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

B. M. Matthew and C. Anastasio

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 μL 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 μl 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 μl of HFBA (not 50 μl 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 µm (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 $Br^{\bullet}$, Br_2, and 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 = $Br^{\bullet}$, Br_2, and HOBr):

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

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

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

where k_i^{AA} is the total rate constant for the reaction of species i with allyl alcohol, [i]" is the molar concentration of i in the presence of AA, [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 Br*(aq) species as follows:

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

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 $Br^{\bullet}$, Br_2, and HOBr, only the $Br^{\bullet}$ version can be solved. This is because the final equations for Br_2 and 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 ($HO_2^\bullet$) and dibromide radical anion ($^\bullet Br_2^-$)). In the case of $Br^\bullet$, equation S3 can be rewritten as:

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

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

$$R"_F^{Br} = k_{OH}^{Br^-}[OH^\bullet]"[Br^-]Y_{OH}^{Br} \qquad \text{(S5)}$$

$$R"_D^{Br} = k'^{NS}_{Br}[Br^\bullet] + k_{Br}^{AA}[Br^\bullet][AA] \qquad \text{(S6)}$$

where k_m^n is the rate constant for the reaction of species *m* with *n* and Y_{OH}^{Br} is the yield of $Br^\bullet$ formed from the reaction of $^\bullet OH$ with Br^- (section S.5). The rate constant k'^{NS}_{Br} is the pseudo-first-order rate constant for the reaction of $Br^\bullet$ with natural scavengers. In real samples, natural scavengers include all species, other than AA, that react with $Br^\bullet$. The dominant "natural" scavengers in our experimental systems are Br^- and H_2O_2. At steady state, $R"_F^{Br}$ is equal to $R"_D^{Br}$, and therefore

$$[Br^\bullet]" = \frac{k_{OH}^{Br^-}[Br^-][^\bullet OH]"Y_{OH}^{Br}}{k'^{NS}_{Br} + k_{Br}^{AA}[AA]} \qquad \text{(S7)}$$

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

$$R"_D^{OH} = k'^{NS}_{OH}[^\bullet OH] + k_{OH}^{AA}[^\bullet OH]"[AA] \qquad \text{(S8)}$$

where k'^{NS}_{OH} is the pseudo-first-order rate constant for the reaction of $^\bullet OH$ with natural scavengers in the absence of AA, and includes the reaction of $^\bullet OH$ with Br^- and H_2O_2

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

$$[^{\bullet}\text{OH}]'' = \frac{R_F^{OH}}{k'^{NS}_{OH} + k^{AA}_{OH}[\text{AA}]} \tag{S9}$$

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

$$R^{3BPD}_{F,tot} = \frac{k^{AA}_{Br}\, k^{Br^-}_{OH}\, [\text{Br}^-]\, Y^{Br}_{OH}\, R^{OH}_F\, [\text{AA}]\, Y^{3BPD}_{Br}}{F^{3BPD}_{Br}\, (k'^{NS}_{Br} + k^{AA}_{Br}[\text{AA}])(k'^{NS}_{OH} + k^{AA}_{OH}[\text{AA}])} \tag{S10}$$

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 $^{\bullet}$OH and Br$^{\bullet}$ concentrations in the absence of AA) are used to make substitutions:

$$[^{\bullet}\text{OH}] = \frac{R^{OH}_F}{k'^{NS}_{OH}} \tag{S11}$$

$$[\text{Br}^{\bullet}] = \frac{k^{Br^-}_{OH}\, [\text{OH}^{\bullet}][\text{Br}^-] Y^{Br}_{OH}}{k'^{NS}_{Br}} \tag{S12}$$

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

$$\frac{1}{R^{3BPD}_{F,tot}} = a + \frac{b}{[\text{AA}]} + c[\text{AA}] \tag{S13}$$

where

$$a = \frac{(k^{AA}_{OH}\, k'^{NS}_{Br} + k^{AA}_{Br}\, k'^{NS}_{OH}\,)\, F^{3BPD}_{Br}}{R^{Br}_F\, Y^{3BPD}_{Br}\, k^{AA}_{Br}\, k'^{NS}_{OH}} \tag{S14}$$

$$b = \frac{F^{3BPD}_{Br}}{Y^{3BPD}_{Br}\, k^{AA}_{Br}\, [\text{Br}^{\bullet}]} \tag{S15}$$

$$c = \frac{k^{AA}_{OH}\, F^{3BPD}_{Br}}{R^{OH}_F\, Y^{3BPD}_{Br}\, k^{Br^-}_{OH}\, [\text{Br}^-]\, Y^{Br}_{OH}} = \frac{k^{AA}_{OH}\, F^{3BPD}_{Br}}{k'^{NS}_{OH}\, Y^{3BPD}_{Br}\, R^{Br}_F} \tag{S16}$$

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$^\bullet$ (τ_{Br}) in the absence of AA:

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

$$R_F^{Br} = \frac{k_{OH}^{AA}\, F_{Br}^{3BPD}}{c\, k'^{NS}_{OH}\, Y_{Br}^{3BPD}} \qquad \text{(S18)}$$

$$\tau_{Br} = \frac{c\, k'^{NS}_{OH}}{b\, k_{OH}^{AA}\, k_{Br}^{AA}} = \frac{[\mathrm{Br}^\bullet]}{R_F^{Br}} \qquad \text{(S19)}$$

In order to utilize equations S18 and S19 to solve for R_F^{Br} and τ_{Br}, the value of k'^{NS}_{OH} (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:

$$k'^{NS}_{OH} = k_{OH}^{Br^-}[\mathrm{Br}^-] f_{Lost}^{Br^-} + k_{OH}^{H_2O_2}[\mathrm{H_2O_2}] \qquad \text{(S20)}$$

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'^{NS}_{OH} 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''^{i}_{F} (the rate in the presence of AA) ≈ R^{i}_{F} (the rate in the absence of AA)). By making this assumption, the equations no longer need to be written in terms of •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:

$$R^{3BPD}_{F,tot} = \frac{k^{AA}_{i}[i]''[\mathrm{AA}]Y^{3BPD}_{i}}{F^{3BPD}_{i}} \tag{S21}$$

where [*i*]” is equal to

$$[i]'' = \frac{R^{i}_{F}}{k'^{NS}_{i} + k^{AA}_{i}[\mathrm{AA}]} \tag{S22}$$

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

$$R^{3BPD}_{F,tot} = \frac{k^{AA}_{i} R^{i}_{F}[\mathrm{AA}]Y^{3BPD}_{i}}{F^{3BPD}_{i}(k'^{NS}_{i} + k^{AA}_{i}[\mathrm{AA}])} \tag{S23}$$

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:

$$[i] = \frac{R^{i}_{F}}{k'^{NS}_{i}} \tag{S24}$$

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

$$\frac{1}{R^{3BPD}_{F,tot}} = a' + \frac{b'}{[\mathrm{AA}]} \tag{S25}$$

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

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:

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

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

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

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

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

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

These equations are analogous to those derived for the $^{\bullet}$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 $Br^{\bullet}$, Br_2, and 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:

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

Values of $[i]''$ 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, $[Br^-]$, and [AA].

S.5 Calculating the yield of $Br^{\bullet}$ from the reaction of $^{\bullet}OH$ with Br^- (Y_{OH}^{Br}) and the fraction of $^{\bullet}OH$ lost to reaction with Br^- ($f_{Lost}^{Br^-}$) in bromide solutions

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

$^{\bullet}OH + Br^- \rightarrow {}^{\bullet}BrOH^-$ (29)

$^{\bullet}BrOH^- + Br^- \rightarrow {}^{\bullet}Br_2^-$ (30)

$^{\bullet}BrOH^- \rightarrow Br^- + {}^{\bullet}OH$ (35)

$^{\bullet}BrOH^- \rightarrow Br^{\bullet} + OH^-$ (36)

$^{\bullet}BrOH^- + H^+ \rightarrow Br^{\bullet} + H_2O$ (37)

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 $^{\bullet}OH$ (i.e., 30, 36, and 37) also lead to the formation of $Br^{\bullet}$. (Note that reaction 30 is a source of $Br^{\bullet}$ because $^{\bullet}Br_2^-$ rapidly dissociates to $Br^{\bullet}$). Y_{OH}^{Br} and $f_{Lost}^{Br^-}$ are calculated as the sum of the rates of the reactions that lead to $Br^{\bullet}$ formation (or $^{\bullet}OH$ loss), divided by the total rate of $^{\bullet}BrOH^-$ loss. Factoring out $[^{\bullet}BrOH^-]$ in this fraction yields the following expression:

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

where $k_{\to Br^-}^{BrOH^-}$ and $k_{\to Br}^{BrOH^-}$ are the first order rate constants for the dissociation of $^{\bullet}BrOH^-$ into Br^- (reaction 35) and $Br^{\bullet}$ (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 $^{\bullet}BrOH^-$ and $^{\bullet}Br_2^-$ which could lead to the destruction of $^{\bullet}OH$, but not to the formation of

$Br^{\bullet}$ (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 $^{\bullet}BrOH^-$ and $^{\bullet}Br_2^-$.

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

As discussed in section S.2, equation S13 can be used to calculate [$Br^{\bullet}$], R_F^{Br}, and τ_{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 [$Br^{\bullet}$], R_F^{Br}, and τ_{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), $\frac{b}{[\mathrm{AA}]} >> c[\mathrm{AA}]$ and S13 simplifies to:

$$\frac{1}{R_{F,tot}^{3BPD}} = a + \frac{b}{[\mathrm{AA}]} \tag{S33}$$

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 [$Br^{\bullet}$] is calculated as discussed in section S.2 (equation S17) and τ_{Br} can be calculated as [$Br^{\bullet}$]/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:

$$a = \frac{(k_{OH}^{AA}\ k'^{NS}_{Br} + k_{Br}^{AA}\ k'^{NS}_{OH})\ F_{Br}^{3BPD}}{R_F^{Br}\ Y_{Br}^{3BPD}\ k_{Br}^{AA}\ k'^{NS}_{OH}} \tag{S14}$$

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

$$[\mathrm{Br}^{\bullet}] = \frac{R_F^{Br}}{k'^{NS}_{Br}} \qquad \text{(S34)}$$

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

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

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 [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 Br^{-} from NaCl solutions

In agreement with a past report (Wang et al., 1994), we found trace amounts of Br^{-} in solutions made from "pure" NaCl. Because these trace amounts of Br^{-} can bias our experimental results in chloride solutions containing little or no added bromide, we developed a technique to remove 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 Br_2.

Based on these results, we developed a procedure to convert Br^{-} to Br_2 and purge it from solution. In this technique 250 mL of a 3 M NaCl solution containing 0.01 M H_2O_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^{-1} with zero-grade air (Puritan Medical Products) sent through a glass gas dispersion tube (P/N # 9435-23, Ace Glass). Every two hours, fresh H_2O_2 solution was added (61 µL of a 10.4 M H_2O_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 ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), Aldrich) to each aliquot to convert Br^- to Br_2 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^- (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^{-1}) for an additional 8 hours, illuminated for an additional 11 hours without purging, and then purged for ~ 4 hrs (~1.2 L min^{-1}) 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^- (treated and untreated), 75 μM AA and 1.0 mM H_2O_2 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^- 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_2O_2) to the results described in Part 2, section 3.3.1 (measurements of 3BPD and 3CPD as a function of $[Br^-]$ in 0.56 M (treated) NaCl solutions), we estimate that the untreated Aldrich NaCl contained ~ 0.007 mol % Br^-. This is consistent with the value (≤ 0.01 mol % Br^-) reported by Aldrich. In addition, a similar level of Br^- (0.011 mol %) has been reported for NaCl from J.T. Baker (Wang et al., 1994). Because of possible changes in the Cl^- concentration due to evaporation of water or Cl*(g) (i.e., Cl_2 or HOCl), the concentration of Cl^- in the treated solutions was measured with ion chromatography (Zhang and Anastasio, 2001). These measurements showed a slight increase in $[Cl^-]$, indicating that the loss of water was greater than any loss of Cl^- as Cl_2 or HOCl.

S.8 Calculating expected rates of $^\bullet Cl_2^-$ and $Cl^\bullet$ formation ($R_F^{Cl_2^-}$ and R_F^{Cl})

The following reactions lead to the formation of $^\bullet Cl_2^-$ in chloride solutions:

$\mathrm{Cl^- + {}^{\bullet}OH \rightarrow {}^{\bullet}ClOH^-}$ (94)

$\mathrm{{}^{\bullet}ClOH^- + Cl^- \rightarrow {}^{\bullet}Cl_2^- + OH^-}$ (95)

$\mathrm{{}^{\bullet}ClOH^- \rightarrow Cl^- + {}^{\bullet}OH}$ (96)

$\mathrm{{}^{\bullet}ClOH^- + H^+ \rightarrow Cl^{\bullet} + H_2O}$ (97)

$\mathrm{Cl^- + Cl^{\bullet} \rightarrow {}^{\bullet}Cl_2^-}$ (98)

The reaction numbers correspond to those in Table S4. In theory, $R_F^{Cl_2^-}$ should be the sum of the rates from reactions 95 and 98. However, the net rate of $\mathrm{{}^{\bullet}Cl_2^-}$ formation from reaction 98 can be no faster than the rate of formation of $\mathrm{Cl^{\bullet}}$ in reaction 97. Furthermore, essentially all of the $\mathrm{Cl^{\bullet}}$ formed in reaction 97 is converted to $\mathrm{{}^{\bullet}Cl_2^-}$ via reaction 98. Based on this, $R_F^{Cl_2^-}$ is written as the sum of the rates from reactions 95 and 97:

$$R_F^{Cl_2^-} = k_{Cl^-}^{ClOH^-}[\mathrm{Cl^-}][{}^{\bullet}\mathrm{ClOH^-}] + k_{H^+}^{ClOH^-}[{}^{\bullet}\mathrm{ClOH^-}][\mathrm{H^+}] \quad \text{(S36)}$$

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

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

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

where Y_{OH}^{Cl} is the yield of $\mathrm{Cl^{\bullet}}$ from the reaction of $\mathrm{{}^{\bullet}OH}$ with $\mathrm{Cl^-}$ (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 $\mathrm{{}^{\bullet}BrCl^-}$ formation ($R_F^{BrCl^-}$) for the mixed halide system

Because of rapid equilibria established between the following species,

$\mathrm{Br^{\bullet} + Cl^- \rightarrow {}^{\bullet}BrCl^-}$ (175)

$\mathrm{{}^{\bullet}BrCl^- \rightarrow Br^{\bullet} + Cl^-}$ (190)

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

$^{\bullet}\text{ClOH}^{-} + \text{Br}^{-} \rightarrow {}^{\bullet}\text{BrCl}^{-} + \text{OH}^{-}$ (171)

$^{\bullet}\text{BrOH}^{-} + \text{Cl}^{-} \rightarrow {}^{\bullet}\text{BrCl}^{-} + \text{OH}^{-}$ (174)

Based on these reactions, $R_F^{BrCl^-}$ is written as:

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

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_{OH}^{Cl} in chloride solutions

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

$\text{Cl}^{-} + {}^{\bullet}\text{OH} \rightarrow {}^{\bullet}\text{ClOH}^{-}$ (94)

$^{\bullet}\text{ClOH}^{-} + \text{Cl}^{-} \rightarrow {}^{\bullet}\text{Cl}_2^{-} + \text{OH}^{-}$ (95)

$^{\bullet}\text{ClOH}^{-} \rightarrow \text{Cl}^{-} + {}^{\bullet}\text{OH}$ (96)

$^{\bullet}\text{ClOH}^{-} + \text{H}^{+} \rightarrow \text{Cl}^{\bullet} + \text{H}_2\text{O}$ (97)

The overall yield of $\text{Cl}^{\bullet}$ formed from the reaction of $^{\bullet}\text{OH}$ with Cl^{-} (Y_{OH}^{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 $^{\bullet}\text{ClOH}^{-}$ loss. Factoring out $[^{\bullet}\text{ClOH}^{-}]$ from this ratio of rates gives

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

where $k^{ClOH^-}_{\rightarrow Cl^-}$ 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^{Br}_{OH} for the mixed halide system

As discussed in section S.5, the value for Y^{Br}_{OH}, 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^{Br}_{OH} can be rewritten as:

$$Y^{Br}_{OH} = \frac{k^{BrOH^-}_{\rightarrow Br} + k^{H^+}_{BrOH^-}[\mathrm{H}^+] + k^{Br^-}_{BrOH^-}[\mathrm{Br}^-] + k^{Cl^-}_{BrOH^-}[\mathrm{Cl}^-]}{k^{BrOH^-}_{\rightarrow Br^-} + k^{BrOH^-}_{\rightarrow Br} + k^{H^+}_{BrOH^-}[\mathrm{H}^+] + k^{Br^-}_{BrOH^-}[\mathrm{Br}^-] + k^{Cl^-}_{BrOH^-}[\mathrm{Cl}^-]} \qquad \text{(S40)}$$

where $k^{BrOH^-}_{\rightarrow Br^-}$ and $k^{BrOH^-}_{\rightarrow Br}$ 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

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

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*]" 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].

Table S1: Base reactions for Br^{-} Full Model

Rxn #	Reaction	Rate constant ($M^{-1}\ s^{-1}$ or s^{-1})	Reference
Photolysis of H_2O_2 at 313 nm			
1	$H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$	3.1×10^{-6}	Calculated[a]
Non-halogen acid-base equilibria			
2	${}^{\bullet}O_2^{-} + H^{+} \rightarrow HO_2^{\bullet}$	5.0×10^{10}	(Ross et al., 1998)
3	$HO_2^{\bullet} \rightarrow {}^{\bullet}O_2^{-} + H^{+}$	7.9×10^{5}	Calculated with pKa = 4.8
4	$H^{+} + OH^{-} \rightarrow H_2O$	1.0×10^{11}	Assumed Diffusion Limited
5	$H_2O \rightarrow H^{+} + OH^{-}$	1.0×10^{-3}	Calculated with pKw = 14
6	$HCO_3^{-} + H^{+} \rightarrow CO_2$	1.0×10^{10}	Assumed Diffusion Limited
7	$CO_2 \rightarrow H^{+} + HCO_3^{-}$	5.0×10^{3}	Calculated with pKa = 6.3
8	$CO_3^{-2} + H^{+} \rightarrow HCO_3^{-}$	5.0×10^{10}	Assumed Diffusion Limited
9	$HCO_3^{-} \rightarrow H^{+} + CO_3^{-2}$	2.5	Calculated with pKa = 10.3
HO_x/H_2O_2 reactions			
10	$HO_2^{\bullet} + {}^{\bullet}O_2^{-} \rightarrow HO_2^{-}$	9.7×10^{7}	(Ross et al., 1998)
11	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2$	8.3×10^{5}	(Ross et al., 1998)
12	${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$	5.5×10^{9}	(Ross et al., 1998)
13	${}^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2$	7.1×10^{9}	(Ross et al., 1998)
14	${}^{\bullet}OH + {}^{\bullet}O_2^{-} \rightarrow OH^{-}$	1.0×10^{10}	(Ross et al., 1998)
15	$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet}$	2.7×10^{7}	(Ross et al., 1998)
16	${}^{\bullet}OH + HCO_3^{-} \rightarrow {}^{\bullet}CO_3^{-}$	8.5×10^{6}	(Ross et al., 1998)
17	${}^{\bullet}OH + CO_2 \rightarrow {}^{\bullet}CO_3^{-}$	1×10^{6}	(Ross et al., 1998)
18	${}^{\bullet}OH + CO_3^{-2} \rightarrow {}^{\bullet}CO_3^{-} + OH^{-}$	3.9×10^{8}	(Ross et al., 1998)
19	${}^{\bullet}CO_3^{-} + H_2O_2 \rightarrow HCO_3^{-} + HO_2^{\bullet}$	4.3×10^{5}	(Ross et al., 1998)
20	${}^{\bullet}OH + {}^{\bullet}CO_3^{-} \rightarrow$	3×10^{9}	(Ross et al., 1998)
21	${}^{\bullet}CO_3^{-} + HO_2^{-} \rightarrow HCO_3^{-} + {}^{\bullet}O_2^{-}$	3×10^{7}	(Ross et al., 1998)
22	${}^{\bullet}CO_3^{-} + {}^{\bullet}O_2^{-} \rightarrow O_2 + CO_3^{-2}$	6.5×10^{8}	(Ross et al., 1998)

[a] Calculated based on an actinic flux (I_{313}) measured with 2-nitrobenzaldehyde actinometry using a molar absorptivity for H_2O_2 at 313 nm of 0.37 $M^{-1}\ cm^{-1}$ (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.

Table S2: Aqueous phase bromine reactions

Rxn #	Reaction	Rate constant (M^{-1} s^{-1} or s^{-1})	Reference
Photolysis of bromine species at 313 nm			
23	$Br_2 \rightarrow Br^{\bullet} + Br^{\bullet}$	1.5×10^{-5}	Calculated[a]
24	$HOBr \rightarrow Br^{\bullet} + {}^{\bullet}OH$	7.5×10^{-4}	Calculated[a]
Bromine acid-base equilibria			
25	$H^+ + Br^- \rightarrow HBr$	5.0×10^{10}	Assumed Diffusion Limited
26	$HBr \rightarrow H^+ + Br^-$	5.0×10^{19}	Calculated with pKa = -9
27	$H^+ + BrO^- \rightarrow HOBr$	5.0×10^{10}	Assumed Diffusion Limited
28	$HOBr \rightarrow H^+ + BrO^-$	79	Calculated with pKa = 8.8
Bromine aqueous phase reactions			
29	$Br^- + {}^{\bullet}OH \rightarrow {}^{\bullet}BrOH^-$	1.1×10^{10}	(Ross et al., 1998)
30	$Br^- + {}^{\bullet}BrOH^- \rightarrow {}^{\bullet}Br_2^- + OH^-$	1.9×10^{8}	(Zehavi and Rabani, 1972)
31	$Br^- + Br^{\bullet} \rightarrow {}^{\bullet}Br_2^-$	1.5×10^{10}	(Ross et al., 1998)[b]
32	$Br^- + Br_2 \rightarrow Br_3^-$	9.6×10^{8}	(Ershov, 2004)
33	$Br^- + HOBr \rightarrow Br_2OH^-$	5×10^{9}	(Eigen and Kustin, 1962)
34	$Br^- + {}^{\bullet}CO_3^- \rightarrow Br^{\bullet} + CO_3^{-2}$	1×10^{5}	(Ross et al., 1998)[c]
35	${}^{\bullet}BrOH^- \rightarrow Br^- + {}^{\bullet}OH$	3.3×10^{7}	(Zehavi and Rabani, 1972)
36	${}^{\bullet}BrOH^- \rightarrow Br^{\bullet} + OH^-$	4.2×10^{6}	(Zehavi and Rabani, 1972)
37	${}^{\bullet}BrOH^- + H^+ \rightarrow Br^{\bullet} + H_2O$	4.4×10^{10}	(Zehavi and Rabani, 1972)
38	$Br^{\bullet} + H_2O_2 \rightarrow HBr + HO_2^{\bullet}$	4×10^{9}	(Sutton et al., 1965)
39	$Br^{\bullet} + OH^- \rightarrow {}^{\bullet}BrOH^-$	1.3×10^{10}	(Ross et al., 1998)
40	$Br^{\bullet} + H_2O \rightarrow {}^{\bullet}BrOH^- + H^+$	1.4	(Ross et al., 1998)
41	$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$	1×10^{9}	(Klaning and Wolff, 1985), estimate[d]
42	$Br^{\bullet} + HO_2^{\bullet} \rightarrow HBr + O_2$	1.6×10^{8}	(Ross et al., 1998)
43	$Br^{\bullet} + CO_3^{-2} \rightarrow Br^- + {}^{\bullet}CO_3^-$	2×10^{6}	Estimated
44	$Br^{\bullet} + HCO_3^- \rightarrow Br^- + {}^{\bullet}CO_3^-$	1×10^{6}	Estimated
45	${}^{\bullet}Br_2^- + HO_2^{\bullet} \rightarrow Br_2 + HO_2^-$	4.4×10^{9}	(Matthew et al., 2003)
46	${}^{\bullet}Br_2^- + {}^{\bullet}OH \rightarrow HOBr + Br^-$	1×10^{9}	(Wagner and Strehlow, 1987)
47	${}^{\bullet}Br_2^- + {}^{\bullet}O_2^- \rightarrow 2\ Br^- + O_2$	1.7×10^{8}	(Ross et al., 1998)
48	${}^{\bullet}Br_2^- + OH^- \rightarrow {}^{\bullet}BrOH^- + Br^-$	2.7×10^{6}	(Mamou et al., 1977)
49	${}^{\bullet}Br_2^- \rightarrow Br^{\bullet} + Br^-$	6.6×10^{3}	Modeled value[e]
50	${}^{\bullet}Br_2^- + {}^{\bullet}Br_2^- \rightarrow Br_2 + 2\ Br^-$	3.0×10^{9}	(Ershov, 2004)
51	${}^{\bullet}Br_2^- + H_2O_2 \rightarrow 2\ Br^- + HO_2^{\bullet} + H^+$	5.0×10^{2}	(Ross et al., 1998)[f]
52	${}^{\bullet}Br_2^- + CO_3^{-2} \rightarrow {}^{\bullet}CO_3^- + 2\ Br^-$	1.1×10^{5}	(Ross et al., 1998)
53	${}^{\bullet}Br_2^- + HCO_3^- \rightarrow {}^{\bullet}CO_3^- + 2\ Br^- + H^+$	8×10^{4}	Estimated
54	$Br_3^- + HO_2^{\bullet} \rightarrow {}^{\bullet}Br_2^- + HBr + O_2$	1×10^{7}	(Ross et al., 1998)
55	$Br_3^- + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}Br_2^- + Br^- + O_2$	3.8×10^{9}	(Ross et al., 1998)
56	$Br_3^- \rightarrow Br_2 + Br^-$	5.5×10^{7}	(Ershov, 2004)
57	$Br_2 + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}Br_2^- + O_2$	5.6×10^{9}	(Ross et al., 1998)
58	$Br_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}Br_2^- + H^+ + O_2$	1.1×10^{8}	(Ross et al., 1998)
59	$Br_2 + H_2O \rightarrow Br_2OH^- + H^+$	97	(Beckwith et al., 1996)
60	$Br_2 + H_2O_2 \rightarrow 2\ HBr + O_2$	1.3×10^{3}	(Wagner and Strehlow, 1987)
61	$Br_2OH^- + H^+ \rightarrow Br_2 + H_2O$	2×10^{10}	(Eigen and Kustin, 1962)
62	$Br_2OH^- \rightarrow HOBr + Br^-$	5×10^{9}	(Eigen and Kustin, 1962)
63	$HOBr + {}^{\bullet}OH \rightarrow BrO^{\bullet} + H_2O$	2.0×10^{9}	(Ross et al., 1998)
64	$HOBr + {}^{\bullet}O_2^- \rightarrow BrOH^-$	3.5×10^{9}	(Ross et al., 1998)
65	$HOBr + HO_2^{\bullet} \rightarrow BrOH^- + H^+$	3.5×10^{9}	Estimated

Table S2 (continued)

Rxn #	Reaction	Rate constant (M^{-1} s^{-1} or s^{-1})	Reference
Bromine aqueous phase reactions (continued)			
66	$HOBr + H_2O_2 \rightarrow HBr + H_2O + O_2$	3.5×10^4	(Young, 1950)
67	$BrO^- + {}^\bullet OH \rightarrow BrO^\bullet + OH^-$	4.5×10^9	(Ross et al., 1998)
68	$BrO^- + {}^\bullet O_2^- + H_2O \rightarrow Br^\bullet + 2\ OH^- + O_2$	2×10^8	(Ross et al., 1998)[g]
69	$BrO^- + H_2O_2 \rightarrow Br^- + H_2O + O_2$	2×10^5	Estimated[h]

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.

[a] Calculated based on I_{313} measured with 2-nitrobenzaldehyde actinometry using molar absorptivities at 313 nm from Finlayson-Pitts and Pitts (2000) of Br_2 = 0.34 M^{-1} cm^{-1} and HOBr = 33.0 M^{-1} cm^{-1}

[b] Reported value (1.2×10^{10} M^{-1} s^{-1}) was adjusted slightly to better fit our experimental data.

[c] Reported value < 5.0×10^5 M^{-1} s^{-1}

[d] Reactions and estimated rate constants suggested by Klaning and Wolff (1985)

[e] Modeled value. The following values have been suggested: 1.9×10^4 s^{-1} (Merenyi and Lind, 1994) and 640 – 3200 s^{-1} (Sutton et al., 1965).

[f] Reported as < 1.0×10^3 M^{-1} s^{-1}

[g] In the original paper (Schwartz and Bielski, 1986), the reaction is written as $BrO^- + {}^\bullet O_2^- + Br^- + H_2O \rightarrow {}^\bullet Br_2^- + 2\ OH^- + O_2$ with a second-order rate constant of < 2×10^8 M^{-1} s^{-1}. We have assumed that the reaction occurs as written in reaction 68 to form $Br^\bullet$ at the reported upper bound rate constant followed by reaction of $Br^\bullet$ with Br^- (reaction 31) to form ${}^\bullet Br_2^-$.

[h] Value estimated by R. Song, personal communication.

Table S3: Reactions of $^{\bullet}$OH, $^{\bullet}CO_3^-$, and reactive bromide (Br*(aq)) with allyl alcohol (AA)

Rxn #	Reaction	Rate constant (M^{-1} s^{-1})	Reference
Reactions of $^{\bullet}OH$ and $^{\bullet}CO_3^-$ with AA			
70	$^{\bullet}$OH + AA → AAOHr	7.5×10^9	(Ross et al., 1998)[a]
71	AA + AAOHr → AAOH1	2.5	Modeled[b]
72	AA + AAOH1 → AAOH2	0.5	Modeled[b]
73	AA + AAOH2 → AAOH3	0.5	Modeled[b]
74	$^{\bullet}CO_3^-$ + AA → CO3AA	2.9×10^5	(Ross et al., 1998)
Reactions of reactive bromide with AA			
75	$Br^{\bullet}$ + AA → 3BPD	5.2×10^8	(Guha et al., 1993)[c]
76	$Br^{\bullet}$ + AA → BrAA	3.4×10^9	(Guha et al., 1993)[c]
77	AA + BrAA → BrAA1	7	Modeled[b]
78	AA + BrAA1 → BrAA2	7	Modeled[b]
79	AA + BrAA2 → BrAA3	7	Modeled[b]
80	$^{\bullet}Br_2^-$ + AA → 3BPD	2.1×10^2	(Ross et al., 1998)[d]
81	$^{\bullet}Br_2^-$ + AA → Br2AA1	1.8×10^3	(Ross et al., 1998)[d]
82	Br_2 + AA → 3BPD	5.1×10^5	(Atkinson and Bell, 1963)[e]
83	Br_2 + AA → Br2AA2	1.6×10^5	(Atkinson and Bell, 1963)[e]
84	HOBr + AA → 3BPD	5.1×10^5	Assumed $k_{84} = k_{82}$[f]
85	HOBr + AA → Br2AA3	1.6×10^5	Assumed $k_{85} = k_{83}$[f]
86	Br_3^- + AA → 3BPD	5.2×10^4	(Atkinson and Bell, 1963)[g]
87	Br_3^- + AA → Br3AA	1.7×10^4	(Atkinson and Bell, 1963)[g]

[a] Reported value = $(6.0 \pm 1.5)\times10^9$ M^{-1} s^{-1}

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

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

[d] The sum of k_{80} and k_{81} was set equal to the reported upper bound rate constant for the reaction of $^{\bullet}Br_2^-$ with allyl alcohol of 2.0×10^3 M^{-1} s^{-1} (Ross et al., 1998). The yield of 3BPD from the reaction of $^{\bullet}Br_2^-$ with AA (i.e., $k_{80}/(k_{80}+k_{81})$) was assumed to be 0.1 based on the yield for $^{\bullet}Cl_2^-$ with AA (Part 2, section 2.2). Because $^{\bullet}Br_2^-$ 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.

[e] The sum of k_{82} and k_{83} was set equal to the reported rate constant for the reaction of Br_2 with allyl alcohol of 6.7×10^5 M^{-1} s^{-1} (Atkinson and Bell, 1963). The yield of 3BPD from the reaction of Br_2 with AA (0.76) was assumed to be the same as for HOBr.

[f] Values for k_{84} and k_{85} were assumed to be the same as the analogous values for the reaction of 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).

[g] The sum of k_{86} and k_{87} was set equal to the reported rate constant for the reaction of Br_3^- with allyl alcohol of 6.9×10^4 M^{-1} s^{-1} (Atkinson and Bell, 1963). The yield of 3BPD from the reaction of Br_3^- with AA (0.76) was assumed to be the same as the yield from the reaction of Br_2. Because 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 ($M^{-1}\ s^{-1}$ or s^{-1})	Reference
Photolysis reactions at 313 nm			
88	$Cl_2 \rightarrow Cl^{\bullet} + Cl^{\bullet}$	2.3×10^{-3}	Calculated[a]
89	$HOCl \rightarrow {}^{\bullet}OH + Cl^{\bullet}$	3.3×10^{-4}	Calculated[a]
Acid-base equilibria			
90	$H^+ + Cl^- \rightarrow HCl$	5.0×10^{10}	Assumed Diffusion Limited
91	$HCl \rightarrow H^+ + Cl^-$	8.6×10^{16}	Calculated with pKa = -6.24
92	$H^+ + ClO^- \rightarrow HOCl$	5.0×10^{10}	Assumed Diffusion Limited
93	$HOCl \rightarrow H^+ + ClO^-$	1.6×10^{3}	Calculated with pKa = 7.5
Chlorine reactions			
94	$Cl^- + {}^{\bullet}OH \rightarrow {}^{\bullet}ClOH^-$	4.3×10^{9}	(Ross et al., 1998)
95	${}^{\bullet}ClOH^- + Cl^- \rightarrow {}^{\bullet}Cl_2^- + OH^-$	1×10^{5}	(Grigor'ev et al., 1987)[b]
96	${}^{\bullet}ClOH^- \rightarrow Cl^- + {}^{\bullet}OH$	6.1×10^{9}	(Jayson et al., 1973)
97	${}^{\bullet}ClOH^- + H^+ \rightarrow Cl^{\bullet} + H_2O$	2.1×10^{10}	(Jayson et al., 1973)
98	$Cl^- + Cl^{\bullet} \rightarrow {}^{\bullet}Cl_2^-$	6.5×10^{9}	(Klaning and Wolff, 1985)
99	$Cl^- + Cl_2 \rightarrow Cl_3^-$	2×10^{4}	(Ershov, 2004)
100	$Cl^- + HOCl \rightarrow Cl_2OH^-$	1.5×10^{4}	(Wang and Margerum, 1994)
101	$Cl^{\bullet} + H_2O_2 \rightarrow HCl + HO_2^{\bullet}$	4×10^{9}	Estimated
102	$Cl^{\bullet} + OH^- \rightarrow {}^{\bullet}ClOH^-$	1.8×10^{10}	(Klaning and Wolff, 1985)
103	$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$	1×10^{8}	(Wu et al., 1980)
104	$Cl^{\bullet} + H_2O \rightarrow HClOH$	2.5×10^{5}	(McElroy, 1990)
105	$Cl^{\bullet} + CO_3^{-2} \rightarrow {}^{\bullet}CO_3^- + Cl^-$	5×10^{8}	(Ross et al., 1998)
106	$Cl^{\bullet} + HCO_3^- \rightarrow {}^{\bullet}CO_3^- + HCl$	2.2×10^{8}	(Ross et al., 1998)
107	${}^{\bullet}Cl_2^- + HO_2^{\bullet} \rightarrow 2\ Cl^- + H^+ + O_2$	3×10^{9}	(Ross et al., 1998)
108	${}^{\bullet}Cl_2^- + {}^{\bullet}O_2^- \rightarrow 2\ Cl^- + O_2$	1.0×10^{9}	(Ross et al., 1998)
109	${}^{\bullet}Cl_2^- + OH^- \rightarrow {}^{\bullet}ClOH^- + Cl^-$	4.5×10^{7}	(Grigor'ev et al., 1987)
110	${}^{\bullet}Cl_2^- \rightarrow Cl^{\bullet} + Cl^-$	1.1×10^{5}	(Jayson et al., 1973)
111	${}^{\bullet}Cl_2^- + {}^{\bullet}Cl_2^- \rightarrow Cl_2 + 2\ Cl^-$	8.3×10^{8}	(Ross et al., 1998)
112	${}^{\bullet}Cl_2^- + H_2O_2 \rightarrow 2\ Cl^- + HO_2^{\bullet} + H^+$	1.4×10^{5}	(Ross et al., 1998)
113	${}^{\bullet}Cl_2^- + H_2O \rightarrow HClOH + Cl^-$	1.3×10^{3}	(McElroy, 1990)
114	${}^{\bullet}Cl_2^- + {}^{\bullet}OH \rightarrow HOCl + Cl^-$	1×10^{9}	(Ross et al., 1998)
115	${}^{\bullet}Cl_2^- + HCO_3^- \rightarrow 2\ Cl^- + H^+ + {}^{\bullet}CO_3^-$	8×10^{7}	Estimated
116	${}^{\bullet}Cl_2^- + CO_3^{-2} \rightarrow 2\ Cl^- + {}^{\bullet}CO_3^-$	1.6×10^{8}	Estimated
117	$HClOH \rightarrow {}^{\bullet}ClOH^- + H^+$	1×10^{8}	(McElroy, 1990)
118	$HClOH \rightarrow Cl^{\bullet} + H_2O$	100	(McElroy, 1990)[c]
119	$HClOH + Cl^- \rightarrow {}^{\bullet}Cl_2^- + H_2O$	5×10^{9}	(McElroy, 1990)
120	$Cl_3^- + HO_2^{\bullet} \rightarrow {}^{\bullet}Cl_2^- + HCl + O_2$	1×10^{9}	(Bjergbakke et al., 1981)
121	$Cl_3^- + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}Cl_2^- + Cl^- + O_2$	3.8×10^{9}	Estimated
122	$Cl_3^- \rightarrow Cl_2 + Cl^-$	1.1×10^{5}	(Ershov, 2004)
123	$Cl_2 + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}Cl_2^- + O_2$	1×10^{9}	Estimated
124	$Cl_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}Cl_2^- + H^+ + O_2$	1×10^{9}	(Bjergbakke et al., 1981)

Table S4 (continued)

Rxn #	Reaction	Rate constant (M^{-1} s^{-1} or s^{-1})	Reference
Chlorine reactions (continued)			
125	$Cl_2 + H_2O \rightarrow Cl_2OH^- + H^+$	15	(Wang and Margerum, 1994)
126	$Cl_2 + H_2O_2 \rightarrow 2\ HCl + O_2$	1.3×10^4	Estimated
127	$Cl_2OH^- + H^+ \rightarrow Cl_2 + H_2O$	2×10^{10}	Estimated
128	$Cl_2OH^- \rightarrow HOCl + Cl^-$	5.5×10^9	(Wang and Margerum, 1994)
129	$HOCl + {}^\bullet OH \rightarrow ClO^\bullet + H_2O$	2.0×10^9	Estimated
130	$HOCl + {}^\bullet O_2^- \rightarrow Cl^\bullet + OH^- + O_2$	7.5×10^6	(Long and Bielski, 1980)
131	$HOCl + HO_2^\bullet \rightarrow Cl^\bullet + OH^- + O_2$	7.5×10^6	Estimated
132	$HOCl + H_2O_2 \rightarrow HCl + H_2O + O_2$	1.1×10^4	(Connick, 1947)
133	$ClO^- + {}^\bullet OH \rightarrow ClO^\bullet + OH^-$	8.8×10^9	(Buxton and Subhani, 1972)
134	$ClO^- + {}^\bullet O_2^- + H_2O \rightarrow Cl^\bullet + 2\ OH^- + O_2$	2×10^8	Estimated
135	$ClO^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$	1.7×10^5	(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.

[a] Calculated based on I_{313} measured with 2-nitrobenzaldehyde actinometry using molar absorptivities at 313 nm (M^{-1} cm^{-1}) of 51.9 (Cl_2) and 14.8 (HOCl) (Finlayson-Pitts and Pitts, 2000).

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

[c] Reported value < 1.0×10^3 s^{-1}

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

Rxn #	Reaction	Rate constant (M^{-1} s^{-1})	Reference
Reactions of reactive chloride with allyl alcohol			
136	$Cl^{\bullet} + AA \rightarrow 3CPD$	9.0×10^{8}	Modeled[a]
137	$Cl^{\bullet} + AA \rightarrow ClAA$	3.0×10^{9}	Modeled[a]
138	$Cl_2 + AA \rightarrow 3CPD$	1×10^{7}	Estimated[b]
139	$Cl_2 + AA \rightarrow Cl2AA1$	1×10^{8}	Estimated[b]
140	$^{\bullet}Cl_2^{-} + AA \rightarrow 3CPD$	4.7×10^{6}	(Padmaja et al., 1992)[c]
141	$^{\bullet}Cl_2^{-} + AA \rightarrow ClAA$	4.5×10^{7}	(Padmaja et al., 1992)[c]
142	$AA + ClAA \rightarrow ClAA1$	5.5	Modeled[d]
143	$AA + ClAA1 \rightarrow ClAA2$	5.5	Modeled[d]
144	$AA + ClAA2 \rightarrow ClAA3$	5.5	Modeled[d]
145	$HOCl + AA \rightarrow 3CPD$	5.4×10^{5}	Estimated[e]
146	$HOCl + AA \rightarrow Cl2AA2$	1.7×10^{5}	Estimated[e]
Reactions of reactive mixed halogen species with AA			
147	$BrCl + AA \rightarrow 3BPD$	5×10^{7}	Modeled[f]
148	$BrCl + AA \rightarrow 3CPD$	5×10^{3}	Estimated[f]
149	$BrCl + AA \rightarrow AA4$	5×10^{7}	Modeled[f]
150	$^{\bullet}BrCl^{-} + AA \rightarrow 3BPD$	1.7×10^{6}	Modeled[g]
151	$^{\bullet}BrCl^{-} + AA \rightarrow 3CPD$	6.8×10^{4}	Modeled[g]
152	$^{\bullet}BrCl^{-} + AA \rightarrow AA1$	2×10^{7}	Modeled[g]
153	$AA1 + AA \rightarrow AA2$	1	Modeled[d]

Modeled rate constants were estimated from model fits to the experimental data.

[a] The overall rate constant for the reaction of $Cl^{\bullet}$ with allyl alcohol is assumed to be the same as that for $Br^{\bullet}$ (i.e., the sum of k_{136} and k_{137} is equal to the reported k for $Br^{\bullet}$ with oleic acid; see reactions 75 and 76 in Table S3). The yield of 3CPD from the reaction of $Cl^{\bullet}$ with AA was assumed to be ~0.2. Because $Cl^{\bullet}$ is never an important source of 3CPD, this yield value is a rough estimate, and is not constrained by experimental data.

[b] Estimated values. Because Cl_2 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.

[c] Sum of k_{140} and k_{141} is equal to the reported total rate constant for reaction of $^{\bullet}Cl_2^{-}$ with allyl alcohol of 5.0×10^{7} M^{-1} s^{-1} (Padmaja et al., 1992). The yield of 3CPD from the reaction of $^{\bullet}Cl_2^{-}$ with AA (i.e., $k_{140}/(k_{140}+k_{141})$) is 0.095, and was estimated by fitting the model to the experimental data.

[d] Used to account for the radical-initiated polymerization of allyl alcohol (Part 1, section 3.1).

[e] 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.

[f] Rate constants for reactions 147-149 and yields of 3BPD and 3CPD from the reaction of BrCl with AA (0.50 and ~ 5×10^{-5}) 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.

[g] Rate constants for reactions 150 - 153 and the yields of 3CPD (0.0031) and 3BPD (see below) from the reaction of $^{\bullet}BrCl^{-}$ 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 $^{\bullet}BrCl^{-} + AA \rightarrow Br^{-} + Cl^{-}$), 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 ($M^{-1}\ s^{-1}$ or s^{-1})	Reference
Photolysis reactions at 313 nm			
154	$BrCl \rightarrow Br^{\bullet} + Cl^{\bullet}$	8.4×10^{-5}	Calculated[a]
Known mixed halide chemistry			
155	$Cl^- + HOBr + H^+ \rightarrow BrCl + H_2O$	$5.6x10^{9}\ [H^+]$	(Sander et al., 1997)
156	$Br^- + HOCl + H^+ \rightarrow BrCl + H_2O$	$1.3x10^{6}\ [H^+]$	(Sander et al., 1997)
157	$BrCl + H_2O \rightarrow HOBr + Cl^- + H^+$	1.0×10^{5}	(Michalowski et al., 2000)
158	$BrCl + H_2O_2 \rightarrow HBr + HCl + O_2$	1.3×10^{4}	Estimated
159	$BrCl + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}BrCl^- + O_2$	4×10^{9}	Estimated
160	$BrCl + HO_2^{\bullet} \rightarrow {}^{\bullet}BrCl^- + O_2 + H^+$	5×10^{8}	Estimated
161	$BrCl + Cl^- \rightarrow BrCl_2^-$	1.0×10^{4}	(Ershov, 2004)
162	$BrCl_2^- \rightarrow BrCl + Cl^-$	1.7×10^{5}	(Ershov, 2004)
163	$BrCl + Br^- \rightarrow Br_2Cl^-$	3.0×10^{8}	Estimated
164	$Br_2Cl^- \rightarrow BrCl + Br^-$	1.7×10^{4}	Estimated[b]
165	$Br_2 + Cl^- \rightarrow Br_2Cl^-$	5.0×10^{4}	Estimated
166	$Br_2Cl^- \rightarrow Br_2 + Cl^-$	3.8×10^{4}	Estimated[c]
167	$Cl_2 + Br^- \rightarrow BrCl_2^-$	6.0×10^{9}	(Ershov, 2004)
168	$BrCl_2^- \rightarrow Cl_2 + Br^-$	9.0×10^{3}	(Ershov, 2004)
169	$Br_2Cl^- + Cl^- \rightarrow BrCl_2^- + Br^-$	1.0×10^{5}	Estimated[d]
170	$BrCl_2^- + Br^- \rightarrow Br_2Cl^- + Cl^-$	3.0×10^{8}	(Ershov, 2004)
Proposed mixed halide radical reactions			
171	${}^{\bullet}ClOH^- + Br^- \rightarrow {}^{\bullet}BrCl^- + OH^-$	1×10^{9}	Estimated[e]
172	$Cl^{\bullet} + Br^- \rightarrow {}^{\bullet}BrCl^-$	1.2×10^{10}	(Donati, 2002)
173	${}^{\bullet}Cl_2^- + Br^- \rightarrow {}^{\bullet}BrCl^- + Cl^-$	4.0×10^{9}	(Ershov, 2004)
174	${}^{\bullet}BrOH^- + Cl^- \rightarrow {}^{\bullet}BrCl^- + OH^-$	1.9×10^{8}	Estimated[e]
175	$Br^{\bullet} + Cl^- \rightarrow {}^{\bullet}BrCl^-$	1×10^{8}	(Donati, 2002)[f]
176	${}^{\bullet}Br_2^- + Cl^- \rightarrow {}^{\bullet}BrCl^- + Br^-$	4.3×10^{6}	(Ershov, 2004)
177	${}^{\bullet}Br_2^- + {}^{\bullet}Cl_2^- \rightarrow Br_2 + 2\ Cl^-$	4×10^{9}	Estimated[e]
178	${}^{\bullet}BrCl^- + {}^{\bullet}OH \rightarrow BrCl + OH^-$	1×10^{9}	Estimated[e]
179	${}^{\bullet}BrCl^- + HO_2^{\bullet} \rightarrow Br^- + Cl^- + O_2$	1×10^{9}	Estimated[e]
180	${}^{\bullet}BrCl^- + {}^{\bullet}O_2^- \rightarrow Br^- + Cl^- + O_2$	6×10^{8}	Estimated[e]
181	${}^{\bullet}BrCl^- + H_2O_2 \rightarrow HO_2^{\bullet} + Br^- + Cl^- + H^+$	5×10^{3}	Estimated[e]
182	${}^{\bullet}BrCl^- + OH^- \rightarrow {}^{\bullet}ClOH^- + Br^-$	3×10^{6}	Estimated[e]
183	${}^{\bullet}BrCl^- + OH^- \rightarrow {}^{\bullet}BrOH^- + Cl^-$	2×10^{7}	Estimated[e]
184	${}^{\bullet}BrCl^- + HCO_3^- \rightarrow Br^- + Cl^- + H^+ + {}^{\bullet}CO_3^-$	3×10^{6}	Estimated[e]
185	${}^{\bullet}BrCl^- + CO_3^{-2} \rightarrow Br^- + Cl^- + {}^{\bullet}CO_3^-$	6×10^{6}	Estimated[e]
186	${}^{\bullet}BrCl^- + {}^{\bullet}BrCl^- \rightarrow BrCl + Br^- + Cl^-$	4.7×10^{9}	(Donati, 2002)
187	${}^{\bullet}BrCl^- + {}^{\bullet}Cl_2^- \rightarrow 2\ Cl^- + BrCl$	2×10^{9}	Estimated[e]
188	${}^{\bullet}BrCl^- + {}^{\bullet}Br_2^- \rightarrow Br_2 + Br^- + Cl^-$	4×10^{9}	Estimated[e]
189	${}^{\bullet}BrCl^- \rightarrow Cl^{\bullet} + Br^-$	1.9×10^{3}	(Donati, 2002)
190	${}^{\bullet}BrCl^- \rightarrow Br^{\bullet} + Cl^-$	6.1×10^{4}	(Donati, 2002)
191	${}^{\bullet}BrCl^- + Br^- \rightarrow {}^{\bullet}Br_2^- + Cl^-$	8.0×10^{9}	(Ershov, 2004)
192	${}^{\bullet}BrCl^- + Cl^- \rightarrow {}^{\bullet}Cl_2^- + Br^-$	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.

[a] Calculated based on I_{313} measured with 2-nitrobenzaldehyde actinometry using a molar absorptivity for BrCl at 313 nm of 3.67 $M^{-1}\ cm^{-1}$ (Finlayson-Pitts and Pitts, 2000).

Table S6, continued

[b] Rate constant estimated from reaction 163 and a reported equilibrium constant K = 1.8×10^4 (Wang et al., 1994): $k_{164} = k_{163} / K$

[c] Rate constant estimated from reaction 165 and a reported equilibrium constant K = 1.3 (Wang et al., 1994): $k_{166} = k_{165} / K$

[d] Rate constant estimated from reaction 170 and an equilibrium constant K = 3.0×10^3 calculated from data in Wang et al. (1994): $k_{169} = k_{170} / K$

[e] 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.

[f] Reported value is $(2.3 \pm 1.7) \times 10^8\ M^{-1}\ s^{-1}$.

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