

# **Supplementary material for ACP manuscripts “A chemical probe technique for the determination of reactive halogen species in aqueous solution: Parts 1 and 2”**

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## **S.1 Analytical technique for measuring 3BPD and 3CPD**

The analytical technique used for the measurement of 3BPD has been described in detail elsewhere (Matthew and Anastasio, 2000). It is described here briefly along with minor modifications used for the present study.

After a specified illumination time, a known amount (0.100-2.00 mL) of sample was removed and diluted to 5.0 mL total volume with Milli-Q water in a 12 mL glass extraction vial. In order to prevent 3BPD formation after illumination (e.g., during sample extraction), 200  $\mu$ L of a solution containing sodium sulfite (~16 mM) and sodium bisulfite (~19 mM) was added to quench any reactive halogen species. Surrogate compounds were then added to track the recovery of 3BPD during extraction and the sample was saturated with sodium sulfate and extracted twice with 5.0 mL of ethyl acetate. The extracts were combined, an internal standard was added, and the combined extract was concentrated to ~100  $\mu$ L in a heating block (65 °C) under a stream of nitrogen. The extract was dried over sodium sulfate to remove any residual water and then solvent exchanged into ~2 mL of acetonitrile. This was followed by heptafluorobutyric anhydride (HFBA) derivatization to convert the alcohol groups to heptafluorobutyric esters. When borate was present in the samples (i.e., at pH > 5.5), 100  $\mu$ L of HFBA (not 50  $\mu$ L as originally used; Matthew and Anastasio, 2000) was employed to ensure complete derivatization. Once derivatized, the extract was diluted with ~5 mL of water and ~2 mL of saturated sodium bicarbonate solution, and then extracted into 2.0 mL of hexane. The hexane extracts were washed with saturated sodium bicarbonate solution and transferred to GC auto-sampler vials for analysis. Concentrations of halogenated diols in the extracts were measured with a Hewlett Packard (HP) 5890 gas chromatographic system with split/splitless injector. The GC was equipped with a HP 7673A autosampler, a HP 3396A integrator, and a HP 19233 Nickel 63-electron capture detector. The analytical column used

was a 30 m x 0.25 mm I.D. DB5-MS fused-silica capillary column with a phase thickness of 1.0  $\mu\text{m}$  (J & W Scientific).

## S.2 Kinetic derivations for equations describing the non-linear inverse plots and the influence of allyl alcohol in bromide solutions

The kinetic derivation that describes the non-linear inverse plots (e.g., Figure 2 in Part 1), and the effect that allyl alcohol has on the kinetics of these experiments (i.e., the AA effect), are based on the reactions and rate constants from Tables S1-S3. In our experiments, reactions of  $\text{Br}^\bullet$ ,  $\text{Br}_2$ , and  $\text{HOBr}$  with AA are responsible for the formation of 3BPD and, therefore, the total rate of 3BPD formation ( $R_{F,tot}^{3BPD}$ ) is equal to the sum of the rates from these three species ( $i = \text{Br}^\bullet$ ,  $\text{Br}_2$ , and  $\text{HOBr}$ ):

$$R_{F,tot}^{3BPD} = \sum_i R_{F,i}^{3BPD} \quad (\text{S1})$$

$R_{F,i}^{3BPD}$  here is the rate of 3BPD formation from species  $i$  and is equal to:

$$R_{F,i}^{3BPD} = k_i^{AA} [i]^m [\text{AA}] Y_i^{3BPD} \quad (\text{S2})$$

where  $k_i^{AA}$  is the total rate constant for the reaction of species  $i$  with allyl alcohol,  $[i]^m$  is the molar concentration of  $i$  in the presence of AA,  $[\text{AA}]$  is the molar concentration of AA, and  $Y_i^{3BPD}$  is the yield of 3BPD from the reaction of species  $i$  with AA (Part 1, section 2.2.3 and equation E1).

A complete kinetic derivation including all three species that takes into account the AA effect is extremely difficult and could not be solved analytically. However, equation S1 can be written in terms of an individual  $\text{Br}^\bullet(\text{aq})$  species as follows:

$$R_{F,tot}^{3BPD} = \frac{R_{F,i}^{3BPD}}{F_i^{3BPD}} \quad (\text{S3})$$

where  $F_i^{3BPD}$  is the fraction of total 3BPD that was formed from the reaction of species  $i$  with allyl alcohol (section S.4).

While versions of equation S3 can be derived separately for  $\text{Br}^\bullet$ ,  $\text{Br}_2$ , and  $\text{HOBr}$ , only the  $\text{Br}^\bullet$  version can be solved. This is because the final equations for  $\text{Br}_2$  and  $\text{HOBr}$  contain terms

that are currently unknown or that are difficult to estimate (e.g., the rates of formation and pseudo-first-order rate constants for destruction of hydroperoxyl radical ( $\text{HO}_2^\bullet$ ) and dibromide radical anion ( $\text{Br}_2^{\bullet-}$ ). In the case of  $\text{Br}^\bullet$ , equation S3 can be rewritten as:

$$R_{F,tot}^{3BPD} = \frac{k_{Br}^{AA} [\text{Br}^\bullet]^n [\text{AA}] Y_{Br}^{3BPD}}{F_{Br}^{3BPD}} \quad (\text{S4})$$

where  $[\text{Br}^\bullet]^n$  is the molar concentration of  $\text{Br}^\bullet$  in the presence of AA. In order to have equation S4 account for the AA effect, it must be written in terms of  $\bullet\text{OH}$ . This is done by assuming steady-state conditions for  $\text{Br}^\bullet(\text{aq})$  and  $\bullet\text{OH}$  and solving for the concentrations of  $\text{Br}^\bullet$  and  $\bullet\text{OH}$  in the presence of AA (i.e.,  $[\text{Br}^\bullet]^n$  and  $[\bullet\text{OH}]^n$ ). In our experimental system, the rates of  $\text{Br}^\bullet$  formation ( $R_F^{Br}$ ) and destruction ( $R_D^{Br}$ ) in the presence of AA can be written as:

$$R_F^{Br} = k_{OH}^{Br^-} [\text{OH}^\bullet]^n [\text{Br}^-] Y_{OH}^{Br} \quad (\text{S5})$$

$$R_D^{Br} = k_{Br}^{NS} [\text{Br}^\bullet] + k_{Br}^{AA} [\text{Br}^\bullet]^n [\text{AA}] \quad (\text{S6})$$

where  $k_m^n$  is the rate constant for the reaction of species  $m$  with  $n$  and  $Y_{OH}^{Br}$  is the yield of  $\text{Br}^\bullet$  formed from the reaction of  $\bullet\text{OH}$  with  $\text{Br}^-$  (section S.5). The rate constant  $k_{Br}^{NS}$  is the pseudo-first-order rate constant for the reaction of  $\text{Br}^\bullet$  with natural scavengers. In real samples, natural scavengers include all species, other than AA, that react with  $\text{Br}^\bullet$ . The dominant “natural” scavengers in our experimental systems are  $\text{Br}^-$  and  $\text{H}_2\text{O}_2$ . At steady state,  $R_F^{Br}$  is equal to  $R_D^{Br}$ , and therefore

$$[\text{Br}^\bullet]^n = \frac{k_{OH}^{Br^-} [\text{Br}^-] [\bullet\text{OH}]^n Y_{OH}^{Br}}{k_{Br}^{NS} + k_{Br}^{AA} [\text{AA}]} \quad (\text{S7})$$

Similarly, the steady-state  $\bullet\text{OH}$  concentration in the presence of AA can be determined using the same procedure. For  $\bullet\text{OH}$ , we do not need to explicitly solve for  $R_F^{OH}$  (since this can be measured or calculated in our experiments and, unlike  $\text{Br}^\bullet(\text{aq})$ , is unaffected by the addition of AA), but we must solve for the rate of  $\bullet\text{OH}$  destruction in the presence of AA ( $R_D^{OH}$ ):

$$R_D^{OH} = k_{OH}^{NS} [\bullet\text{OH}] + k_{OH}^{AA} [\bullet\text{OH}]^n [\text{AA}] \quad (\text{S8})$$

where  $k_{OH}^{NS}$  is the pseudo-first-order rate constant for the reaction of  $\bullet\text{OH}$  with natural scavengers in the absence of AA, and includes the reaction of  $\bullet\text{OH}$  with  $\text{Br}^-$  and  $\text{H}_2\text{O}_2$

(equation S20). Note that the second term in equation S8 takes into account the effect of allyl alcohol on  $[\bullet\text{OH}]$ . At steady state  $R_F^{OH} = R_D^{OH}$  (in the presence of AA) and therefore

$$[\bullet\text{OH}] = \frac{R_F^{OH}}{k_{OH}^{NS} + k_{OH}^{AA}[\text{AA}]} \quad (\text{S9})$$

Combining equations S7 and S9 into S4 yields an expression for  $R_{F,tot}^{3BPD}$  based on  $\text{Br}\bullet$  kinetics and written in terms of  $\bullet\text{OH}$ :

$$R_{F,tot}^{3BPD} = \frac{k_{Br}^{AA} k_{OH}^{Br^-} [\text{Br}^-] Y_{OH}^{Br} R_F^{OH} [\text{AA}] Y_{Br}^{3BPD}}{F_{Br}^{3BPD} (k_{Br}^{NS} + k_{Br}^{AA}[\text{AA}])(k_{OH}^{NS} + k_{OH}^{AA}[\text{AA}])} \quad (\text{S10})$$

By taking the inverse of both sides of S10, the equation is linearly transformed (as described by Zhou and Mopper (1990)). Like terms in the linearized equation are then combined and the following two equations (which represent  $\bullet\text{OH}$  and  $\text{Br}\bullet$  concentrations in the absence of AA) are used to make substitutions:

$$[\bullet\text{OH}] = \frac{R_F^{OH}}{k_{OH}^{NS}} \quad (\text{S11})$$

$$[\text{Br}\bullet] = \frac{k_{OH}^{Br^-} [\text{OH}\bullet] [\text{Br}^-] Y_{OH}^{Br}}{k_{Br}^{NS}} \quad (\text{S12})$$

The result of these steps is an equation that describes the linear inverse plot over all AA concentrations:

$$\frac{1}{R_{F,tot}^{3BPD}} = a + \frac{b}{[\text{AA}]} + c[\text{AA}] \quad (\text{S13})$$

where

$$a = \frac{(k_{OH}^{AA} k_{Br}^{NS} + k_{Br}^{AA} k_{OH}^{NS}) F_{Br}^{3BPD}}{R_F^{Br} Y_{Br}^{3BPD} k_{Br}^{AA} k_{OH}^{NS}} \quad (\text{S14})$$

$$b = \frac{F_{Br}^{3BPD}}{Y_{Br}^{3BPD} k_{Br}^{AA} [\text{Br}\bullet]} \quad (\text{S15})$$

$$c = \frac{k_{OH}^{AA} F_{Br}^{3BPD}}{R_F^{OH} Y_{Br}^{3BPD} k_{OH}^{Br^-} [\text{Br}^-] Y_{OH}^{Br}} = \frac{k_{OH}^{AA} F_{Br}^{3BPD}}{k_{OH}^{NS} Y_{Br}^{3BPD} R_F^{Br}} \quad (\text{S16})$$

Values for  $a$ ,  $b$ , and  $c$  are determined by fitting the experimental data ( $1/R_{F,tot}^{3BPD}$  and  $1/[AA]$ ) to the functional form of equation S13 using Sigmaplot (version 4.0). By rearranging the  $a$ ,  $b$ , and  $c$  terms, it is possible to solve for  $[Br^\bullet]$ ,  $R_F^{Br}$ , and the lifetime of  $Br^\bullet$  ( $\tau_{Br}$ ) in the absence of AA:

$$[Br^\bullet] = \frac{F_{Br}^{3BPD}}{b Y_{Br}^{3BPD} k_{Br}^{AA}} \quad (S17)$$

$$R_F^{Br} = \frac{k_{OH}^{AA} F_{Br}^{3BPD}}{c k_{OH}^{NS} Y_{Br}^{3BPD}} \quad (S18)$$

$$\tau_{Br} = \frac{c k_{OH}^{NS}}{b k_{OH}^{AA} k_{Br}^{AA}} = \frac{[Br^\bullet]}{R_F^{Br}} \quad (S19)$$

In order to utilize equations S18 and S19 to solve for  $R_F^{Br}$  and  $\tau_{Br}$ , the value of  $k_{OH}^{NS}$  (pseudo-first-order rate constant for  $\bullet OH$  loss in the absence of AA) must first be determined. If the system is well defined (i.e., the major sinks of  $\bullet OH$  are known), it is relatively straightforward to calculate this value. For example, in our system  $Br^-$  and  $H_2O_2$  are the dominant “natural scavengers” of  $\bullet OH$  and thus:

$$k_{OH}^{NS} = k_{OH}^{Br^-} [Br^-] f_{Lost}^{Br^-} + k_{OH}^{H_2O_2} [H_2O_2] \quad (S20)$$

where  $f_{Lost}^{Br^-}$  is the fraction of  $\bullet OH$  reacting with  $Br^-$  that is “lost” (see S.5). In solutions with bromide only,  $f_{Lost}^{Br^-}$  is equivalent to the yield of  $Br^\bullet$  from the reaction of  $\bullet OH$  with  $Br^-$  ( $Y_{OH}^{Br}$ ) (section S.4). In cases where  $k_{OH}^{NS}$  cannot be readily calculated (e.g., in natural samples) it can be measured directly with the BA chemical probe technique discussed in Part 1, section 2.2.3.

### S.3 Kinetic derivations for equations describing the linear portion of the inverse plot

Because the equations in section S.2 can only be applied to  $Br^\bullet$  kinetics, we sought a more general set of equations that could be used for all forms of  $Br^*(aq)$ . One approach is to assume that at low concentrations allyl alcohol has minimal impact on  $[\bullet OH]$  and, therefore,

little effect on the rate of formation of Br\*(aq) (i.e.,  $R_{F}^{ii}$  (the rate in the presence of AA)  $\approx$   $R_{F}^i$  (the rate in the absence of AA)). By making this assumption, the equations no longer need to be written in terms of  $\bullet$ OH, which greatly simplifies the derivations and allows equations to be written for each Br\*(aq) species. Under these conditions, equation S4 can be rewritten to represent any Br\*(aq) species:

$$R_{F,tot}^{3BPD} = \frac{k_i^{AA} [i]'' [AA] Y_i^{3BPD}}{F_i^{3BPD}} \quad (S21)$$

where  $[i]''$  is equal to

$$[i]'' = \frac{R_{F}^i}{k_i^{NS} + k_i^{AA} [AA]} \quad (S22)$$

and  $k_i^{NS}$  is the pseudo-first-order rate constant for the reaction of species  $i$  with natural scavengers. Substituting S22 into S21 yields

$$R_{F,tot}^{3BPD} = \frac{k_i^{AA} R_{F}^i [AA] Y_i^{3BPD}}{F_i^{3BPD} (k_i^{NS} + k_i^{AA} [AA])} \quad (S23)$$

As with equation S10, equation S23 can be linearly transformed by taking the inverse of both sides of the equation. Like terms are then combined and the following equation (which represents steady-state concentrations of  $i$  in the absence of AA) is used to make substitutions:

$$[i] = \frac{R_{F}^i}{k_i^{NS}} \quad (S24)$$

The final result is an equation that describes the linear portion of the inverse plot:

$$\frac{1}{R_{F,tot}^{3BPD}} = a' + \frac{b'}{[AA]} \quad (S25)$$

Note that this equation follows directly from equation S13 under conditions of low allyl alcohol concentrations where  $\frac{b}{[AA]} \gg c[AA]$  and it is assumed that AA has a minimal affect on  $R_{F}^i$ .

The parameters  $a'$  and  $b'$  in equation S25 are the y-intercept and slope of the linear portion of the inverse plot that can be expressed as:

$$a' = \frac{F_i^{3BPD}}{Y_i^{3BPD} R_F^i} \quad (S26)$$

$$b' = \frac{F_i^{3BPD}}{Y_i^{3BPD} k_i^{AA} [i]} \quad (S27)$$

These two terms can be rearranged to solve for values of  $[i]$ ,  $R_F^i$ , and  $\tau_i$  in the absence of AA as follows:

$$[i] = \frac{F_i^{3BPD}}{b' Y_i^{3BPD} k_i^{AA}} \quad (S28)$$

$$R_F^i = \frac{F_i^{3BPD}}{a' Y_i^{3BPD}} \quad (S29)$$

$$\tau_i = \frac{a'}{b' k_i^{AA}} = \frac{[i]}{R_F^i} \quad (S30)$$

These equations are analogous to those derived for the  $\bullet\text{OH}$  system with BA as the probe (Zhou and Mopper, 1990; Anastasio and McGregor, 2001).

#### S.4 Calculating the fraction of 3BPD formed from the reaction of species $i$ with AA ( $F_i^{3BPD}$ ) in bromide solutions

As discussed earlier, in our experimental system 3BPD formation can be attributed to the reactions of  $\text{Br}\bullet$ ,  $\text{Br}_2$ , and  $\text{HOBr}$  with AA. The fraction of 3BPD formed from each species can be calculated by dividing the rate of 3BPD formation attributed to species  $i$  by the total rate of 3BPD formation:

$$F_i^{3BPD} = \frac{R_{F,i}^{3BPD}}{R_{F,tot}^{3BPD}} = \frac{k_i^{AA} [i]^m [\text{AA}] Y_i^{3BPD}}{\sum_i (k_i^{AA} [i]^m [\text{AA}] Y_i^{3BPD})} \quad (S31)$$

Values of  $[i]^m$  were determined using the kinetic model under a given set of conditions. It is important to note that  $F_i^{3BPD}$  changes as a function of pH,  $[\text{Br}^-]$ , and  $[\text{AA}]$ .

## S.5 Calculating the yield of Br• from the reaction of •OH with Br<sup>-</sup> ( $Y_{OH}^{Br}$ ) and the fraction of •OH lost to reaction with Br<sup>-</sup> ( $f_{Lost}^{Br^-}$ ) in bromide solutions

In our experimental system, the yield of Br• from the reaction of •OH with Br<sup>-</sup> ( $Y_{OH}^{Br}$ ) is equivalent to the fraction of •OH lost during reaction with Br<sup>-</sup> ( $f_{Lost}^{Br^-}$ ). These two values are determined by the fate of •BrOH<sup>-</sup>, which is formed from the initial reaction of •OH with Br<sup>-</sup> (reaction 29) and controlled by subsequent reactions (Table S2):



The values for  $Y_{OH}^{Br}$  and  $f_{Lost}^{Br^-}$  are equivalent in our experimental system because the reactions that lead to the destruction of •OH (i.e., 30, 36, and 37) also lead to the formation of Br•. (Note that reaction 30 is a source of Br• because •Br<sub>2</sub><sup>-</sup> rapidly dissociates to Br•).  $Y_{OH}^{Br}$  and  $f_{Lost}^{Br^-}$  are calculated as the sum of the rates of the reactions that lead to Br• formation (or •OH loss), divided by the total rate of •BrOH<sup>-</sup> loss. Factoring out [•BrOH<sup>-</sup>] in this fraction yields the following expression:

$$Y_{OH}^{Br} = \frac{k_{\rightarrow Br}^{BrOH^-} + k_{BrOH^-}^{H^+} [\text{H}^+] + k_{BrOH^-}^{Br^-} [\text{Br}^-]}{k_{\rightarrow Br^-}^{BrOH^-} + k_{\rightarrow Br}^{BrOH^-} + k_{BrOH^-}^{H^+} [\text{H}^+] + k_{BrOH^-}^{Br^-} [\text{Br}^-]} \quad (\text{S32})$$

where  $k_{\rightarrow Br^-}^{BrOH^-}$  and  $k_{\rightarrow Br}^{BrOH^-}$  are the first order rate constants for the dissociation of •BrOH<sup>-</sup> into Br<sup>-</sup> (reaction 35) and Br• (reaction 36), respectively.

Although  $Y_{OH}^{Br}$  and  $f_{Lost}^{Br^-}$  are equivalent for our experimental system, this may not be true for other systems. For example, in actual samples there might be species present that can react with •BrOH<sup>-</sup> and •Br<sub>2</sub><sup>-</sup> which could lead to the destruction of •OH, but not to the formation of



$\text{Br}^\bullet$  (i.e., reactions with dissolved organic material). In such cases,  $f_{Lost}^{Br^-}$  would be larger than  $Y_{OH}^{Br}$  and, in order to calculate  $f_{Lost}^{Br^-}$ , equation S32 would need to be modified to account for the additional reactions of  $\bullet\text{BrOH}^-$  and  $\bullet\text{Br}_2^-$ .

### S.6 Alternative method for calculating the rate of $\text{Br}^\bullet$ formation ( $R_F^{Br}$ ) in bromide solutions using equation S13

As discussed in section S.2, equation S13 can be used to calculate  $[\text{Br}^\bullet]$ ,  $R_F^{Br}$ , and  $\tau_{\text{Br}}$  in cases where the entire non-linear inverse plot has been defined. In theory, it should also be possible to use S13 to calculate  $[\text{Br}^\bullet]$ ,  $R_F^{Br}$ , and  $\tau_{\text{Br}}$  in cases where only the linear portion of the curve has been defined. In the linear portion of the inverse plot (i.e., at low AA concentrations),  $\frac{b}{[\text{AA}]} \gg c[\text{AA}]$  and S13 simplifies to:

$$\frac{1}{R_{F,tot}^{3BPD}} = a + \frac{b}{[\text{AA}]} \quad (\text{S33})$$

Note this equation is different from equation S25 (section S.3) in that the  $a$  and  $b$  terms have not been rewritten in terms of all three species (i.e.,  $a$  and  $b$  are still defined by equations S14 and S15, respectively). In the linear range, the  $a$  and  $b$  terms are equivalent to the y-intercept and slope of the linear inverse plot, respectively.

When working in the linear range  $[\text{Br}^\bullet]$  is calculated as discussed in section S.2 (equation S17) and  $\tau_{\text{Br}}$  can be calculated as  $[\text{Br}^\bullet]/R_F^{Br}$ . However, in the original derivation,  $R_F^{Br}$  was derived with the  $c$  term, and because the  $c$  term has been removed, the  $a$  term must now be used to calculate  $R_F^{Br}$ . In section S.2 the  $a$  term was defined as:

$$a = \frac{(k_{OH}^{AA} k_{Br}^{NS} + k_{Br}^{AA} k_{OH}^{NS}) F_{Br}^{3BPD}}{R_F^{Br} Y_{Br}^{3BPD} k_{Br}^{AA} k_{OH}^{NS}} \quad (\text{S14})$$

Note that this equation has two unknowns,  $R_F^{Br}$  and  $k_{Br}^{NS}$ . In order to solve this equation for  $R_F^{Br}$  the equation must be written in terms of  $[\text{Br}^\bullet]$ , which can be calculated with equation S17. This is done by substituting with

$$[\text{Br}^\bullet] = \frac{R_F^{Br}}{k_{Br}^{NS}} \quad (\text{S34})$$

By rearranging S14 and using equation S34,  $R_F^{Br}$  can be written as:

$$R_F^{Br} = \frac{F_{Br}^{3BPD} [\text{Br}^\bullet] Y_{Br}^{3BPD} k_{Br}^{AA} k_{OH}^{NS}}{Y_{Br}^{3BPD} [ (a[\text{Br}^\bullet] Y_{Br}^{3BPD} k_{Br}^{AA} k_{OH}^{NS}) - (k_{OH}^{AA} F_{Br}^{3BPD}) ]} \quad (\text{S35})$$

This equation, in conjunction with the y-intercept from the linear inverse plot of the raw data (i.e., without any AA or  $F_i^{3BPD}$  corrections) and the  $[\text{Br}^\bullet]$  calculated with equation S17, was used to calculate  $R_F^{Br}$  for several of the experiments. This “data treatment” only provides good results in cases where  $F_{Br}^{3BPD}$  is very large and, overall, these results are no better (and typically much worse) than those obtained from data treatment C.

## S.7 Technique for removing small amounts of $\text{Br}^-$ from NaCl solutions

In agreement with a past report (Wang et al., 1994), we found trace amounts of  $\text{Br}^-$  in solutions made from "pure" NaCl. Because these trace amounts of  $\text{Br}^-$  can bias our experimental results in chloride solutions containing little or no added bromide, we developed a technique to remove  $\text{Br}^-$  from concentrated chloride solutions.

In preliminary experiments to develop this technique, 3 M solutions of pure NaCl (Aldrich, 99.999%) at pH ~ 2 were illuminated for ~24 hours with 254 nm light in a cylindrical reactor (RPR-100; Southern New England Ultraviolet Company, Inc.) equipped with 16 mercury lamps (RPR-2537 Å, 25 W). After illumination allyl alcohol was added to the solutions and, surprisingly, large amounts of 3BPD were formed, indicating the presence of reactive bromide species such as  $\text{Br}_2$ .

Based on these results, we developed a procedure to convert  $\text{Br}^-$  to  $\text{Br}_2$  and purge it from solution. In this technique 250 mL of a 3 M NaCl solution containing 0.01 M  $\text{H}_2\text{O}_2$  was adjusted to pH 1.5 and then divided equally into four separate 130 mL quartz vessels (P/N # 7892, Ace Glass). The vessels were illuminated for 8 hrs in the cylindrical photoreactor while simultaneously being purged at ~ 0.35 L min<sup>-1</sup> with zero-grade air (Puritan Medical Products) sent through a glass gas dispersion tube (P/N # 9435-23, Ace Glass). Every two hours, fresh  $\text{H}_2\text{O}_2$  solution was added (61 µL of a 10.4 M  $\text{H}_2\text{O}_2$  stock solution). After illumination,

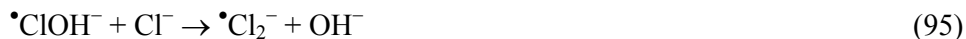
bromide levels were monitored by taking 0.40 mL of illuminated solution from each vessel, adding 5 mg of Oxone (monopersulfate compound (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>), Aldrich) to each aliquot to convert Br<sup>-</sup> to Br<sub>2</sub> and letting the solutions react in the dark for 1.5 hrs. After this, 1.6 mL of Milli-Q water and 2.3 μL of 66 mM AA solution were added, and the mixture was allowed to react for 1 hr, at which time the sample was extracted and analyzed for 3BPD (Matthew and Anastasio, 2000). Although there was a reduction in Br<sup>-</sup> (as indicated by a reduction in the amount of 3BPD formed compared to amounts in untreated chloride), these initial tests revealed that there was still measurable levels of bromide present in the solutions.

The solutions were then illuminated and purged (~1.2 L min<sup>-1</sup>) for an additional 8 hours, illuminated for an additional 11 hours without purging, and then purged for ~ 4 hrs (~1.2 L min<sup>-1</sup>) without illumination. Based on the “Oxone test” described above, there was very little bromide remaining in these treated solutions. To further confirm this, solutions of 0.56 M Cl<sup>-</sup> (treated and untreated), 75 μM AA and 1.0 mM H<sub>2</sub>O<sub>2</sub> were illuminated at pH 5.5 with 313 nm light for 1 hr. The 3BPD peak area was reduced by ~ 60 times in the treated sample compared to the area in the untreated NaCl, indicating that ~ 98% of the Br<sup>-</sup> in the NaCl was removed by treatment. While this treatment removed most of the bromide, further tests would need to be conducted before it could be used on a routine basis.

By comparing the formation rate of 3BPD in untreated 0.56 M chloride solutions (pH 5.5, 75 μM AA, and 1.0 mM H<sub>2</sub>O<sub>2</sub>) to the results described in Part 2, section 3.3.1 (measurements of 3BPD and 3CPD as a function of [Br<sup>-</sup>] in 0.56 M (treated) NaCl solutions), we estimate that the untreated Aldrich NaCl contained ~ 0.007 mol % Br<sup>-</sup>. This is consistent with the value (≤ 0.01 mol % Br<sup>-</sup>) reported by Aldrich. In addition, a similar level of Br<sup>-</sup> (0.011 mol %) has been reported for NaCl from J.T. Baker (Wang et al., 1994). Because of possible changes in the Cl<sup>-</sup> concentration due to evaporation of water or Cl\*(g) (i.e., Cl<sub>2</sub> or HOCl), the concentration of Cl<sup>-</sup> in the treated solutions was measured with ion chromatography (Zhang and Anastasio, 2001). These measurements showed a slight increase in [Cl<sup>-</sup>], indicating that the loss of water was greater than any loss of Cl<sup>-</sup> as Cl<sub>2</sub> or HOCl.

## **S.8 Calculating expected rates of •Cl<sub>2</sub><sup>-</sup> and Cl• formation ( $R_F^{Cl_2^-}$ and $R_F^{Cl}$ )**

The following reactions lead to the formation of •Cl<sub>2</sub><sup>-</sup> in chloride solutions:



The reaction numbers correspond to those in Table S4. In theory,  $R_F^{\text{Cl}_2^-}$  should be the sum of the rates from reactions 95 and 98. However, the net rate of  $\bullet\text{Cl}_2^-$  formation from reaction 98 can be no faster than the rate of formation of  $\text{Cl}^\bullet$  in reaction 97. Furthermore, essentially all of the  $\text{Cl}^\bullet$  formed in reaction 97 is converted to  $\bullet\text{Cl}_2^-$  via reaction 98. Based on this,  $R_F^{\text{Cl}_2^-}$  is written as the sum of the rates from reactions 95 and 97:

$$R_F^{\text{Cl}_2^-} = k_{\text{Cl}^-}^{\text{ClOH}^-} [\text{Cl}^-][\bullet\text{ClOH}^-] + k_{\text{H}^+}^{\text{ClOH}^-} [\bullet\text{ClOH}^-][\text{H}^+] \quad (\text{S36})$$

where  $k_m^n$  is the rate constant for the reaction of species  $m$  with species  $n$ .

Analogous to the case for  $\text{Br}^\bullet$ , all of the  $\text{Cl}^\bullet$  in our system originates from the reaction of  $\bullet\text{OH}$  with  $\text{Cl}^-$  (reaction 94), which means that the rate of formation of  $\text{Cl}^\bullet$  is:

$$R_F^{\text{Cl}^\bullet} = k_{\text{OH}^-}^{\text{Cl}^-} [\bullet\text{OH}][\text{Cl}^-] Y_{\text{OH}^-}^{\text{Cl}^\bullet} \quad (\text{S37})$$

where  $Y_{\text{OH}^-}^{\text{Cl}^\bullet}$  is the yield of  $\text{Cl}^\bullet$  from the reaction of  $\bullet\text{OH}$  with  $\text{Cl}^-$  (see section S.10). The concentrations for the species in equations S36 and S37 are taken directly from the model output produced for a given set of experimental conditions.

### S.9 Calculating the expected rate of $\bullet\text{BrCl}^-$ formation ( $R_F^{\text{BrCl}^-}$ ) for the mixed halide system

Because of rapid equilibria established between the following species,



and the equivalent reactions for  $\text{Cl}^\bullet$  (172 and 189), it is difficult to calculate the formation rate of “new”  $\text{BrCl}^\bullet$  that is separate from the rate of recirculating  $\text{BrCl}^\bullet$  established from these equilibria. To estimate the formation of “new”  $\text{BrCl}^\bullet$  we have used the contributions from 171 and 174:



Based on these reactions,  $R_F^{\text{BrCl}^\bullet}$  is written as:

$$R_F^{\text{BrCl}^\bullet} = k_{\text{BrOH}^\bullet}^{\text{Cl}^-} [\text{BrOH}^\bullet][\text{Cl}^-] + k_{\text{ClOH}^\bullet}^{\text{Br}^-} [\text{ClOH}^\bullet][\text{Br}^-] \quad (\text{S38})$$

As was the case for equations S36 and S37, the concentrations of the species in S38 are obtained directly from the model.

### S.10 Calculation of $Y_{\text{OH}}^{\text{Cl}}$ in chloride solutions

The yield of  $\text{Cl}^\bullet$  from the reaction of  $\text{Cl}^-$  with  $\text{OH}^\bullet$  is based on the fate of  $\text{ClOH}^\bullet$ , which is formed by  $\text{OH}^\bullet$  reacting with  $\text{Cl}^-$  (94) and destroyed via 95-97:



The overall yield of  $\text{Cl}^\bullet$  formed from the reaction of  $\text{OH}^\bullet$  with  $\text{Cl}^-$  ( $Y_{\text{OH}}^{\text{Cl}}$ ) is calculated as the sum of the rates of those reactions that lead to  $\text{Cl}^\bullet$  formation, divided by the total rate of  $\text{ClOH}^\bullet$  loss. Factoring out  $[\text{ClOH}^\bullet]$  from this ratio of rates gives

$$Y_{\text{OH}}^{\text{Cl}} = \frac{k_{\text{ClOH}^\bullet}^{\text{H}^+} [\text{H}^+] + k_{\text{ClOH}^\bullet}^{\text{Cl}^-} [\text{Cl}^-]}{k_{\text{ClOH}^\bullet \rightarrow \text{Cl}^\bullet}^{\text{Cl}^-} + k_{\text{ClOH}^\bullet}^{\text{H}^+} [\text{H}^+] + k_{\text{ClOH}^\bullet}^{\text{Cl}^-} [\text{Cl}^-]} \quad (\text{S39})$$

where  $k_{\rightarrow Cl^-}^{ClOH^-}$  is the first-order rate constant for the dissociation of  $\bullet ClOH^-$  to  $Cl^-$  and  $\bullet OH$  (reaction 96). Reaction 95 must be considered as a source of  $Cl^\bullet$  because  $\bullet Cl_2^-$  establishes a very fast equilibrium with  $Cl^\bullet$  and  $Cl^-$  (reactions 98 and 110, Table S4).

### S.11 Calculation of $Y_{OH}^{Br}$ for the mixed halide system

As discussed in section S.5, the value for  $Y_{OH}^{Br}$ , the yield of  $Br^\bullet$  from the reaction of  $\bullet OH$  with  $Br^-$ , is determined by the fate of  $\bullet BrOH^-$ . In addition to the reactions of  $\bullet BrOH^-$  listed in section S.5, the reaction of  $\bullet BrOH^-$  with  $Cl^-$  to form  $\bullet BrCl^-$  (reaction 174, Table S6) is also a source of  $Br^\bullet$  because the dominant fate of  $\bullet BrCl^-$  is to combine with  $Br^-$  to form  $\bullet Br_2^-$  (reaction 191) or dissociate to yield  $Br^\bullet$  (reaction 190). Using equation S29 from section S.3 as the base equation,  $Y_{OH}^{Br}$  can be rewritten as:

$$Y_{OH}^{Br} = \frac{k_{\rightarrow Br}^{BrOH^-} + k_{BrOH^-}^{H^+} [H^+] + k_{BrOH^-}^{Br^-} [Br^-] + k_{BrOH^-}^{Cl^-} [Cl^-]}{k_{\rightarrow Br^-}^{BrOH^-} + k_{\rightarrow Br}^{BrOH^-} + k_{BrOH^-}^{H^+} [H^+] + k_{BrOH^-}^{Br^-} [Br^-] + k_{BrOH^-}^{Cl^-} [Cl^-]} \quad (S40)$$

where  $k_{\rightarrow Br^-}^{BrOH^-}$  and  $k_{\rightarrow Br}^{BrOH^-}$  are the first-order rate constants for the dissociation of  $\bullet BrOH^-$  into  $Br^- + \bullet OH$  and  $Br^\bullet + OH^-$ , respectively (reactions 35 and 36 in Table S2).

### S.12 Calculation of $F_i^{3XPD}$ in the chloride and mixed halide solutions

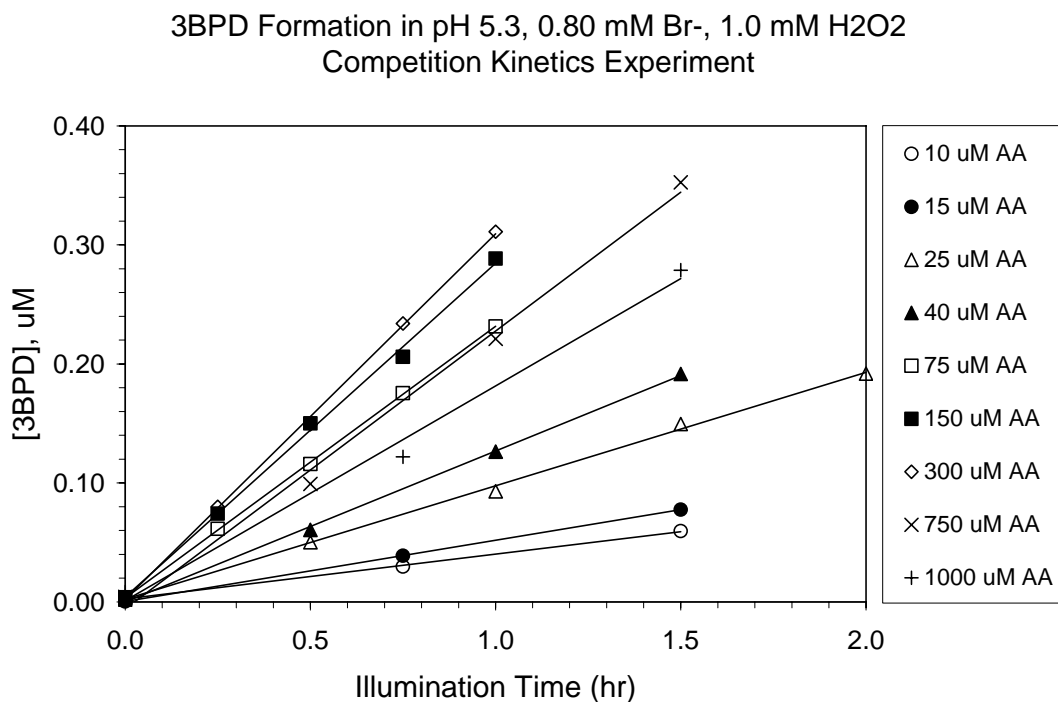
In chloride and mixed halide solutions the fraction of 3XPD (i.e., 3BPD or 3CPD) formed from species  $i$  is calculated as described for bromide solutions (section S.4), except that different species are included in the calculations. In the chloride system the important species are  $\bullet Cl_2^-$  and  $Cl^\bullet$ , while in the mixed halide system the species  $Br^\bullet$ ,  $Br_2$ ,  $\bullet Cl_2^-$ ,  $\bullet BrCl^-$ , and  $BrCl$  are primarily responsible for 3XPD formation. Under other experimental conditions other species might also need to be considered. The general equation for the calculation of  $F_i^{3XPD}$  is

$$F_i^{3XPD} = \frac{R_i^{3XPD}}{R_{F,tot}^{3XPD}} = \frac{k_i^{AA} [i]^n Y_i^{3XPD}}{\sum_i (k_i^{AA} [i]^n Y_i^{3XPD})} \quad (S41)$$

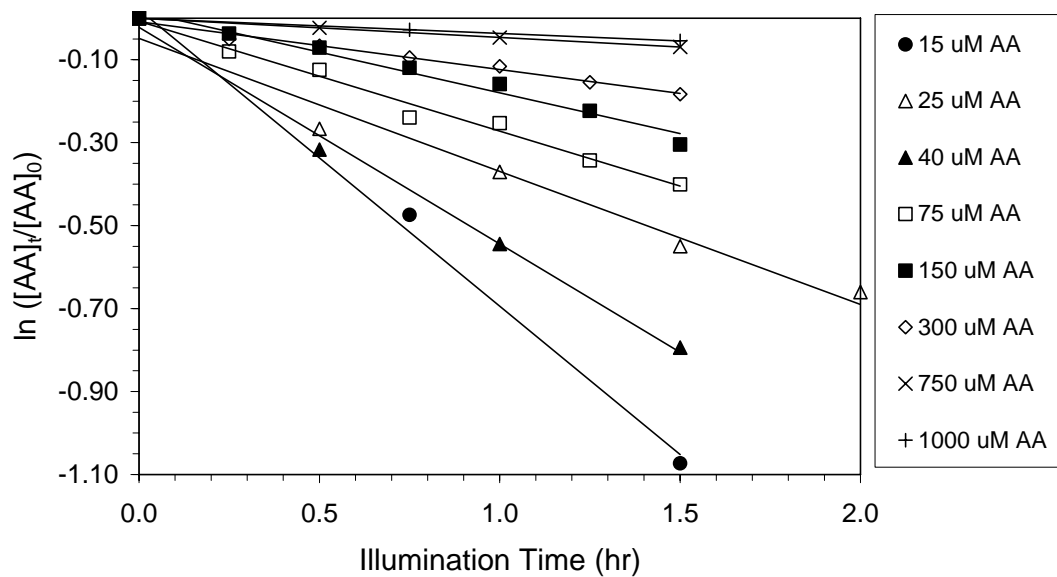
where  $k_i^{AA}$  is the rate constant for reactive halogen species  $i$  reacting with AA,  $Y_i^{3XPD}$  is the yield of 3XPD formed from the reaction of  $i$  with AA, and  $[i]^{ss}$  is the concentration of  $i$  in the presence of AA obtained from the kinetic model. As for  $F_i^{3BPD}$  in the bromide system (section S.4), it is important to note that  $F_i^{3XPD}$  changes as a function pH,  $[Br^-]$ ,  $[Cl^-]$ , and  $[AA]$ .

### S.13 Examples of plots of 3BPD formation and AA loss

The following two figures show examples of the rates of 3BPD formation and allyl alcohol loss in the bromide-only competition kinetics Experiment 1 (pH 5.3, 0.80 mM  $Br^-$ , 1.0 mM  $H_2O_2$ , 10–1000  $\mu M$  AA, 313nm illumination). These are the measurements that were used to construct Figs. 5a and 5b in Part 1. Note that there is no data for allyl alcohol loss at 10  $\mu M$  AA because of problems with this portion of the experiment.



AA Loss in pH 5.3, 0.80 mM Br<sup>-</sup>, 1.0 mM H<sub>2</sub>O<sub>2</sub>  
Competition Kinetics Experiment





**Table S1:** Base reactions for Br<sup>-</sup> Full Model

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	Reference
<i>Photolysis of H<sub>2</sub>O<sub>2</sub> at 313 nm</i>			
1	H <sub>2</sub> O <sub>2</sub> → •OH + •OH	3.1×10 <sup>-6</sup>	Calculated <sup>a</sup>
<i>Non-halogen acid-base equilibria</i>			
2	•O <sub>2</sub> <sup>-</sup> + H <sup>+</sup> → HO <sub>2</sub> •	5.0×10 <sup>10</sup>	(Ross et al., 1998)
3	HO <sub>2</sub> • → •O <sub>2</sub> <sup>-</sup> + H <sup>+</sup>	7.9×10 <sup>5</sup>	Calculated with pKa = 4.8
4	H <sup>+</sup> + OH <sup>-</sup> → H <sub>2</sub> O	1.0×10 <sup>11</sup>	Assumed Diffusion Limited
5	H <sub>2</sub> O → H <sup>+</sup> + OH <sup>-</sup>	1.0×10 <sup>-3</sup>	Calculated with pKw = 14
6	HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> → CO <sub>2</sub>	1.0×10 <sup>10</sup>	Assumed Diffusion Limited
7	CO <sub>2</sub> → H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	5.0×10 <sup>3</sup>	Calculated with pKa = 6.3
8	CO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup> → HCO <sub>3</sub> <sup>-</sup>	5.0×10 <sup>10</sup>	Assumed Diffusion Limited
9	HCO <sub>3</sub> <sup>-</sup> → H <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup>	2.5	Calculated with pKa = 10.3
<i>HO<sub>x</sub>/H<sub>2</sub>O<sub>2</sub> reactions</i>			
10	HO <sub>2</sub> • + •O <sub>2</sub> <sup>-</sup> → HO <sub>2</sub> <sup>-</sup>	9.7×10 <sup>7</sup>	(Ross et al., 1998)
11	HO <sub>2</sub> • + HO <sub>2</sub> • → H <sub>2</sub> O <sub>2</sub>	8.3×10 <sup>5</sup>	(Ross et al., 1998)
12	•OH + •OH → H <sub>2</sub> O <sub>2</sub>	5.5×10 <sup>9</sup>	(Ross et al., 1998)
13	•OH + HO <sub>2</sub> • → H <sub>2</sub> O + O <sub>2</sub>	7.1×10 <sup>9</sup>	(Ross et al., 1998)
14	•OH + •O <sub>2</sub> <sup>-</sup> → OH <sup>-</sup>	1.0×10 <sup>10</sup>	(Ross et al., 1998)
15	H <sub>2</sub> O <sub>2</sub> + •OH → HO <sub>2</sub> •	2.7×10 <sup>7</sup>	(Ross et al., 1998)
16	•OH + HCO <sub>3</sub> <sup>-</sup> → •CO <sub>3</sub> <sup>-</sup>	8.5×10 <sup>6</sup>	(Ross et al., 1998)
17	•OH + CO <sub>2</sub> → •CO <sub>3</sub> <sup>-</sup>	1×10 <sup>6</sup>	(Ross et al., 1998)
18	•OH + CO <sub>3</sub> <sup>2-</sup> → •CO <sub>3</sub> <sup>-</sup> + OH <sup>-</sup>	3.9×10 <sup>8</sup>	(Ross et al., 1998)
19	•CO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → HCO <sub>3</sub> <sup>-</sup> + HO <sub>2</sub> •	4.3×10 <sup>5</sup>	(Ross et al., 1998)
20	•OH + •CO <sub>3</sub> <sup>-</sup> →	3×10 <sup>9</sup>	(Ross et al., 1998)
21	•CO <sub>3</sub> <sup>-</sup> + HO <sub>2</sub> <sup>-</sup> → HCO <sub>3</sub> <sup>-</sup> + •O <sub>2</sub> <sup>-</sup>	3×10 <sup>7</sup>	(Ross et al., 1998)
22	•CO <sub>3</sub> <sup>-</sup> + •O <sub>2</sub> <sup>-</sup> → O <sub>2</sub> + CO <sub>3</sub> <sup>2-</sup>	6.5×10 <sup>8</sup>	(Ross et al., 1998)

<sup>a</sup> Calculated based on an actinic flux (I<sub>313</sub>) measured with 2-nitrobenzaldehyde actinometry using a molar absorptivity for H<sub>2</sub>O<sub>2</sub> at 313 nm of 0.37 M<sup>-1</sup> cm<sup>-1</sup> (T. Arakaki, personal communication). Because photon fluxes vary slightly between experiments, the value of the photolysis rate constant in a given experiment can be slightly different from the typical value listed here. Note that the listed rate constant is the value for the loss of H<sub>2</sub>O<sub>2</sub>. This value needs to be multiplied by a factor of two to calculate the rate of formation of •OH because of the reaction stoichiometry.

**Table S2:** Aqueous phase bromine reactions

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	Reference
<i>Photolysis of bromine species at 313 nm</i>			
23	Br <sub>2</sub> → Br• + Br•	1.5×10 <sup>-5</sup>	Calculated <sup>a</sup>
24	HOBr → Br• + •OH	7.5×10 <sup>-4</sup>	Calculated <sup>a</sup>
<i>Bromine acid-base equilibria</i>			
25	H <sup>+</sup> + Br <sup>-</sup> → HBr	5.0×10 <sup>10</sup>	Assumed Diffusion Limited
26	HBr → H <sup>+</sup> + Br <sup>-</sup>	5.0×10 <sup>19</sup>	Calculated with pKa = -9
27	H <sup>+</sup> + BrO <sup>-</sup> → HOBr	5.0×10 <sup>10</sup>	Assumed Diffusion Limited
28	HOBr → H <sup>+</sup> + BrO <sup>-</sup>	79	Calculated with pKa = 8.8
<i>Bromine aqueous phase reactions</i>			
29	Br <sup>-</sup> + •OH → •BrOH <sup>-</sup>	1.1×10 <sup>10</sup>	(Ross et al., 1998)
30	Br <sup>-</sup> + •BrOH <sup>-</sup> → •Br <sub>2</sub> <sup>-</sup> + OH <sup>-</sup>	1.9×10 <sup>8</sup>	(Zehavi and Rabani, 1972)
31	Br <sup>-</sup> + Br• → •Br <sub>2</sub> <sup>-</sup>	1.5×10 <sup>10</sup>	(Ross et al., 1998) <sup>b</sup>
32	Br <sup>-</sup> + Br <sub>2</sub> → Br <sub>3</sub> <sup>-</sup>	9.6×10 <sup>8</sup>	(Ershov, 2004)
33	Br <sup>-</sup> + HOBr → Br <sub>2</sub> OH <sup>-</sup>	5×10 <sup>9</sup>	(Eigen and Kustin, 1962)
34	Br <sup>-</sup> + •CO <sub>3</sub> <sup>2-</sup> → Br• + CO <sub>3</sub> <sup>2-</sup>	1×10 <sup>5</sup>	(Ross et al., 1998) <sup>c</sup>
35	•BrOH <sup>-</sup> → Br <sup>-</sup> + •OH	3.3×10 <sup>7</sup>	(Zehavi and Rabani, 1972)
36	•BrOH <sup>-</sup> → Br• + OH <sup>-</sup>	4.2×10 <sup>6</sup>	(Zehavi and Rabani, 1972)
37	•BrOH <sup>-</sup> + H <sup>+</sup> → Br• + H <sub>2</sub> O	4.4×10 <sup>10</sup>	(Zehavi and Rabani, 1972)
38	Br• + H <sub>2</sub> O <sub>2</sub> → HBr + HO <sub>2</sub> •	4×10 <sup>9</sup>	(Sutton et al., 1965)
39	Br• + OH <sup>-</sup> → •BrOH <sup>-</sup>	1.3×10 <sup>10</sup>	(Ross et al., 1998)
40	Br• + H <sub>2</sub> O → •BrOH <sup>-</sup> + H <sup>+</sup>	1.4	(Ross et al., 1998)
41	Br• + Br• → Br <sub>2</sub>	1×10 <sup>9</sup>	(Klaning and Wolff, 1985), estimate <sup>d</sup>
42	Br• + HO <sub>2</sub> • → HBr + O <sub>2</sub>	1.6×10 <sup>8</sup>	(Ross et al., 1998)
43	Br• + CO <sub>3</sub> <sup>2-</sup> → Br <sup>-</sup> + •CO <sub>3</sub> <sup>-</sup>	2×10 <sup>6</sup>	Estimated
44	Br• + HCO <sub>3</sub> <sup>-</sup> → Br <sup>-</sup> + •CO <sub>3</sub> <sup>-</sup>	1×10 <sup>6</sup>	Estimated
45	•Br <sub>2</sub> <sup>-</sup> + HO <sub>2</sub> • → Br <sub>2</sub> + HO <sub>2</sub> <sup>-</sup>	4.4×10 <sup>9</sup>	(Matthew et al., 2003)
46	•Br <sub>2</sub> <sup>-</sup> + •OH → HOBr + Br <sup>-</sup>	1×10 <sup>9</sup>	(Wagner and Strehlow, 1987)
47	•Br <sub>2</sub> <sup>-</sup> + •O <sub>2</sub> <sup>-</sup> → 2 Br <sup>-</sup> + O <sub>2</sub>	1.7×10 <sup>8</sup>	(Ross et al., 1998)
48	•Br <sub>2</sub> <sup>-</sup> + OH <sup>-</sup> → •BrOH <sup>-</sup> + Br <sup>-</sup>	2.7×10 <sup>6</sup>	(Mamou et al., 1977)
49	•Br <sub>2</sub> <sup>-</sup> → Br• + Br <sup>-</sup>	6.6×10 <sup>3</sup>	Modeled value <sup>e</sup>
50	•Br <sub>2</sub> <sup>-</sup> + •Br <sub>2</sub> <sup>-</sup> → Br <sub>2</sub> + 2 Br <sup>-</sup>	3.0×10 <sup>9</sup>	(Ershov, 2004)
51	•Br <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → 2 Br <sup>-</sup> + HO <sub>2</sub> • + H <sup>+</sup>	5.0×10 <sup>2</sup>	(Ross et al., 1998) <sup>f</sup>
52	•Br <sub>2</sub> <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup> → •CO <sub>3</sub> <sup>-</sup> + 2 Br <sup>-</sup>	1.1×10 <sup>5</sup>	(Ross et al., 1998)
53	•Br <sub>2</sub> <sup>-</sup> + HCO <sub>3</sub> <sup>-</sup> → •CO <sub>3</sub> <sup>-</sup> + 2 Br <sup>-</sup> + H <sup>+</sup>	8×10 <sup>4</sup>	Estimated
54	Br <sub>3</sub> <sup>-</sup> + HO <sub>2</sub> • → •Br <sub>2</sub> <sup>-</sup> + HBr + O <sub>2</sub>	1×10 <sup>7</sup>	(Ross et al., 1998)
55	Br <sub>3</sub> <sup>-</sup> + •O <sub>2</sub> <sup>-</sup> → •Br <sub>2</sub> <sup>-</sup> + Br <sup>-</sup> + O <sub>2</sub>	3.8×10 <sup>9</sup>	(Ross et al., 1998)
56	Br <sub>3</sub> <sup>-</sup> → Br <sub>2</sub> + Br <sup>-</sup>	5.5×10 <sup>7</sup>	(Ershov, 2004)
57	Br <sub>2</sub> + •O <sub>2</sub> <sup>-</sup> → •Br <sub>2</sub> <sup>-</sup> + O <sub>2</sub>	5.6×10 <sup>9</sup>	(Ross et al., 1998)
58	Br <sub>2</sub> + HO <sub>2</sub> • → •Br <sub>2</sub> <sup>-</sup> + H <sup>+</sup> + O <sub>2</sub>	1.1×10 <sup>8</sup>	(Ross et al., 1998)
59	Br <sub>2</sub> + H <sub>2</sub> O → Br <sub>2</sub> OH <sup>-</sup> + H <sup>+</sup>	97	(Beckwith et al., 1996)
60	Br <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> → 2 HBr + O <sub>2</sub>	1.3×10 <sup>3</sup>	(Wagner and Strehlow, 1987)
61	Br <sub>2</sub> OH <sup>-</sup> + H <sup>+</sup> → Br <sub>2</sub> + H <sub>2</sub> O	2×10 <sup>10</sup>	(Eigen and Kustin, 1962)
62	Br <sub>2</sub> OH <sup>-</sup> → HOBr + Br <sup>-</sup>	5×10 <sup>9</sup>	(Eigen and Kustin, 1962)
63	HOBr + •OH → BrO• + H <sub>2</sub> O	2.0×10 <sup>9</sup>	(Ross et al., 1998)
64	HOBr + •O <sub>2</sub> <sup>-</sup> → BrOH <sup>-</sup>	3.5×10 <sup>9</sup>	(Ross et al., 1998)
65	HOBr + HO <sub>2</sub> • → BrOH <sup>-</sup> + H <sup>+</sup>	3.5×10 <sup>9</sup>	Estimated

**Table S2 (continued)**

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	Reference
<i>Bromine aqueous phase reactions (continued)</i>			
66	HOBr + H <sub>2</sub> O <sub>2</sub> → HBr + H <sub>2</sub> O + O <sub>2</sub>	3.5×10 <sup>4</sup>	(Young, 1950)
67	BrO <sup>-</sup> + •OH → BrO• + OH <sup>-</sup>	4.5×10 <sup>9</sup>	(Ross et al., 1998)
68	BrO <sup>-</sup> + •O <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O → Br• + 2 OH <sup>-</sup> + O <sub>2</sub>	2×10 <sup>8</sup>	(Ross et al., 1998) <sup>g</sup>
69	BrO <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → Br <sup>-</sup> + H <sub>2</sub> O + O <sub>2</sub>	2×10 <sup>5</sup>	Estimated <sup>h</sup>

The concentration of water has been included in all rate constants for reactions where water is a reactant. All estimated rate constants were done so in this work unless otherwise noted.

<sup>a</sup> Calculated based on I<sub>313</sub> measured with 2-nitrobenzaldehyde actinometry using molar absorptivities at 313 nm from Finlayson-Pitts and Pitts (2000) of Br<sub>2</sub> = 0.34 M<sup>-1</sup> cm<sup>-1</sup> and HOBr = 33.0 M<sup>-1</sup> cm<sup>-1</sup>

<sup>b</sup> Reported value (1.2×10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>) was adjusted slightly to better fit our experimental data.

<sup>c</sup> Reported value < 5.0×10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>

<sup>d</sup> Reactions and estimated rate constants suggested by Klaning and Wolff (1985)

<sup>e</sup> Modeled value. The following values have been suggested: 1.9×10<sup>4</sup> s<sup>-1</sup> (Merenyi and Lind, 1994) and 640 – 3200 s<sup>-1</sup> (Sutton et al., 1965).

<sup>f</sup> Reported as < 1.0×10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup>

<sup>g</sup> In the original paper (Schwartz and Bielski, 1986), the reaction is written as BrO<sup>-</sup> + •O<sub>2</sub><sup>-</sup> + Br<sup>-</sup> + H<sub>2</sub>O → •Br<sub>2</sub><sup>-</sup> + 2 OH<sup>-</sup> + O<sub>2</sub> with a second-order rate constant of < 2×10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>. We have assumed that the reaction occurs as written in reaction 68 to form Br• at the reported upper bound rate constant followed by reaction of Br• with Br<sup>-</sup> (reaction 31) to form •Br<sub>2</sub><sup>-</sup>.

<sup>h</sup> Value estimated by R. Song, personal communication.

**Table S3:** Reactions of  $\bullet\text{OH}$ ,  $\bullet\text{CO}_3^-$ , and reactive bromide ( $\text{Br}^*(\text{aq})$ ) with allyl alcohol (AA)

Rxn #	Reaction	Rate constant ( $\text{M}^{-1} \text{s}^{-1}$ )	Reference
<i>Reactions of <math>\bullet\text{OH}</math> and <math>\bullet\text{CO}_3^-</math> with AA</i>			
70	$\bullet\text{OH} + \text{AA} \rightarrow \text{AAOHR}$	$7.5 \times 10^9$	(Ross et al., 1998) <sup>a</sup>
71	$\text{AA} + \text{AAOHR} \rightarrow \text{AAOH1}$	2.5	Modeled <sup>b</sup>
72	$\text{AA} + \text{AAOH1} \rightarrow \text{AAOH2}$	0.5	Modeled <sup>b</sup>
73	$\text{AA} + \text{AAOH2} \rightarrow \text{AAOH3}$	0.5	Modeled <sup>b</sup>
74	$\bullet\text{CO}_3^- + \text{AA} \rightarrow \text{CO3AA}$	$2.9 \times 10^5$	(Ross et al., 1998)
<i>Reactions of reactive bromide with AA</i>			
75	$\text{Br}^* + \text{AA} \rightarrow 3\text{BPD}$	$5.2 \times 10^8$	(Guha et al., 1993) <sup>c</sup>
76	$\text{Br}^* + \text{AA} \rightarrow \text{BrAA}$	$3.4 \times 10^9$	(Guha et al., 1993) <sup>c</sup>
77	$\text{AA} + \text{BrAA} \rightarrow \text{BrAA1}$	7	Modeled <sup>b</sup>
78	$\text{AA} + \text{BrAA1} \rightarrow \text{BrAA2}$	7	Modeled <sup>b</sup>
79	$\text{AA} + \text{BrAA2} \rightarrow \text{BrAA3}$	7	Modeled <sup>b</sup>
80	$\bullet\text{Br}_2^- + \text{AA} \rightarrow 3\text{BPD} + \text{Br}^-$	$2.1 \times 10^2$	(Ross et al., 1998) <sup>d</sup>
81	$\bullet\text{Br}_2^- + \text{AA} \rightarrow \text{Br2AA1} + \text{Br}^-$	$1.8 \times 10^3$	(Ross et al., 1998) <sup>d</sup>
82	$\text{Br}_2 + \text{AA} \rightarrow 3\text{BPD} + \text{Br}^*$	$5.1 \times 10^5$	(Atkinson and Bell, 1963) <sup>e</sup>
83	$\text{Br}_2 + \text{AA} \rightarrow \text{Br2AA} + \text{Br}^*$	$1.6 \times 10^5$	(Atkinson and Bell, 1963) <sup>e</sup>
84	$\text{HOBr} + \text{AA} \rightarrow 3\text{BPD}$	$5.1 \times 10^5$	Assumed $k_{84} = k_{82}^f$
85	$\text{HOBr} + \text{AA} \rightarrow \text{Br2AA}$	$1.6 \times 10^5$	Assumed $k_{85} = k_{83}^f$
86	$\text{Br}_3^- + \text{AA} \rightarrow 3\text{BPD} + \bullet\text{Br}_2^-$	$5.2 \times 10^4$	(Atkinson and Bell, 1963) <sup>g</sup>
87	$\text{Br}_3^- + \text{AA} \rightarrow \text{Br2AA} + \bullet\text{Br}_2^-$	$1.6 \times 10^4$	(Atkinson and Bell, 1963) <sup>g</sup>

<sup>a</sup> Reported value =  $(6.0 \pm 1.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$

<sup>b</sup> Reactions added to account for the radical-initiated polymerization of allyl alcohol with rate constants estimated from model fits to the experimental data.

<sup>c</sup> The sum of  $k_{75}$  and  $k_{76}$  was set equal to the reported rate constant for the reaction of  $\text{Br}^*$  with oleic acid of  $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Guha et al., 1993). The yield of 3BPD from the reaction of  $\text{Br}^*$  with AA (i.e.,  $k_{75}/(k_{75}+k_{76})$ ) is 0.13, and was estimated by fitting the model to experimental data.

<sup>d</sup> The sum of  $k_{80}$  and  $k_{81}$  was set equal to the reported upper bound rate constant for the reaction of  $\bullet\text{Br}_2^-$  with allyl alcohol of  $2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  (Ross et al., 1998). The yield of 3BPD from the reaction of  $\bullet\text{Br}_2^-$  with AA (i.e.,  $k_{80}/(k_{80}+k_{81})$ ) was assumed to be 0.1 based on the yield for  $\bullet\text{Cl}_2^-$  with AA (Part 2, section 2.2). Because  $\bullet\text{Br}_2^-$  is never an important source of 3BPD for our experimental conditions, this yield value is a rough estimate and is not constrained by experimental data.

<sup>e</sup> The sum of  $k_{82}$  and  $k_{83}$  was set equal to the reported rate constant for the reaction of  $\text{Br}_2$  with allyl alcohol of  $6.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  (Atkinson and Bell, 1963). The yield of 3BPD from the reaction of  $\text{Br}_2$  with AA (0.76) was assumed to be the same as for HOBr.

<sup>f</sup> Values for  $k_{84}$  and  $k_{85}$  were assumed to be the same as the analogous values for the reaction of  $\text{Br}_2$  with AA (reactions 82 and 83). The yield of 3BPD from the reaction of HOBr with AA (i.e.,  $k_{84}/(k_{84}+k_{85})$ ) was estimated to be 0.76 based on the yield of product formed from the reaction of HOBr with propene in aqueous solution (Loudon, 1988) and HOCl with AA in water (De La Mare and Pritchard, 1954).

<sup>g</sup> The sum of  $k_{86}$  and  $k_{87}$  was set equal to the reported rate constant for the reaction of  $\text{Br}_3^-$  with allyl alcohol of  $6.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (Atkinson and Bell, 1963). The yield of 3BPD from the reaction of  $\text{Br}_3^-$  with AA (0.76) was assumed to be the same as the yield from the reaction of  $\text{Br}_2$ . Because  $\text{Br}_3^-$  is never an important source of 3BPD for our experimental conditions, this yield value is a rough estimate that is not constrained by experimental data.

**Table S4** Chloride reactions

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	Reference
<i>Photolysis reactions at 313 nm</i>			
88	Cl <sub>2</sub> → Cl <sup>•</sup> + Cl <sup>•</sup>	2.3×10 <sup>-3</sup>	Calculated <sup>a</sup>
89	HOCl → <sup>•</sup> OH + Cl <sup>•</sup>	3.3×10 <sup>-4</sup>	Calculated <sup>a</sup>
<i>Acid-base equilibria</i>			
90	H <sup>+</sup> + Cl <sup>-</sup> → HCl	5.0×10 <sup>10</sup>	Assumed Diffusion Limited
91	HCl → H <sup>+</sup> + Cl <sup>-</sup>	8.6×10 <sup>16</sup>	Calculated with pKa = -6.24
92	H <sup>+</sup> + ClO <sup>-</sup> → HOCl	5.0×10 <sup>10</sup>	Assumed Diffusion Limited
93	HOCl → H <sup>+</sup> + ClO <sup>-</sup>	1.6×10 <sup>3</sup>	Calculated with pKa = 7.5
<i>Chlorine reactions</i>			
94	Cl <sup>-</sup> + <sup>•</sup> OH → <sup>•</sup> ClOH <sup>-</sup>	4.3×10 <sup>9</sup>	(Ross et al., 1998)
95	<sup>•</sup> ClOH <sup>-</sup> + Cl <sup>-</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + OH <sup>-</sup>	1×10 <sup>5</sup>	(Grigor'ev et al., 1987) <sup>b</sup>
96	<sup>•</sup> ClOH <sup>-</sup> → Cl <sup>-</sup> + <sup>•</sup> OH	6.1×10 <sup>9</sup>	(Jayson et al., 1973)
97	<sup>•</sup> ClOH <sup>-</sup> + H <sup>+</sup> → Cl <sup>•</sup> + H <sub>2</sub> O	2.1×10 <sup>10</sup>	(Jayson et al., 1973)
98	Cl <sup>-</sup> + Cl <sup>•</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup>	6.5×10 <sup>9</sup>	(Klaning and Wolff, 1985)
99	Cl <sup>-</sup> + Cl <sub>2</sub> → Cl <sub>3</sub> <sup>-</sup>	2×10 <sup>4</sup>	(Ershov, 2004)
100	Cl <sup>-</sup> + HOCl → Cl <sub>2</sub> OH <sup>-</sup>	1.5×10 <sup>4</sup>	(Wang and Margerum, 1994)
101	Cl <sup>•</sup> + H <sub>2</sub> O <sub>2</sub> → HCl + HO <sub>2</sub> <sup>•</sup>	4×10 <sup>9</sup>	Estimated
102	Cl <sup>•</sup> + OH <sup>-</sup> → <sup>•</sup> ClOH <sup>-</sup>	1.8×10 <sup>10</sup>	(Klaning and Wolff, 1985)
103	Cl <sup>•</sup> + Cl <sup>•</sup> → Cl <sub>2</sub>	1×10 <sup>8</sup>	(Wu et al., 1980)
104	Cl <sup>•</sup> + H <sub>2</sub> O → HClOH	2.5×10 <sup>5</sup>	(McElroy, 1990)
105	Cl <sup>•</sup> + CO <sub>3</sub> <sup>2-</sup> → <sup>•</sup> CO <sub>3</sub> <sup>-</sup> + Cl <sup>-</sup>	5×10 <sup>8</sup>	(Ross et al., 1998)
106	Cl <sup>•</sup> + HCO <sub>3</sub> <sup>-</sup> → <sup>•</sup> CO <sub>3</sub> <sup>-</sup> + HCl	2.2×10 <sup>8</sup>	(Ross et al., 1998)
107	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + HO <sub>2</sub> <sup>•</sup> → 2 Cl <sup>-</sup> + H <sup>+</sup> + O <sub>2</sub>	3×10 <sup>9</sup>	(Ross et al., 1998)
108	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + <sup>•</sup> O <sub>2</sub> <sup>-</sup> → 2 Cl <sup>-</sup> + O <sub>2</sub>	1.0×10 <sup>9</sup>	(Ross et al., 1998)
109	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + OH <sup>-</sup> → <sup>•</sup> ClOH <sup>-</sup> + Cl <sup>-</sup>	4.5×10 <sup>7</sup>	(Grigor'ev et al., 1987)
110	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> → Cl <sup>•</sup> + Cl <sup>-</sup>	1.1×10 <sup>5</sup>	(Jayson et al., 1973)
111	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> → Cl <sub>2</sub> + 2 Cl <sup>-</sup>	8.3×10 <sup>8</sup>	(Ross et al., 1998)
112	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → 2 Cl <sup>-</sup> + HO <sub>2</sub> <sup>•</sup> + H <sup>+</sup>	1.4×10 <sup>5</sup>	(Ross et al., 1998)
113	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O → HClOH + Cl <sup>-</sup>	1.3×10 <sup>3</sup>	(McElroy, 1990)
114	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + <sup>•</sup> OH → HOCl + Cl <sup>-</sup>	1×10 <sup>9</sup>	(Ross et al., 1998)
115	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + HCO <sub>3</sub> <sup>-</sup> → 2 Cl <sup>-</sup> + H <sup>+</sup> + <sup>•</sup> CO <sub>3</sub> <sup>-</sup>	8×10 <sup>7</sup>	Estimated
116	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup> → 2 Cl <sup>-</sup> + <sup>•</sup> CO <sub>3</sub> <sup>-</sup>	1.6×10 <sup>8</sup>	Estimated
117	HClOH → <sup>•</sup> ClOH <sup>-</sup> + H <sup>+</sup>	1×10 <sup>8</sup>	(McElroy, 1990)
118	HClOH → Cl <sup>•</sup> + H <sub>2</sub> O	100	(McElroy, 1990) <sup>c</sup>
119	HClOH + Cl <sup>-</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O	5×10 <sup>9</sup>	(McElroy, 1990)
120	Cl <sub>3</sub> <sup>-</sup> + HO <sub>2</sub> <sup>•</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + HCl + O <sub>2</sub>	1×10 <sup>9</sup>	(Bjergbakke et al., 1981)
121	Cl <sub>3</sub> <sup>-</sup> + <sup>•</sup> O <sub>2</sub> <sup>-</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + Cl <sup>-</sup> + O <sub>2</sub>	3.8×10 <sup>9</sup>	Estimated
122	Cl <sub>3</sub> <sup>-</sup> → Cl <sub>2</sub> + Cl <sup>-</sup>	1.1×10 <sup>5</sup>	(Ershov, 2004)
123	Cl <sub>2</sub> + <sup>•</sup> O <sub>2</sub> <sup>-</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + O <sub>2</sub>	1×10 <sup>9</sup>	Estimated
124	Cl <sub>2</sub> + HO <sub>2</sub> <sup>•</sup> → <sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + H <sup>+</sup> + O <sub>2</sub>	1×10 <sup>9</sup>	(Bjergbakke et al., 1981)

**Table S4 (continued)**

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	Reference
<i>Chlorine reactions (continued)</i>			
125	Cl <sub>2</sub> + H <sub>2</sub> O → Cl <sub>2</sub> OH <sup>-</sup> + H <sup>+</sup>	15	(Wang and Margerum, 1994)
126	Cl <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> → 2 HCl + O <sub>2</sub>	1.3×10 <sup>4</sup>	Estimated
127	Cl <sub>2</sub> OH <sup>-</sup> + H <sup>+</sup> → Cl <sub>2</sub> + H <sub>2</sub> O	2×10 <sup>10</sup>	Estimated
128	Cl <sub>2</sub> OH <sup>-</sup> → HOCl + Cl <sup>-</sup>	5.5×10 <sup>9</sup>	(Wang and Margerum, 1994)
129	HOCl + •OH → ClO• + H <sub>2</sub> O	2.0×10 <sup>9</sup>	Estimated
130	HOCl + •O <sub>2</sub> <sup>-</sup> → Cl• + OH <sup>-</sup> + O <sub>2</sub>	7.5×10 <sup>6</sup>	(Long and Bielski, 1980)
131	HOCl + HO <sub>2</sub> • → Cl• + OH <sup>-</sup> + O <sub>2</sub>	7.5×10 <sup>6</sup>	Estimated
132	HOCl + H <sub>2</sub> O <sub>2</sub> → HCl + H <sub>2</sub> O + O <sub>2</sub>	1.1×10 <sup>4</sup>	(Connick, 1947)
133	ClO <sup>-</sup> + •OH → ClO• + OH <sup>-</sup>	8.8×10 <sup>9</sup>	(Buxton and Subhani, 1972)
134	ClO <sup>-</sup> + •O <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O → Cl• + 2 OH <sup>-</sup> + O <sub>2</sub>	2×10 <sup>8</sup>	Estimated
135	ClO <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → Cl <sup>-</sup> + H <sub>2</sub> O + O <sub>2</sub>	1.7×10 <sup>5</sup>	(Connick, 1947)

The concentration of water has been included in all rate constants for reactions where water is a reactant. All estimated rate constants were done so in this work unless otherwise noted.

<sup>a</sup> Calculated based on I<sub>313</sub> measured with 2-nitrobenzaldehyde actinometry using molar absorptivities at 313 nm (M<sup>-1</sup> cm<sup>-1</sup>) of 51.9 (Cl<sub>2</sub>) and 14.8 (HOCl) (Finlayson-Pitts and Pitts, 2000).

<sup>b</sup> Modeled value. Reported rate constants (M<sup>-1</sup> s<sup>-1</sup>) are a function of [Cl<sup>-</sup>]: 1.0×10<sup>4</sup> at 1.2 M Cl<sup>-</sup>, 2.4×10<sup>4</sup> at 3.5 M Cl<sup>-</sup>, 1.9×10<sup>5</sup> at 6.8 M Cl<sup>-</sup>, and 2.5×10<sup>5</sup> at 10.1 M.

<sup>c</sup> Reported value < 1.0×10<sup>3</sup> s<sup>-1</sup>

**Table S5** Reactions of reactive chloride and mixed halide species with allyl alcohol (AA).

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> )	Reference
<i>Reactions of reactive chloride with allyl alcohol</i>			
136	Cl <sup>•</sup> + AA → 3CPD	9.0×10 <sup>8</sup>	Modeled <sup>a</sup>
137	Cl <sup>•</sup> + AA → CIAA	3.0×10 <sup>9</sup>	Modeled <sup>a</sup>
138	Cl <sub>2</sub> + AA → 3CPD + Cl <sup>•</sup>	1×10 <sup>7</sup>	Estimated <sup>b</sup>
139	Cl <sub>2</sub> + AA → CIAA2 + Cl <sup>•</sup>	1×10 <sup>8</sup>	Estimated <sup>b</sup>
140	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + AA → 3CPD + Cl <sup>-</sup>	4.7×10 <sup>6</sup>	(Padmaja et al., 1992) <sup>c</sup>
141	<sup>•</sup> Cl <sub>2</sub> <sup>-</sup> + AA → CIAA2 + Cl <sup>-</sup>	4.5×10 <sup>7</sup>	(Padmaja et al., 1992) <sup>c</sup>
142	AA + CIAA → CIAA1	5.5	Modeled <sup>d</sup>
143	AA + CIAA1 → CIAA2	5.5	Modeled <sup>d</sup>
144	AA + CIAA2 → CIAA3	5.5	Modeled <sup>d</sup>
145	HOCl + AA → 3CPD	5.4×10 <sup>5</sup>	Estimated <sup>e</sup>
146	HOCl + AA → Cl <sub>2</sub> AA2	1.7×10 <sup>5</sup>	Estimated <sup>e</sup>
<i>Reactions of reactive mixed halogen species with AA</i>			
147	BrCl + AA → 3BPD + Cl <sup>•</sup>	5×10 <sup>7</sup>	Modeled <sup>f</sup>
148	BrCl + AA → 3CPD + Br <sup>•</sup>	5×10 <sup>3</sup>	Estimated <sup>f</sup>
149	BrCl + AA → AA4	2×10 <sup>7</sup>	Modeled <sup>f</sup>
150	<sup>•</sup> BrCl <sup>-</sup> + AA → 3BPD + Cl <sup>-</sup>	1.7×10 <sup>6</sup>	Modeled <sup>g</sup>
151	<sup>•</sup> BrCl <sup>-</sup> + AA → 3CPD + Br <sup>-</sup>	6.8×10 <sup>4</sup>	Modeled <sup>g</sup>
152	<sup>•</sup> BrCl <sup>-</sup> + AA → AA1	2×10 <sup>7</sup>	Modeled <sup>g</sup>
153	AA1 + AA → AA2	1	Modeled <sup>d</sup>

Modeled rate constants were estimated by adjusting the model values (Cl<sup>-</sup> Full Model for Cl<sup>•</sup>(aq) reactions and Mix Full Model for reactions 147 – 153) to fit the experimental data.

- <sup>a</sup> The overall rate constant for the reaction of Cl<sup>•</sup> with allyl alcohol is assumed to be the same as that for Br<sup>•</sup> (i.e., the sum of  $k_{136}$  and  $k_{137}$  is equal to the reported  $k$  for Br<sup>•</sup> with oleic acid; see reactions 75 and 76 in Table S3). The yield of 3CPD from the reaction of Cl<sup>•</sup> with AA was assumed to be ~0.2. Because Cl<sup>•</sup> is never an important source of 3CPD, this yield value is a rough estimate, and is not constrained by experimental data.
- <sup>b</sup> Estimated values. Because Cl<sub>2</sub> is never an important source of 3CPD in our experiments, the rate constants and 3CPD yield (0.091) are not well constrained by experimental data.
- <sup>c</sup> Sum of  $k_{140}$  and  $k_{141}$  is equal to the reported total rate constant for reaction of <sup>•</sup>Cl<sub>2</sub><sup>-</sup> with allyl alcohol of 5.0×10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> (Padmaja et al., 1992). The yield of 3CPD from the reaction of <sup>•</sup>Cl<sub>2</sub><sup>-</sup> with AA (i.e.,  $k_{140}/(k_{140}+k_{141})$ ) is 0.095, and was estimated by fitting the model to the experimental data.
- <sup>d</sup> Used to account for the radical-initiated polymerization of allyl alcohol (Part 1, section 3.1).
- <sup>e</sup> Rate constants are based on reactions of HOBr with allyl alcohol (reactions 84 and 85, Table S3) and a reported yield of 3CPD from HOCl with AA of 0.76 (De La Mare and Pritchard, 1954). Because HOCl is not an important source of 3CPD in our experiments these values are not constrained by our modeling.
- <sup>f</sup> Rate constants for reactions 147-149 and yields of 3BPD and 3CPD from the reaction of BrCl with AA (0.71 and ~7×10<sup>-5</sup>) were estimated by fitting models to the experimental data. Since BrCl is minor source of 3CPD in our experiments, the value for  $k_{148}$  is not well constrained.
- <sup>g</sup> Rate constants for reactions 150 - 153 and the yields of 3CPD (0.0031) and 3BPD (see below) from the reaction of <sup>•</sup>BrCl<sup>-</sup> with AA were estimated by fitting models to experimental data. The 3BPD yield is a function of pH: 0.078 at pH ≤ 5.5, 0 at pH ≥ 6.5 (where reaction 150 was treated as <sup>•</sup>BrCl<sup>-</sup> + AA → Br<sup>-</sup> + Cl<sup>-</sup>), and varying linearly between these pH values. Values for  $k_{151}$  and  $k_{152}$  were independent of pH.

**Table S6** Known and proposed mixed halide reactions.

Rxn #	Reaction	Rate constant (M <sup>-1</sup> s <sup>-1</sup> or s <sup>-1</sup> )	Reference
<i>Photolysis reactions at 313 nm</i>			
154	BrCl → Br• + Cl•	8.4×10 <sup>-5</sup>	Calculated <sup>a</sup>
<i>Known mixed halide chemistry</i>			
155	Cl <sup>-</sup> + HOBr + H <sup>+</sup> → BrCl + H <sub>2</sub> O	5.6×10 <sup>9</sup> [H <sup>+</sup> ]	(Sander et al., 1997)
156	Br <sup>-</sup> + HOCl + H <sup>+</sup> → BrCl + H <sub>2</sub> O	1.3×10 <sup>6</sup> [H <sup>+</sup> ]	(Sander et al., 1997)
157	BrCl + H <sub>2</sub> O → HOBr + Cl <sup>-</sup> + H <sup>+</sup>	1.0×10 <sup>5</sup>	(Michalowski et al., 2000)
158	BrCl + H <sub>2</sub> O <sub>2</sub> → HBr + HCl + O <sub>2</sub>	1.3×10 <sup>4</sup>	Estimated
159	BrCl + •O <sub>2</sub> <sup>-</sup> → •BrCl <sup>-</sup> + O <sub>2</sub>	4×10 <sup>9</sup>	Estimated
160	BrCl + HO <sub>2</sub> • → •BrCl <sup>-</sup> + O <sub>2</sub> + H <sup>+</sup>	5×10 <sup>8</sup>	Estimated
161	BrCl + Cl <sup>-</sup> → BrCl <sub>2</sub> <sup>-</sup>	1.0×10 <sup>6</sup>	(Ershov, 2004)
162	BrCl <sub>2</sub> <sup>-</sup> → BrCl + Cl <sup>-</sup>	1.7×10 <sup>5</sup>	(Ershov, 2004)
163	BrCl + Br <sup>-</sup> → Br <sub>2</sub> Cl <sup>-</sup>	3.0×10 <sup>8</sup>	Estimated
164	Br <sub>2</sub> Cl <sup>-</sup> → BrCl + Br <sup>-</sup>	1.7×10 <sup>4</sup>	Estimated <sup>b</sup>
165	Br <sub>2</sub> + Cl <sup>-</sup> → Br <sub>2</sub> Cl <sup>-</sup>	5.0×10 <sup>4</sup>	Estimated
166	Br <sub>2</sub> Cl <sup>-</sup> → Br <sub>2</sub> + Cl <sup>-</sup>	3.8×10 <sup>4</sup>	Estimated <sup>c</sup>
167	Cl <sub>2</sub> + Br <sup>-</sup> → BrCl <sub>2</sub> <sup>-</sup>	6.0×10 <sup>9</sup>	(Ershov, 2004)
168	BrCl <sub>2</sub> <sup>-</sup> → Cl <sub>2</sub> + Br <sup>-</sup>	9.0×10 <sup>3</sup>	(Ershov, 2004)
169	Br <sub>2</sub> Cl <sup>-</sup> + Cl <sup>-</sup> → BrCl <sub>2</sub> <sup>-</sup> + Br <sup>-</sup>	1.0×10 <sup>5</sup>	Estimated <sup>d</sup>
170	BrCl <sub>2</sub> <sup>-</sup> + Br <sup>-</sup> → Br <sub>2</sub> Cl <sup>-</sup> + Cl <sup>-</sup>	3.0×10 <sup>8</sup>	(Ershov, 2004)
<i>Proposed mixed halide radical reactions</i>			
171	•ClOH + Br <sup>-</sup> → •BrCl <sup>-</sup> + OH <sup>-</sup>	1×10 <sup>9</sup>	Estimated <sup>e</sup>
172	Cl <sup>•</sup> + Br <sup>-</sup> → •BrCl <sup>-</sup>	1.2×10 <sup>10</sup>	(Donati, 2002)
173	•Cl <sub>2</sub> <sup>-</sup> + Br <sup>-</sup> → •BrCl <sup>-</sup> + Cl <sup>-</sup>	4.0×10 <sup>9</sup>	(Ershov, 2004)
174	•BrOH + Cl <sup>-</sup> → •BrCl <sup>-</sup> + OH <sup>-</sup>	1.9×10 <sup>8</sup>	Estimated <sup>e</sup>
175	Br <sup>•</sup> + Cl <sup>-</sup> → •BrCl <sup>-</sup>	1×10 <sup>8</sup>	(Donati, 2002) <sup>f</sup>
176	•Br <sub>2</sub> <sup>-</sup> + Cl <sup>-</sup> → •BrCl <sup>-</sup> + Br <sup>-</sup>	4.3×10 <sup>6</sup>	(Ershov, 2004)
177	•Br <sub>2</sub> <sup>-</sup> + •Cl <sub>2</sub> <sup>-</sup> → Br <sub>2</sub> + 2 Cl <sup>-</sup>	4×10 <sup>9</sup>	Estimated <sup>e</sup>
178	•BrCl <sup>-</sup> + •OH → BrCl + OH <sup>-</sup>	1×10 <sup>9</sup>	Estimated <sup>e</sup>
179	•BrCl <sup>-</sup> + HO <sub>2</sub> • → Br <sup>-</sup> + Cl <sup>-</sup> + O <sub>2</sub>	1×10 <sup>9</sup>	Estimated <sup>e</sup>
180	•BrCl <sup>-</sup> + •O <sub>2</sub> <sup>-</sup> → Br <sup>-</sup> + Cl <sup>-</sup> + O <sub>2</sub>	6×10 <sup>8</sup>	Estimated <sup>e</sup>
181	•BrCl <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → HO <sub>2</sub> • + Br <sup>-</sup> + Cl <sup>-</sup> + H <sup>+</sup>	5×10 <sup>3</sup>	Estimated <sup>e</sup>
182	•BrCl <sup>-</sup> + OH <sup>-</sup> → •ClOH + Br <sup>-</sup>	3×10 <sup>6</sup>	Estimated <sup>e</sup>
183	•BrCl <sup>-</sup> + OH <sup>-</sup> → •BrOH + Cl <sup>-</sup>	2×10 <sup>7</sup>	Estimated <sup>e</sup>
184	•BrCl <sup>-</sup> + HCO <sub>3</sub> <sup>-</sup> → Br <sup>-</sup> + Cl <sup>-</sup> + H <sup>+</sup> + •CO <sub>3</sub> <sup>-</sup>	3×10 <sup>6</sup>	Estimated <sup>e</sup>
185	•BrCl <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup> → Br <sup>-</sup> + Cl <sup>-</sup> + •CO <sub>3</sub> <sup>-</sup>	6×10 <sup>6</sup>	Estimated <sup>e</sup>
186	•BrCl <sup>-</sup> + •BrCl <sup>-</sup> → BrCl + Br <sup>-</sup> + Cl <sup>-</sup>	4.7×10 <sup>9</sup>	(Donati, 2002)
187	•BrCl <sup>-</sup> + •Cl <sub>2</sub> <sup>-</sup> → 2 Cl <sup>-</sup> + BrCl	2×10 <sup>9</sup>	Estimated <sup>e</sup>
188	•BrCl <sup>-</sup> + •Br <sub>2</sub> <sup>-</sup> → Br <sub>2</sub> + Br <sup>-</sup> + Cl <sup>-</sup>	4×10 <sup>9</sup>	Estimated <sup>e</sup>
189	•BrCl <sup>-</sup> → Cl <sup>•</sup> + Br <sup>-</sup>	1.9×10 <sup>3</sup>	(Donati, 2002)
190	•BrCl <sup>-</sup> → Br <sup>•</sup> + Cl <sup>-</sup>	6.1×10 <sup>4</sup>	(Donati, 2002)
191	•BrCl <sup>-</sup> + Br <sup>-</sup> → •Br <sub>2</sub> <sup>-</sup> + Cl <sup>-</sup>	8.0×10 <sup>9</sup>	(Ershov, 2004)
192	•BrCl <sup>-</sup> + Cl <sup>-</sup> → •Cl <sub>2</sub> <sup>-</sup> + Br <sup>-</sup>	110	(Ershov, 2004)

The concentration of water has been included in all rate constants for reactions where water is a reactant. All estimated rate constants were done so in this work unless otherwise noted.

<sup>a</sup> Calculated based on I<sub>313</sub> measured with 2-nitrobenzaldehyde actinometry using a molar absorptivity for BrCl at 313 nm of 3.67 M<sup>-1</sup> cm<sup>-1</sup> (Finlayson-Pitts and Pitts, 2000).



**Table S6**, continued

- <sup>b</sup> Rate constant estimated from reaction 163 and a reported equilibrium constant  $K = 1.8 \times 10^4$  (Wang et al., 1994):  $k_{164} = k_{163} / K$
- <sup>c</sup> Rate constant estimated from reaction 165 and a reported equilibrium constant  $K = 1.3$  (Wang et al., 1994):  $k_{166} = k_{165} / K$
- <sup>d</sup> Rate constant estimated from reaction 170 and an equilibrium constant  $K = 3.0 \times 10^3$  calculated from data in Wang et al. (1994):  $k_{169} = k_{170} / K$
- <sup>e</sup> Rate constants were estimated based upon analogous reactions in solutions containing only bromide or chloride as well as considerations of the electronegativities of the reactants.
- <sup>f</sup> Reported value is  $(2.3 \pm 1.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

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