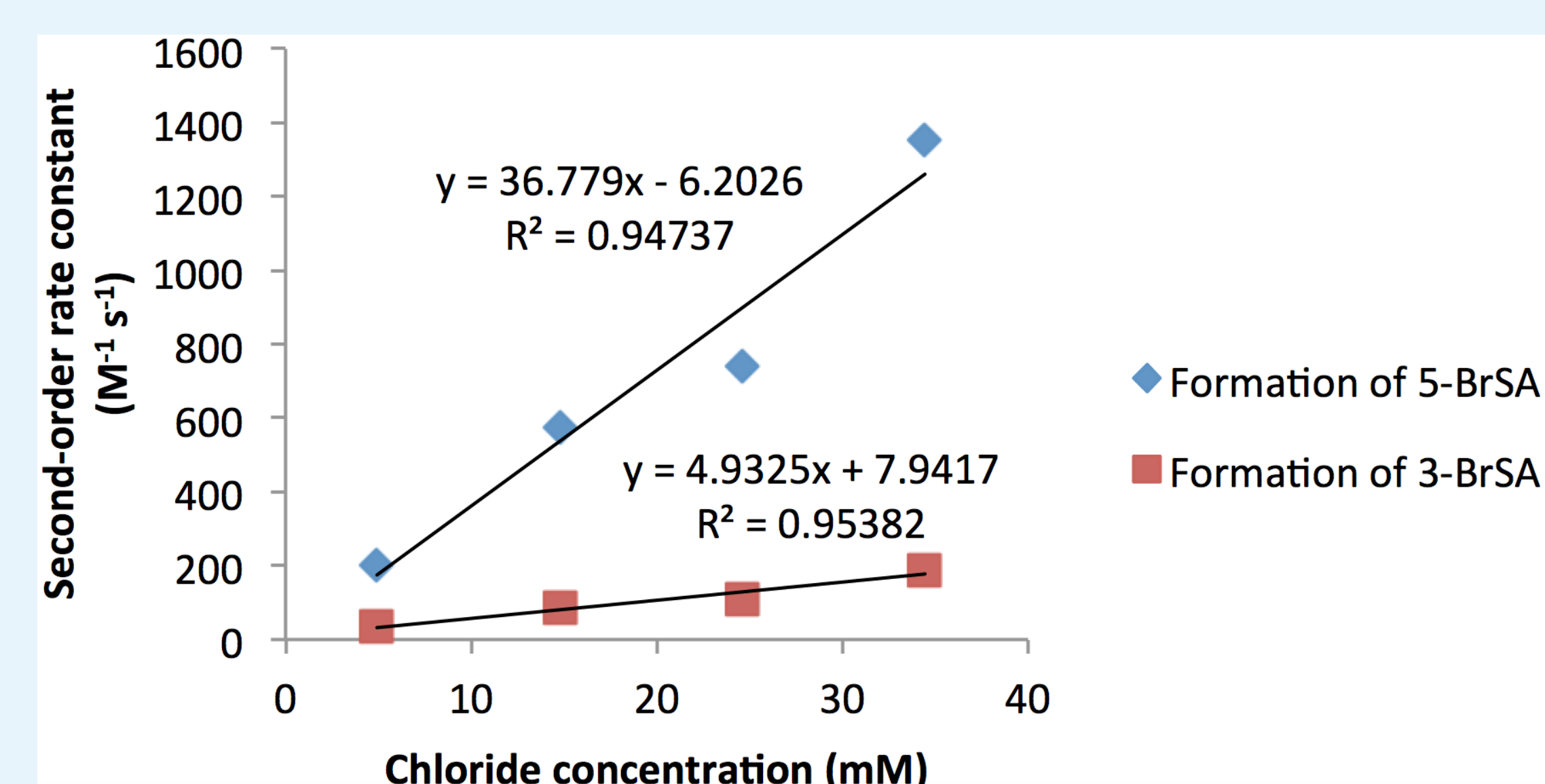


Figure 9. Regiospecific rate constants for SA bromination as a function of chloride concentration at pH 6.96.

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).

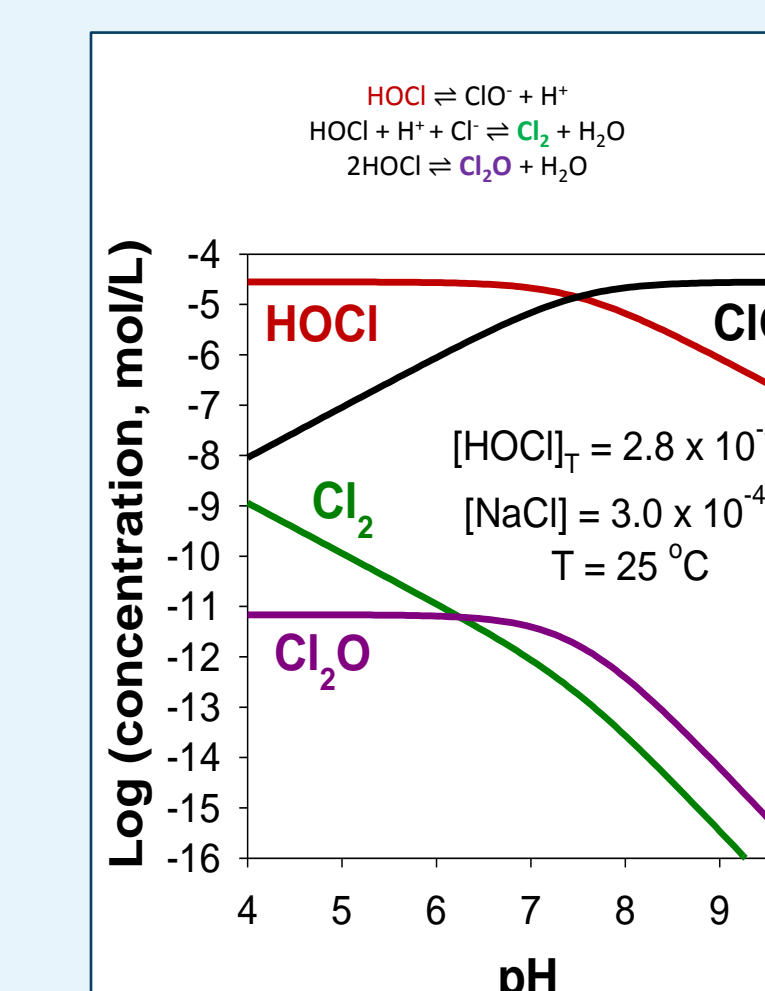


Figure 10. Speciation diagram of aqueous free chlorine.

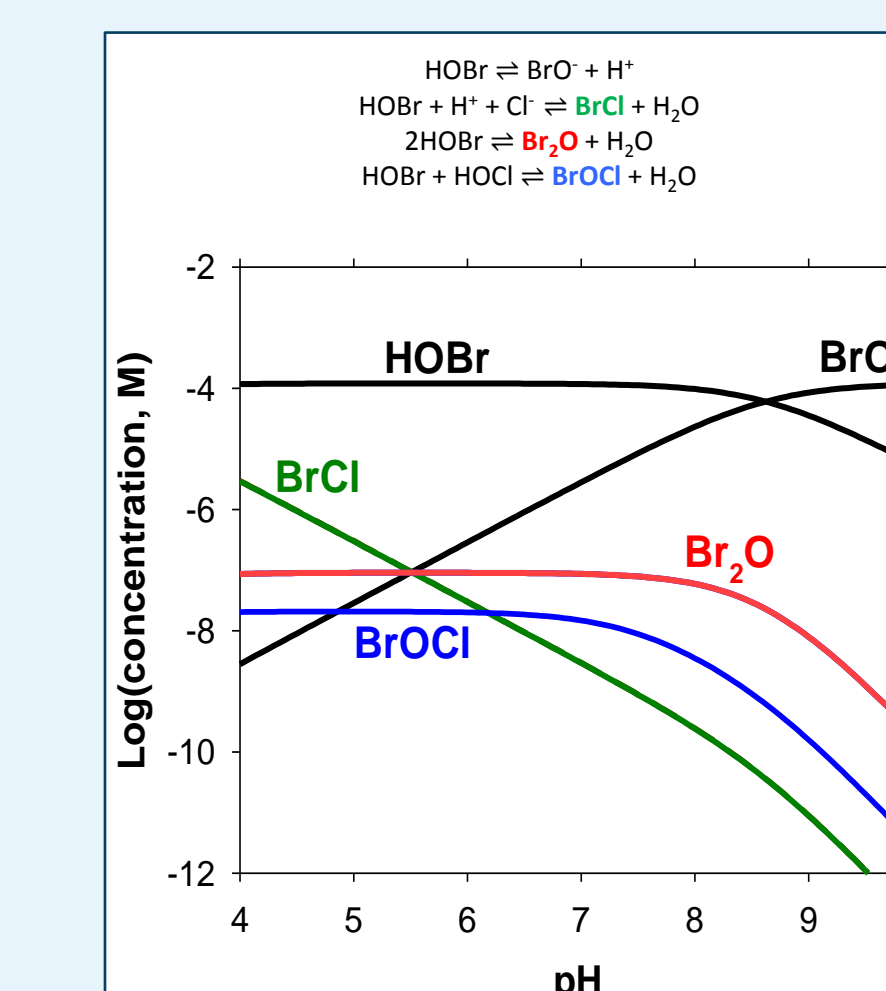


Figure 11. Speciation diagram of aqueous free bromine in the presence of excess free chlorine.

- 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).⁵⁻⁷
- Previous work has also shown that $BrCl$ is ~ 7 orders of magnitude more inherently reactive than is HOBr in reactions with anisole.⁸
- Our work indicates that $BrCl$ and Cl_2 can influence the rate and regioselectivity of SA bromination and chlorination, respectively.

Acknowledgements

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References

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