Environmental Science & Technology

pubs.acs.org/est

Article

Effects of Halides on Organic Compound Degradation during Plasma Treatment of Brines

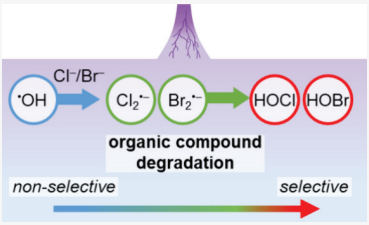
Moshan Chen, Dillon Moher, Jacqueline Rogers, Shurik Yatom, Elijah Thimsen, and Kimberly M. Parker*

Cite This: *Environ. Sci. Technol.* 2024, 58, 5139−5152

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Plasma has been proposed as an alternative strategy to treat organic contaminants in brines. Chemical degradation in these systems is expected to be partially driven by halogen oxidants, which have been detected in halide-containing solutions exposed to plasma. In this study, we characterized specific mechanisms involving the formation and reactions of halogen oxidants during plasma treatment. We first demonstrated that addition of halides accelerated the degradation of a probe compound known to react quickly with halogen oxidants (i.e., *para*-hydroxybenzoate) but did not affect the degradation of a less reactive probe compound (i.e., benzoate). This effect was attributed to the degradation of *para*-hydroxybenzoate by hypohalous acids, which were produced via a mechanism involving halogen radicals as intermediates. We applied this mechanistic insight to investigate the impact of constituents in brines on reactions driven by halogen oxidants during plasma treatment. Bromide, which is expected to occur alongside chloride in brines, was required to enable halogen oxidant formation, consistent with the generation of halogen radicals from the oxidation of halides by hydroxyl radical. Other constituents typically present in brines (i.e., carbonates, organic matter) slowed the degradation of organic compounds, consistent with their ability to scavenge species involved during plasma treatment.



KEYWORDS: *brine treatment, plasma, halides, hypohalous acids, halogen radicals*

1. INTRODUCTION

Plasma technology has been recently proposed as a promising tool for water treatment due to its simplicity, cost, and effectiveness toward destroying toxic organic compounds.[1−7] Unlike ultraviolet/oxidant advanced oxidation processes (UV/oxidant AOPs), plasma operates without requiring chemical consumables (e.g., hydrogen peroxide, H_2O_2; hypochlorous acid, HOCl).[5] In addition, though the energy requirement may be substantial, plasma treatment of some organic contaminants has been reported to be competitive against other treatment options including UV/oxidant AOPs, electrochemical treatment, and sonolysis.[6,7] Plasma-based water treatment generates an array of oxidative species (e.g., hydroxyl radical, •OH; oxygen atom, O; ozone, O_3; hydrogen peroxide, H_2O_2)[8−11] via processes in the plasma or at the plasma−water interface,[4,8] among which •OH, known to react with a wide spectrum of organic contaminants,[12] is frequently determined to drive the degradation of several organic contaminants (e.g., pesticides,[13−15] pharmaceuticals,[16,17] algal toxins[18−20]). Plasma also generates reductive species (i.e., hydrated electron, e^-_{aq},[21−24] or its conjugate acid hydrogen atom, H•,[8,25] pK_a 9.6[12]) that degrade contaminants such as per- and polyfluoroalkyl substances and halogenated disinfection byproducts in plasma[7,26,27] or other treatment technologies.[28−33]

Among possible applications, plasma has particular advantages when applied to degrade organic compounds in brines. Contaminated brines encompass a wide array of waste streams from diverse sources (ion exchange,[34,35] reverse osmosis,[36−38] pharmaceutical production,[39] hydraulic fracturing,[40,41] landfill,[42] textile manufacturing[43]), but all share high concentrations of salts and other constituents that present multiple opportunities for plasma treatment. First, relative to conventional AOPs, plasma appears to be less susceptible to inhibition by constituents in complex wastewaters that scavenge reactive species.[38,44] For example, organic compound degradation by plasma was observed to be less sensitive to the inclusion of co-occurring constituents in complex mixtures (i.e., reverse osmosis brine,[38] urine[44]) compared to •OH-based AOPs. Second, because reactive species are concentrated at or above the plasma−water interface,[8] salting-out effects in brines can improve the degradation efficiency of some contaminants (i.e., surfactants).[45] For example, the degradation of perfluorooctanoic acid (PFOA), which is known to occur at or above the plasma−water interface,[26] was accelerated upon the addition of salts,[45] consistent with salts causing PFOA to more favorably partition to the water surface.[46−48] Third, increased conductivity at elevated salt concentrations affects plasma

Received: August 31, 2023
Revised: February 12, 2024
Accepted: February 12, 2024
Published: March 6, 2024

properties such as the plasma volume and the contact area between plasma and water.[49] These changes can increase the production of reactive species (e.g., $^{\bullet}OH$),[50] though notably, the opposite trend has been observed in other reactors.[44,49] Depending on the impact of conductivity on reactive species production in the specific reactor, the addition of salts has been reported to either accelerate[51,52] or decelerate[45,53,54] the degradation of organic compounds during plasma treatment.

Beyond these contributions, halides present in brines may specifically enable new pathways due to their potential to form halogen oxidants during plasma treatment. For example, studies have invoked halogen oxidants, including HOCl and halogen radicals (i.e., $Cl^{\bullet}$, $Cl_2^{\bullet-}$, $ClOH^{\bullet-}$), to explain compound degradation during plasma treatment of solutions containing chloride (Cl^-).[45,54−56] HOCl has been measured to occur in Cl^--containing solutions treated by plasma.[57−59] The specific mechanisms proposed to be responsible for halogen oxidant formation depend on the plasma reactor setup. The inclusion of oxygen (i.e., at 0.1−1%) in the feed gas of some plasma systems enabled the generation of OCl^-, the conjugate base of HOCl, via the reaction between O and Cl^- (eq 1).[57−59] In other plasma systems, an alternative mechanism involving the reaction between $^{\bullet}OH$ and Cl^- (eq 2) to form $Cl^{\bullet}$ (eq 3) and $Cl_2^{\bullet-}$ (eqs 4 and 5) has been proposed in multiple studies,[45,54−56] which may either react with organic compounds themselves[54,56] or recombine to form HOCl (eqs 6−8)[60−62] that drives compound degradation (Table S1).[45,54,55]

$$O + Cl^- \rightarrow OCl^- \quad (1)$$

$$Cl^- + {}^{\bullet}OH \leftrightarrow ClOH^{\bullet-} k_{2,f} = 4.3 \times 10^9\ M^{-1}\ s^{-1},\ k_{2,r} = 6.1 \times 10^9\ s^{-1},\ K_2 = 0.70\ M^{-1} \quad (2)$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O k_3 = 2.1 \times 10^{10}\ M^{-1}\ s^{-1} \quad (3)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-} k_4 = 8.8 \times 10^7\ M^{-1}\ s^{-1} \quad (4)$$

$$ClOH^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} + OH^- k_5 = 1.0 \times 10^4\ M^{-1}\ s^{-1} \quad (5)$$

$$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2 k_6 = 8.8 \times 10^7\ M^{-1}\ s^{-1} \quad (6)$$

$$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + 2Cl^- k_7 = 9.0 \times 10^8\ M^{-1}\ s^{-1} \quad (7)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- k_8 = 22\ M^{-1}\ s^{-1} \quad (8)$$

These studies characterizing halogen oxidants in plasma-treated water have only investigated the impact of Cl^-,[45,54−59] which cannot account for the unique roles of other chemical species occurring in brines. In particular, brines, like natural waters,[63] also contain some bromide (Br^-) typically present at 0.1−1 mol % Cl^-,[41,64,65] which is particularly relevant for mechanisms involving halogen radicals.[66] Whereas HOCl formation from O can proceed in Cl^--only systems,[57−59] the presence of Br^- (even a trace contaminant in the Cl^- reagent)[67,68] is known to dominate the oxidation of halides by $^{\bullet}OH$, leading to Br-containing halogen radicals (eqs 9−13) and their recombination products (e.g., hypobromous acid, HOBr, eqs 14−16, Table S1).[66] Specifically, Cl^- itself is ineffective in scavenging $^{\bullet}OH$ to produce halogen radicals due to the fast reverse reaction of the intermediate $ClOH^{\bullet-}$ to regenerate the initial reactants (eq 2),[66] whereas $BrOH^{\bullet-}$ generated in the presence of Br^- (eq 9) predominantly reacts further to produce halogen radicals (eqs 10−13, e.g., >99.99% of $ClOH^{\bullet-}$ regenerates the reactants[69−71] compared to 14% of $BrOH^{\bullet-}$,[72−74] Text S1).[66] Therefore, the previously proposed mechanism involving halogen radical formation in Cl^--only systems treated by plasma[45,54−56] has been typically considered negligible in other contexts (e.g., conventional AOPs).[66] Beyond the effect of Br^-, other brine constituents (i.e., carbonates, organic matter) may also impact the formation and reactions of halogen oxidants during plasma treatment depending on the specific reactive species involved.[64,67,68,75]

$$Br^- + {}^{\bullet}OH \leftrightarrow BrOH^{\bullet-} k_{9,f} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1},\ k_{9,r} = 3.3 \times 10^7\ s^{-1},\ K_9 = 330\ M^{-1} \quad (9)$$

$$BrOH^{\bullet-} + H^+ \rightarrow Br^{\bullet} + H_2O k_{10} = 4.4 \times 10^{10}\ M^{-1}\ s^{-1} \quad (10)$$

$$Br^{\bullet} + Br^- \rightarrow Br_2^{\bullet-} k_{11} = 1.2 \times 10^{10}\ M^{-1}\ s^{-1} \quad (11)$$

$$BrOH^{\bullet-} + Br^- \rightarrow Br_2^{\bullet-} + OH^- k_{12} = 1.9 \times 10^8\ M^{-1}\ s^{-1} \quad (12)$$

$$BrOH^{\bullet-} + Cl^- \rightarrow ClBr^{\bullet-} + OH^- k_{13} = 1.9 \times 10^8\ M^{-1}\ s^{-1} \quad (13)$$

$$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2 k_{14} = 1.2 \times 10^8\ M^{-1}\ s^{-1} \quad (14)$$

$$Br_2^{\bullet-} + Br_2^{\bullet-} \rightarrow Br_2 + 2Br^- k_{15} = 3.0 \times 10^9\ M^{-1}\ s^{-1} \quad (15)$$

$$Br_2 + H_2O \rightarrow HOBr + H^+ + Br^- k_{16} = 97\ M^{-1}\ s^{-1} \quad (16)$$

In this study, we evaluated the role of halogen oxidants during plasma treatment of halide-containing waters to incorporate consideration of Br^- and other constituents (i.e., carbonates, organic matter) occurring in brines alongside Cl^-. We specifically focused on the formation of halogen oxidants mediated by halogen radicals (eqs 2−16) rather than by O (eq 1) because we anticipated that the inclusion of Br^- would play a key role in this mechanism. To this end, we measured the degradation of probe compounds to provide insight into the formation of halogen oxidants in solutions of different chemistries, as well as to evaluate whether halogen radicals reacted with these compounds directly or recombined to form hypohalous acids (Table S1)[60−62,73,76−80] that drove degradation instead. We complemented our experiments with the characterization of reactive species in plasma over solutions with and without halides. We applied our mechanistic insight to evaluate organic compound degradation in the presence of brine constituents, including known competitors for radicals (i.e., carbonates, organic matter).[64,67,68] Overall, our work enables the formation mechanism and reactions of halogen oxidants to be accurately understood in the presence of key additional constituents beyond Cl^- during plasma treatment of contaminated brines.

2. MATERIALS AND METHODS

2.1. Reagents. All chemicals used in this work are listed in the Supporting Information (Table S2). All experimental solutions were prepared in Milli-Q water. Stock solutions of HOCl and HOBr (~1.5−1.6 mM) were prepared from sodium hypochlorite (5−6%) directly or by reacting with a

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

stoichiometric amount of Br^- and standardized spectrophotometrically at 292[81] or 329 nm,[82] respectively.

2.2. Plasma Reactor Setup. The plasma reactor consisted of a flask with two electrodes and a high-voltage power supply, as detailed in Text S2 and Figure S1. To control the headspace pressure and gas composition, the flask was connected to a gas port equipped with a vacuum pump and a gas inlet. An ice bath (4 °C) and a vapor condenser were used to minimize water loss during plasma treatment, which was confirmed to be negligible (Figure S2). Exposure to plasma was found to promote internal mixing (Figure S3), such that mechanical mixing (e.g., a stir bar) was not required. We omitted components required for stirring to avoid additional complexities in the reactor design. Salts found to be deposited on the electrode after plasma treatment of halide-containing solutions were analyzed for composition using a scanning electron microscope (Thermo Fisher Scientific).

We used 99.999% argon (Linde Gas & Equipment, Inc.) as the feed gas in our system. Argon was selected to achieve a high plasma density (i.e., relative to helium)[83] and avoid the formation of reactive nitrogen species (as opposed to nitrogen gas or air).[14] The absence of oxygen in the feed gas is consistent with feed gas compositions previously shown to lead to negligible hypohalous acid formation mediated by O (eq 1),[59] consistent with our goal to investigate pathways mediated by halogen radicals (eqs 2−16). While O-mediated hypohalous acid formation is negligible without oxygen in the feed gas (i.e., <2 ppm_v, Table S2), some O may be generated due to the presence of low amounts of oxygen from other sources (e.g., ambient air, residual air, oxygen impurity in the feed gas).[84] Trace oxygen may also scavenge electrons,[85] but this effect is not expected to be relevant to the processes studied herein.

2.3. Treatment of Solutions by Plasma. To investigate the mechanism by which halides contributed to organic compound degradation, two probe compounds (i.e., benzoate and *para*-hydroxybenzoate) were used during the plasma treatment. Solutions (50 mL) were prepared with 10 mM phosphate buffer (pH 7), 50 μM of each probe compound, and halides at indicated concentrations. In experiments containing both Br^- and Cl^-, Br^- was added at 1 mol % Cl^-, corresponding to molar ratios reported in brines (i.e., 0.1−1 mol %, Table S3).[35,39,41,42,64,65,86−111] When isolating the effect of Cl^- alone, different experiments were performed with both lower-purity (i.e., ≥99.0%, 0.004 mol % Br^-, Text S3[67,112] and Figure S4) and higher-purity (99.999%) Cl^- reagents as indicated in corresponding figures. When Br^- was added, lower-purity Cl^- was used because the trace Br^- in the Cl^- reagent is negligible relative to the added Br^-. Perchlorate (ClO_4^-) was used to control ionic strength. Because conductivity affects reactive species production during plasma exposure,[44,49,50] we confirmed that halide- and ClO_4^--containing solutions at the same ionic strength had comparable solution conductivity (Figure S5). Consequently, controls for ionic strength using ClO_4^- also served to control solution conductivity. Isopropanol (50 mM) was added in specific experiments as a scavenger for radicals.

Prior to all experiments, the system was held at a low pressure (i.e., 25 Torr) for 5 min to degas solutions. Then, the flask headspace was purged three times before being filled with argon at 100 Torr. This subatmospheric pressure was selected to achieve greater radical density during plasma treatment.[113] We confirmed that the degradation of probe compounds at 100 Torr was faster than at atmospheric pressure (i.e., 760 Torr) in both halide- and ClO_4^--containing solutions and that the effect of halides was consistent at both pressures (Figure S6). After exposure to plasma at indicated times, aliquots (each 0.5 mL) were collected by a syringe through a septum. Then, each aliquot was transferred to a 2 mL amber vial, quenched by 5 μL of 0.1 M ascorbic acid, and analyzed for probe compound concentrations. Concentrations of hypohalous acids were measured by sampling 2 mL aliquots either at the end of the experiment (if a single concentration was determined) or at multiple time points in experiments separate from probe compound measurements. All sampling removed <24% of the overall solution volume over the experiment duration.

Additional experiments were performed by further modifying the solution composition. In addition to the probe compounds used above, four organic contaminants (i.e., salicylate, acetaminophen, sulfamethoxazole, anthranilate) were selected based on their different reactivities toward halogen oxidants (Table S4).[62,77,114−119] Like Cl^- and Br^-, additional constituents (i.e., sulfate, SO_4^{2-}; nitrate, NO_3^-; carbonates; organic matter) were added at brine-relevant concentrations (Table S3).[35,39,41,42,64,65,86−111] Some of these constituents have known reactivities with the reactive species of interest (Table S5).[12,64,75,120−128] All salts used in this study contained sodium as the cation. While calcium and magnesium are present in some brines (Table S3),[35,39,41,42,64,65,86−111] these cations were excluded from the present study to avoid precipitation of solids with some anions (i.e., SO_4^{2-} and carbonates).[129−131] When included, carbonates were introduced to the solution using a syringe after the headspace was filled with argon to prevent the loss of carbonates as carbon dioxide during degassing. The ionic strength of all solutions was adjusted to a constant value (2.0 M) using ClO_4^-.

2.4. Analysis of Dissolved Species. The summed concentrations of hypohalous acids (i.e., HOCl and HOBr) were measured by the *N*,*N*-diethyl-phenylenediamine (DPD) colorimetric method[132] using a UV−vis spectrophotometer (Varian Cary) or a Nanodrop (Thermo Fisher Scientific). The total concentrations of hypohalous acids were calculated by standard curves for HOCl or HOBr, which were found to be identical (Figure S7). The concentrations of organic compounds were quantified on an Agilent 1260 Infinity II high-pressure liquid chromatography instrument with UV detection as described in Text S4. The retention times, UV wavelengths, and the limits of detection (LOD) of organic compounds are reported in Table S6.

2.5. Analysis of Species in Plasma by Optical Emission Spectroscopy (OES). To investigate reactive species present in plasma over solutions of different chemistries, analysis using two different OES spectrometers was carried out using a glass vessel with optical windows (quartz) as a custom feature made in the Department of Chemistry at Washington University in St. Louis (modified from the aforementioned reactor design as shown in Figure S1). First, a low-resolution OES spectrometer (Ocean Optics HR4000 CG-UV-NIR) was used to obtain broadband OES spectra (i.e., 200−1100 nm) to identify species with strong emission intensities in plasma. Second, a high-resolution OES spectrometer (Princeton Instruments SpectraPro HRS-750) was used over narrow ranges of wavelengths to observe species with weak emission intensities. The identification of species by each OES spectrometer was achieved by comparing wavelengths to those reported previously (Table S7).[133−136] While OES provides information about the presence of observable

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

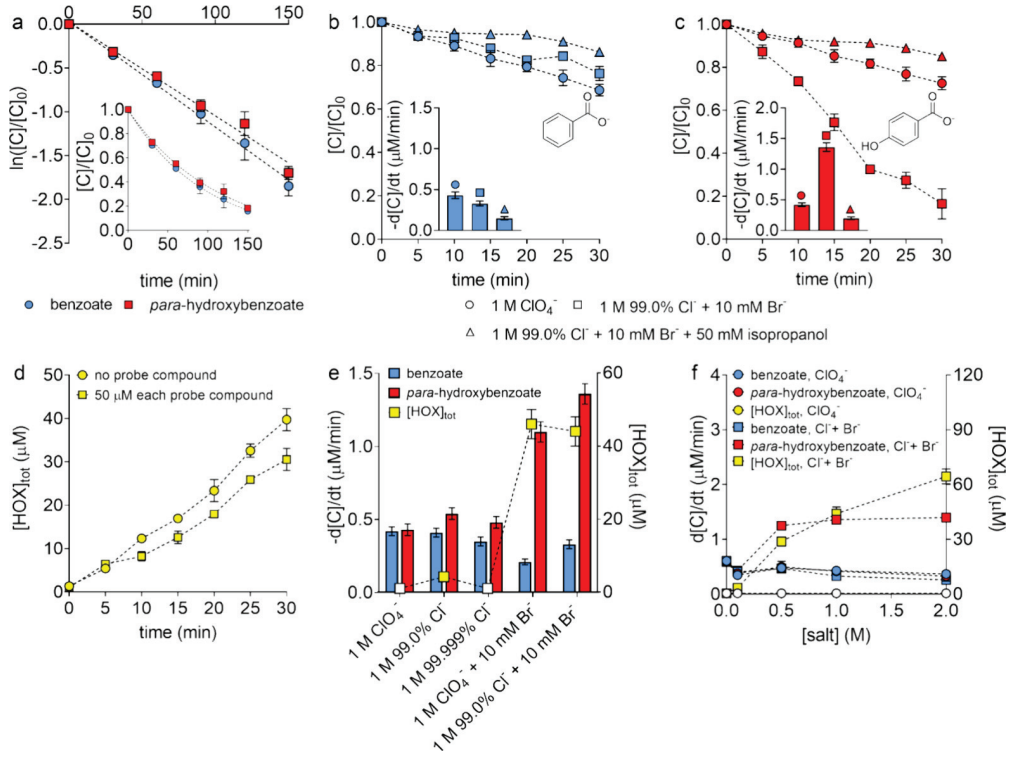


Figure 1. Degradation of probe compounds (i.e., benzoate, *para*-hydroxybenzoate) and formation of hypohalous acids during plasma treatment of solutions with varying chemical constituents (all containing 10 mM phosphate buffer, pH 7). (a) Degradation of benzoate and *para*-hydroxybenzoate (each initially present at 50 μM) in the presence of 1 M ClO_4^-. (b,c) Degradation of (b) benzoate and (c) *para*-hydroxybenzoate in the presence of salts and/or isopropanol. (d) Formation of hypohalous acids in the presence of 1 M Cl^- and 10 mM Br^-. (e) Degradation rates of probe compounds and hypohalous acid concentrations (plotted on the right *y*-axis) in solutions with different halide combinations after plasma treatment for 30 min. For corresponding conditions, results in (e) are from the same experiments used to obtain results presented in (b) and (c), while results presented in (d) were collected independently to reduce the volume of solution removed during the experiments. The measured concentrations of hypohalous acids at 30 min under the same conditions (with probe compounds and halides) in (d) and (e) were not significantly different. (f) Degradation rates of probe compounds and hypohalous acid concentrations (plotted on the right *y*-axis) over 30 min in the presence of ClO_4^- or halides (i.e., Cl^-, purity: 99.0%, with 1 mol % added Br^-); results collected with 1 M salt are reproduced from (b) and (c) for probe compound degradation rates and (e) for hypohalous acid concentration. White squares (in e) and circles (in f) represent measurements below the LOD ($[HOX]_{tot}$ = 0.8 μM). Errors in concentrations represent the range of measurements from duplicate experiments, while errors in degradation rates represent the standard errors on the slopes obtained from linear regression.

species, it does not directly provide information about species concentrations in plasma.

2.6. Statistical Analysis. All experiments were conducted in duplicate. Errors in concentrations represent the range of measurements from duplicate experiments, while errors in degradation rate constants and rates represent the standard errors on the slopes obtained from linear regression. The significance of differences was evaluated using GraphPad Prism with a confidence level set to be $\leq$0.05.

3. RESULTS AND DISCUSSION

3.1. Effects of Halides on Probe Compound Degradation. We first evaluated whether halogen oxidants were generated during plasma treatment of solutions containing mixed halides (i.e., 1 M Cl^- along with 10 mM Br^-). In addition to the chlorine-relevant species (i.e., $Cl^{\bullet}$, $Cl_2^{\bullet-}$, HOCl) invoked in prior studies,[45,54−56] Br^- is also expected to enable the formation of bromine-relevant radicals (i.e., $Br^{\bullet}$, $Br_2^{\bullet-}$), mixed halogen radicals (i.e., $ClBr^{\bullet-}$), and HOBr.[66] To this end, we compared the degradation rates of two probe compounds, benzoate and *para*-hydroxybenzoate, selected due to their reported bimolecular rate constants with both chlorine and bromine species (Table S4).[62,77,114−117] In the absence of halides, both probe compounds were expected to degrade at similar rates due to their similar rate constants for reactions with common species generated by plasma (e.g., $^{\bullet}OH$, e_{aq}^-, $H^{\bullet}$, Table S4).[137−141] In contrast, if halogen oxidants were formed in the presence of halides, *para*-hydroxybenzoate was expected to degrade more quickly than benzoate, corresponding to its substantially higher bimolecular rate constants with both halogen radicals[115−117] and hypohalous acids.[62,114]

In the absence of halides, benzoate and *para*-hydroxybenzoate degraded at similar rates in a solution with 1 M ClO_4^- added to increase the ionic strength (Figure 1a). Consistent with the reported kinetics of other organic compounds treated by plasma,[7,13,15,26,30,44] the degradation of both compounds followed pseudo-first-order kinetics, resulting in rate constants of 0.0121 ± 0.0007 and 0.0108 ± 0.0006 min^{-1} for the degradation of benzoate and *para*-hydroxybenzoate, respectively (Figure 1a). To determine the effect of ionic strength in our reactor, we measured probe compound degradation in solutions without ClO_4^-, finding that each rate constant increased by 40−50% (i.e., to 0.017 ± 0.001 min^{-1} for benzoate and 0.016 ± 0.001 min^{-1} for *para*-hydroxybenzoate (Figure S8). This result suggested that the ionic strength and conductivity in our reactor slightly suppressed probe

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

compound degradation, but reactive species with comparable reactivities toward both compounds (i.e., $^{\bullet}OH$, Table S4)[137,138] dominated the reaction regardless of ionic strength.

Consistent with our hypothesis, the addition of halides (i.e., 1 M Cl^- and 10 mM Br^-) marginally affected benzoate degradation (Figure 1b) but accelerated *para*-hydroxybenzoate degradation (Figure 1c). However, before proceeding with quantitative analysis of these effects, we were first required to address our observation that the kinetics of *para*-hydroxybenzoate degradation in the presence of halides appeared to deviate from pseudo-first-order kinetics (Figure 1c). Additional residual analysis supported our observation that unlike the probe compound degradation in the presence of ClO_4^-, *para*-hydroxybenzoate degradation in the presence of halides more closely followed zero-order kinetics (Figure S9). Because benzoate was degraded by <20% over the same time frame in the presence of halides, analysis of the reaction order was not attempted. To facilitate comparisons among probe compound degradation in different chemistries that alter the reaction order, we opted to report observed zero-order degradation rates of each compound during the first 30 min of exposure to plasma (Figure 1b,c). Using this approach, we determined that the degradation rate of benzoate was not significantly impacted by replacing ClO_4^- with halides, while the degradation rate of *para*-hydroxybenzoate was increased by 3-fold.

In addition to affecting our quantitative analysis, the degradation of *para*-hydroxybenzoate by observed zero-order kinetics also enabled us to evaluate the potential for each class of halogen oxidants (i.e., halogen radicals or hypohalous acids) to contribute directly (i.e., as opposed to acting as intermediates) to the accelerated rate in the presence of halides. If halogen radicals directly reacted with *para*-hydroxybenzoate, we expected that the reaction would follow pseudo-first-order kinetics, consistent with organic compound degradation in UV/oxidant AOP treatment of halide-containing waters.[67,68,142] Therefore, we instead hypothesized that hypohalous acids, which form from the recombination of radical species,[66] reacted with *para*-hydroxybenzoate. Our hypothesis was based on the observation that the overall concentration of hypohalous acids, both in the absence and presence of probe compounds, increased as the solution exposure to plasma increased (Figure 1d), which might allow the reaction rate to be maintained even as *para*-hydroxybenzoate concentration diminished.

To determine if the increasing amount of hypohalous acids was quantitatively consistent with the observed zero-order kinetics of *para*-hydroxybenzoate, we analyzed the instantaneous rate of *para*-hydroxybenzoate loss at each time point using the following equation:

$$-\mathrm{d[C]}/\mathrm{d}t = k_{\mathrm{C,HOCl}}[\mathrm{HOCl}][\mathrm{C}] + k_{\mathrm{C,HOBr}}[\mathrm{HOBr}][\mathrm{C}] \quad (17)$$

where [C] represents the measured concentration of *para*-hydroxybenzoate (Figure 1c in the presence of halides), t represents the duration of exposure to plasma, $k_{\mathrm{C,HOCl}}$ and $k_{\mathrm{C,HOBr}}$ represent the apparent bimolecular rate constant between *para*-hydroxybenzoate and each hypohalous acid (either found in or estimated from the literature, Text S5 and Table S4),[77,114] and [HOCl] and [HOBr] represent the concentrations of HOCl and HOBr, respectively. Reactions involving the conjugate bases of HOCl and HOBr were assumed to be negligible due to both their lower concentrations at the experimental pH and their slower reactivities toward substituted aromatics.[77,143]

To further simplify this equation, we defined the term f_{HOCl} as the fraction of hypohalous acid present as HOCl (i.e., $f_{\mathrm{HOCl}} = [\mathrm{HOCl}]/[\mathrm{HOX}]_{\mathrm{tot}}$, where $[\mathrm{HOX}]_{\mathrm{tot}}$ is the total concentration of hypohalous acids). Then, [HOCl] and [HOBr] in eq 17 were substituted with $f_{\mathrm{HOCl}}[\mathrm{HOX}]_{\mathrm{tot}}$ and $(1 - f_{\mathrm{HOCl}})[\mathrm{HOX}]_{\mathrm{tot}}$, respectively, to generate

$$-\mathrm{d[C]}/\mathrm{d}t = [k_{\mathrm{C,HOCl}} f_{\mathrm{HOCl}} + k_{\mathrm{C,HOBr}}(1 - f_{\mathrm{HOCl}})][\mathrm{HOX}]_{\mathrm{tot}}[\mathrm{C}] \quad (18)$$

Due to the constant pH and near-constant concentrations of Cl^- and Br^-, f_{HOCl} is expected to be approximately constant during the experiment.[77] Consequently, *para*-hydroxybenzoate is calculated to degrade upon reactions with hypohalous acids following observed zero-order kinetics (i.e., $\mathrm{d[C]}/\mathrm{d}t$ is constant) if the multiplication product of the concentrations of *para*-hydroxybenzoate and total hypohalous acids (i.e., $[\mathrm{HOX}]_{\mathrm{tot}}[\mathrm{C}]$) is nearly constant. When we calculated this term using experimental concentrations of *para*-hydroxybenzoate (Figure 1c, condition: with halides) and hypohalous acids (Figure 1d, condition: with probe compounds), we found that the value of $[\mathrm{HOX}]_{\mathrm{tot}}[\mathrm{C}]$ did not vary during the experimental period (i.e., a slope of 0 ± 2 μM^2/min, Figure S10), consistent with the observed zero-order kinetics of *para*-hydroxybenzoate degradation.

In addition to confirming that measured hypohalous acid concentrations were consistent with the observed reaction order, we also evaluated if the amount of hypohalous acids measured in our system could feasibly account for the observed rate of *para*-hydroxybenzoate degradation using bimolecular rate constants available or estimated from literature.[77,114] Assuming all hypohalous acid was present as HOCl (i.e., $f_{\mathrm{HOCl}} = 1$), the calculated *para*-hydroxybenzoate degradation rate (i.e., 0.22 ± 0.09 μM/min, Figure S11) is lower than but within the same order of magnitude as the measured rate (i.e., 1.36 ± 0.07 μM/min, Figure 1c). Conversely, if HOBr is assumed to be exclusively present (i.e., $f_{\mathrm{HOCl}} = 0$), the calculated rate (i.e., 900 ± 400 μM/min, Figure S11) is >2 orders of magnitude higher than the measured rate. Because HOBr has been modeled to occur at higher concentrations than HOCl in seawater containing 0.0015 mol Br^-/mol Cl^-,[144] HOBr is expected to also dominate in our system, which has both higher halide concentrations and Br^-/Cl^- ratio. Consequently, our measured $[\mathrm{HOX}]_{\mathrm{tot}}$, if present primarily as HOBr, overpredicts the observed degradation rate of *para*-hydroxybenzoate, possibly due to an overestimation of the bimolecular rate constant between *para*-hydroxybenzoate and HOBr (Table S4). Recently, reactions with organic compounds involving previously overlooked species (e.g., Br_2O, Br_2) have been found to contribute to rate constants for reactions attributed to HOBr being overestimated by similar orders of magnitude.[145,146] While re-evaluation of this bimolecular rate constant is beyond the scope of this work, our analysis with currently available values suggests that hypohalous acids are present at sufficient concentrations, if not in excess, to account for the observed rate of *para*-hydroxybenzoate degradation.

While our results are consistent with hypohalous acids acting as the primary species directly reacting with *para*-hydroxybenzoate to accelerate its degradation in the presence of halides, we still hypothesized that radicals (i.e., $^{\bullet}OH$, halogen

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

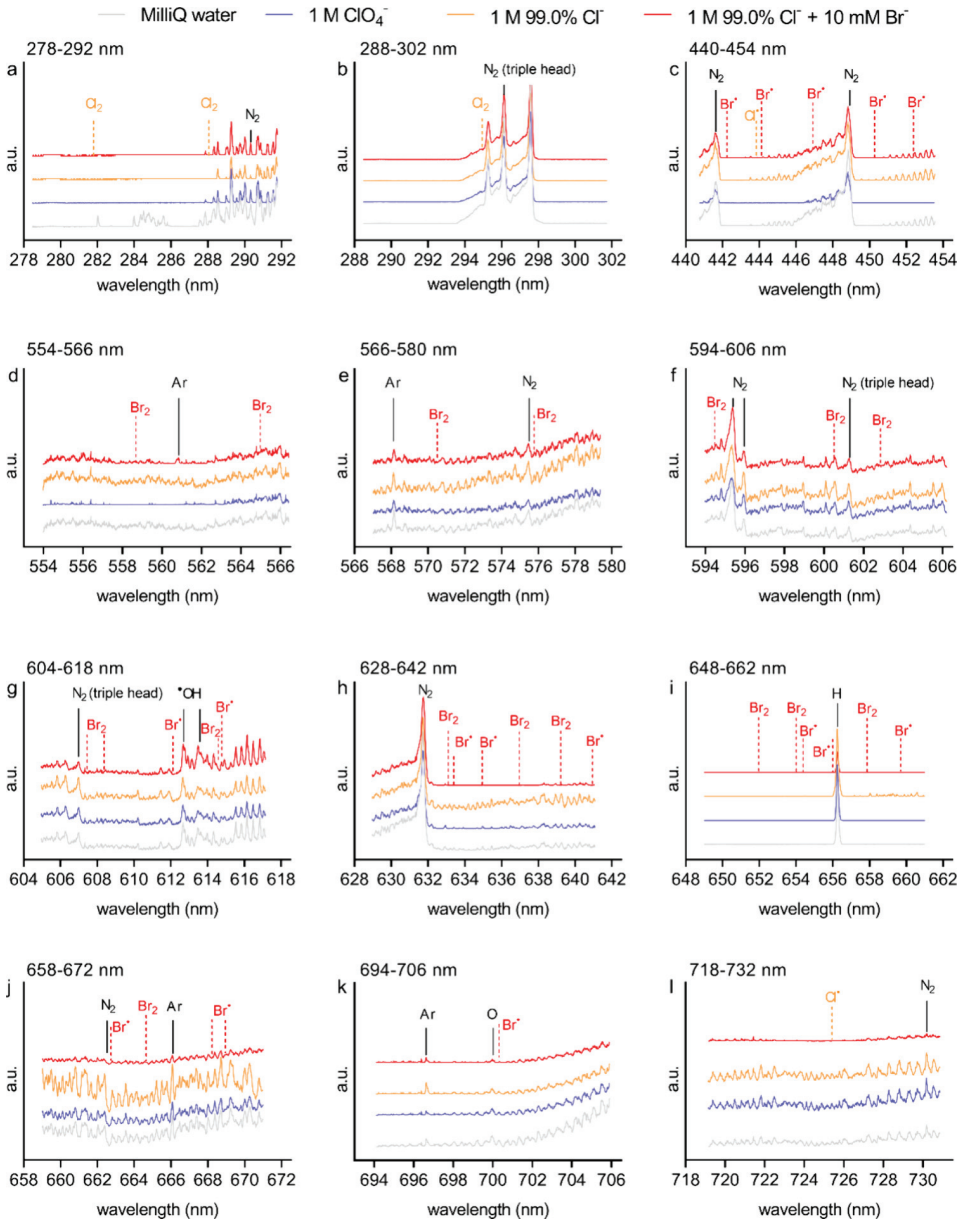


Figure 2. High-resolution OES spectra at selected wavelengths from 278 to 732 nm in plasma over either Milli-Q water or solutions containing salts. Solutions containing salts also contained 10 mM phosphate buffer (pH 7) and 50 μM each of benzoate and *para*-hydroxybenzoate. The black solid lines indicate wavelengths where oxygen, nitrogen, and argon species were identified. The orange and red dashed lines indicate wavelengths where halogen radicals and molecular halogens were previously reported (Table S7)[133,134] but not identified in this study.

radicals) act as intermediates that go on to form hypohalous acids via recombination reactions.[66] To test this hypothesis, we repeated our experiments in solutions including 50 mM isopropanol, a known scavenger of both $^{\bullet}OH$ (i.e., $k_{isopropanol,^{\bullet}OH} = 1.9 \times 10^9\ M^{-1}\ s^{-1}$)[12] and halogen radicals (e.g., $k_{isopropanol,Cl_2^{\bullet-}} = 1.2 \times 10^5\ M^{-1}\ s^{-1}$,[115] $k_{isopropanol,Br^{\bullet}} = 6.6 \times 10^6\ M^{-1}\ s^{-1}$).[73] In addition, isopropanol is not expected to quench hypohalous acids directly due to slow reported rate constants (e.g., $k_{isopropanol,HOBr} < 3.9 \times 10^{-4}\ M^{-1}\ s^{-1}$),[147] which we confirmed by demonstrating that isopropanol did not impact *para*-hydroxybenzoate degradation by hypohalous acids added directly as HOCl to halide-containing solutions (Figure S12). The addition of isopropanol to halide-containing solutions decreased the degradation rate of *para*-hydroxybenzoate to 0.20 ± 0.02 μM/min, which was 6-fold lower than the rate measured in halide-containing solutions without isopropanol (Figure 1c). Consistent with our proposed pathway of hypohalous acid formation from radical recombination, we determined that the addition of isopropanol reduced the concentration of hypohalous acids after plasma treatment to below their LOD (Figure S13).

The above evidence supports our expectation that our plasma system generates hypohalous acids through a radical-mediated pathway (i.e., recombination of halogen radicals formed from halide oxidation by $^{\bullet}OH$) in solutions containing Cl^- and Br^- together. This pathway has been invoked previously to explain results obtained during plasma treatment of solutions containing Cl^- as the sole halide,[45,54−56] which contradicts prior work that suggests Cl^- oxidation by $^{\bullet}OH$ is negligible.[66] This discrepancy was possibly due to a trace

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

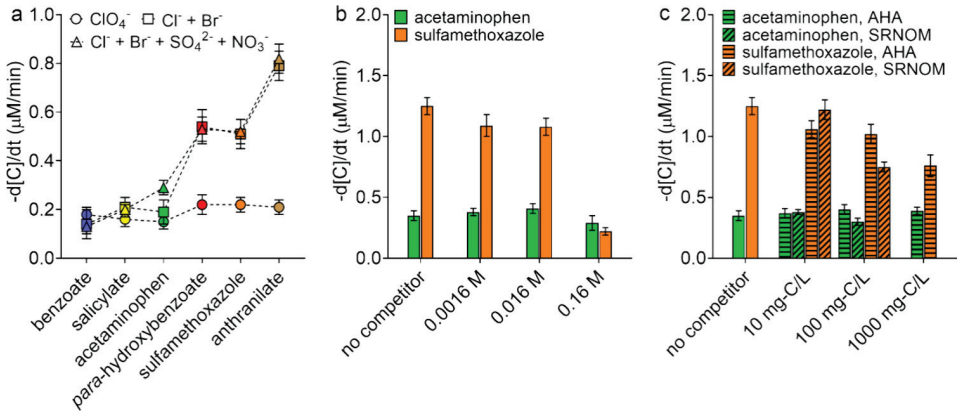


Figure 3. Degradation rates of selected compounds during plasma treatment of solutions with additional brine constituents. All solutions contained 10 mM phosphate buffer (pH 7) and had an ionic strength adjusted to 2.0 M by ClO_4^-. (a) Degradation rates of benzoate, salicylate, acetaminophen, *para*-hydroxybenzoate, sulfamethoxazole, and anthranilate (each initially present at 50 μM) in the presence of salts. The concentrations of Cl^-, Br^-, SO_4^{2-}, and NO_3^-, when present, were 1 M, 10 mM, 0.25 M, and 0.08 M, respectively. (b,c) Degradation rates of acetaminophen and sulfamethoxazole (each initially present at 50 μM) in the presence of (b) carbonates or (c) organic matter (i.e., Aldrich humic acid, AHA; Suwannee River natural organic matter, SRNOM). All solutions in (b) and (c) initially contained Cl^-, Br^-, SO_4^{2-}, and NO_3^- at concentrations that are used in (a). The data in (b) and (c) for the degradation rates of acetaminophen and sulfamethoxazole in the absence of competitors were obtained from the same experiments. Errors on degradation rates represent the standard errors on the slopes obtained from linear regression.

amount of Br^- impurity occurring in the Cl^- reagent, which has previously been implicated in halogen radical formation.[67,68] We found that the inclusion of 1 M Cl^- added as a low-purity reagent (i.e., ≥99.0% with 0.004 mol % Br^-) increased the degradation rate of *para*-hydroxybenzoate by 22 ± 9% relative to the ionic strength control (p = 0.02, Figure 1e). In contrast, the inclusion of 1 M Cl^- added as a high-purity reagent (i.e., 99.999%) did not increase the rate relative to that of the control (Figure 1e). Similarly, hypohalous acid concentrations after treatment for 30 min were measurable in solutions prepared with low-purity Cl^- (i.e., 4.2 ± 0.8 μM) but below the LOD (i.e., 0.8 μM) in solutions prepared with either ClO_4^- or high-purity Cl^- (Figure 1e). These results suggest that plasma treatment of solutions containing Cl^- as the sole halide is unlikely to generate hypohalous acids via a radical-mediated pathway as well as indicate that a trace amount of Br^- impurity, which varies in magnitude among Cl^- reagents, may contribute to some effects previously attributed to Cl^- alone during plasma treatment.

While the effect of 1 M Cl^- as the sole halide was negligible in our system, the inclusion of 10 mM Br^- (along with 1 M ClO_4^- to control the ionic strength) affected both compound degradation and hypohalous acid formation to similar extents with or without 1 M Cl^- present (Figure 1e). The degradation rate of *para*-hydroxybenzoate in the Br^--only solution was 81 ± 7% of the rate when Br^- and Cl^- were present together, and the concentration of hypohalous acid was indistinguishable between the two solutions after 30 min of exposure to plasma. In $^{\bullet}OH$-initiated pathways, lower concentrations of Br^- alone (i.e., 0.001−0.1 mM) have been previously reported to negligibly affect downstream reactions,[142,148,149] whereas higher concentrations of Br^- alone (i.e., 1 mM) accelerated organic compound degradation.[149] Consistent with these findings, the elevated Br^- concentration used in our study (10 mM, corresponding to 1 mol % Cl^-) appears to be sufficient to account for the halide-dependent reactions in our plasma system regardless of the presence of Cl^-.

Though the amount of Br^- compared to Cl^- is relatively consistent in brines (i.e., 0.1−1 mol % Br^-, Table S3), the absolute concentrations of halides vary substantially (e.g., 0.007−2 M Cl^-, Table S3).[35,39,41,42,64,65,86−111] Therefore, we expanded our experiments to evaluate the effect of halides at different concentrations but at a constant ratio of Br^- to Cl^- (i.e., 0.1−2 M Cl^- with 1 mol % Br^-). The inclusion of halides at concentrations higher than 0.5 M Cl^- and 5 mM Br^- increased the degradation rate of *para*-hydroxybenzoate by 2- to 4-fold relative to ClO_4^- at the same ionic strength and conductivity (Figure 1f). We also observed hypohalous acid formation across all tested halide concentrations (Figure 1f). Both the acceleration of *para*-hydroxybenzoate degradation and hypohalous acid formation increased to lesser degrees upon increasing the addition of halides at high concentrations, possibly due to other limitations (e.g., $^{\bullet}OH$ generation by plasma).

3.2. Effects of Halides on Reactive Species in Plasma.

We next investigated reactive species in plasma using both low-resolution OES (Figure S14) and high-resolution OES (Figure 2 and Figure S15). Consistent with our proposed mechanism to generate halogen oxidants from halide oxidation by $^{\bullet}OH$ (eqs 2−16), we detected the presence of $^{\bullet}OH$ in plasma by both the low-resolution and high-resolution OES above all solutions regardless of the presence of halides or ionic strength (Figures S14 and S15 and Table S7). Although our feed gas did not include oxygen in amounts required to generate hypohalous acids from O (eq 1),[59] O was also detected by high-resolution OES (Figure 2k, Table S7), though not by low-resolution OES (Figure S14). The presence of O in plasma has been previously observed even when oxygen was not added in the feed gas.[84]

The collected OES spectra also afforded us the opportunity to determine if halogen species (i.e., $Cl^{\bullet}$, $Br^{\bullet}$, as well as molecular halogens, i.e., Cl_2, Br_2) could be detected in the plasma phase during treatment of halide-containing solutions. In addition to their possible generation at the interface of the plasma and liquid in our reactor,[8] we also noticed evidence that halide-containing aerosols, which may allow heterogeneous oxidation of halides by $^{\bullet}OH$ at their interface,[150−152] were generated in our system during plasma treatment.

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

Specifically, we noted salt deposition on the electrode after plasma treatment, which we determined to be primarily composed of sodium chloride (Figures S16 and S17) likely transferred to the electrode by aerosols generated during plasma exposure.[8] Using low-resolution OES, we also observed a large sodium (Na) peak above solutions containing either halides (i.e., 1 M Cl^- and 10 mM Br^-) or 1 M ClO_4^-, suggesting that salts in solutions may generate plasma species (Figure S14). However, no halogen species were detected in the plasma regardless of the presence of halides (Figure 2, Table S7), suggesting either that these species were present below their LOD (which could not be quantified for the OES) or that halogen oxidants were primarily confined to the liquid phase of the reactor.

3.3. Effects of Brine Constituents on Organic Contaminant Degradation. We expanded our experiments to include four organic contaminants selected due to their reported bimolecular rate constants toward hypohalous acids, which span orders of magnitude (Table S4).[62,77,114,119] In the ionic strength control, all contaminants degraded at rates comparable to the probe compounds (Figure 3a), in agreement with their similar bimolecular rate constants toward species generated by plasma in the absence of halides (e.g., $^{\bullet}OH$, e_{aq}^-, Table S4).[137−139,153−156] The addition of halides selectively accelerated the degradation of two contaminants (i.e., sulfamethoxazole, anthranilate) to extents similar to or greater than *para*-hydroxybenzoate (Figure 3a); like *para*-hydroxybenzoate, the accelerated degradation of these contaminants (e.g., anthranilate) also followed zero-order kinetics (Figure S18). The acceleration of degradation rates of the compounds upon halide addition correlated with their reactivity toward hypohalous acids, which occurred at measurable concentrations (i.e., 35 ± 5 μM after 30 min of exposure to plasma, Figure S19). Specifically, the bimolecular rate constants for the reactions of five of the six compounds with HOCl (available for all compounds, Table S4,[62,114] which typically trend with rate constants for reactions with HOBr)[77] correlated with greater degradation rates (Figure 3a). The bimolecular rate constants involving HOBr, which have only been reported for three of these compounds (Table S4),[77,119] may explain the one exception: acetaminophen, which did not undergo faster degradation upon halide addition despite reacting with HOCl with a rate constant comparable to *para*-hydroxybenzoate,[62,114] reacts more slowly with HOBr (Table S4).[77,119]

We next evaluated the impact of additional constituents reported to occur in brines (Table S3)[35,39,41,42,64,65,86−111] on the degradation of these compounds in the presence of halides, beginning with two species, SO_4^{2-} and NO_3^-, not expected to affect our proposed pathway. Neither SO_4^{2-} nor NO_3^- scavenges $^{\bullet}OH$ (Table S5);[122,123] though NO_3^- reacts with e_{aq}^- (Table S5),[126] e_{aq}^- is not invoked in the radical-mediated generation of hypohalous acids. Consistent with our expectation, both degradation rates of organic compounds (Figure 3a) and hypohalous acid concentrations (Figure S19) were comparable in the presence of these anions at their median concentrations reported in brines (i.e., 0.25 M SO_4^{2-}, 0.08 M NO_3^-, Table S3).[35,39,41,42,64,65,86−111]

Among the four contaminants, we selected one exhibiting accelerated degradation in the presence of halides and one not (sulfamethoxazole and acetaminophen, respectively) for additional experiments involving brine constituents expected to impact our pathway, beginning with carbonates. Carbonates (i.e., bicarbonate, HCO_3^-; carbonate, CO_3^{2-}) react with both $^{\bullet}OH$ and halogen radicals to produce carbonate radicals ($CO_3^{\bullet-}$, Table S5).[12,120,121,124] $CO_3^{\bullet-}$ reacts rapidly with both contaminants (i.e., $k_{acetaminophen,CO_3^{\bullet-}}$ = 1.9 × 10^9 M^{-1} s^{-1}, $k_{sulfamethoxazole,CO_3^{\bullet-}}$ = 4.4 × 10^8 M^{-1} s^{-1}).[157] However, the scavenging of halogen radicals by carbonates[68] is expected to reduce the formation of hypohalous acids, thereby suppressing resultant contaminant degradation. In the presence of halides without carbonates, the degradation rates of both acetaminophen and sulfamethoxazole were 2-fold higher when isolated as a pair of compounds (Figure 3b) than when present with the four other compounds (Figure 3a); this increase is attributable to the reduced competition for reactive species that also lead to 1.5-fold higher hypohalous acid concentration (i.e., 51 ± 2 μM after 30 min, Figure S20). While the addition of carbonates did not alter the degradation rate of acetaminophen, the degradation rate of sulfamethoxazole was reduced by 6-fold when carbonates were added at 0.16 M (Figure 3b). The addition of carbonates also reduced the formation of hypohalous acids; their measured concentration decreased to 1.5 ± 0.5 μM after solution exposure to plasma for 30 min in the presence of 0.16 M carbonates (Figure S20).

Organic matter is another brine constituent expected to inhibit our proposed pathway due to its known reactions with both radicals (e.g., $^{\bullet}OH$, Table S5)[64,125] and hypohalous acids (Table S5).[75] The addition of organic matter (i.e., Aldrich humic acid, AHA; Suwannee River natural organic matter, SRNOM) to halide-containing solutions did not impact the degradation of acetaminophen but decreased the degradation rate of sulfamethoxazole (Figure 3c). Relative to UV/oxidant AOPs, a higher concentration of organic matter was required to suppress contaminant degradation to a comparable extent during plasma treatment. For example, while the addition of organic matter at 100 mg C/L only decreased the degradation rate of sulfamethoxazole by 19−40% during plasma treatment (Figure 3c), the addition of organic matter at a lower concentration (i.e., 36 mg C/L) to saline waters decreased pharmaceutical degradation by 60−90% during treatment by UV/oxidant AOPs.[64]

3.4. Environmental Implications. In this work, we demonstrated that Br^-, despite occurring only at low concentrations relative to Cl^- in brines, plays a crucial role during plasma treatment of halide-containing solutions. Our finding is consistent with prior work demonstrating that the generation of halogen radicals via halide oxidation by $^{\bullet}OH$ requires Br^- to be present along with Cl^- (Table S1).[66] The dependency of halogen radical formation on the presence of Br^- may be harnessed in future applications to distinguish hypohalous acid formation via halogen radicals from their formation mediated by O, which was reported to require only Cl^- (eq 1),[57−59] in plasma reactors wherein both pathways are feasible. In these applications, the potential for trace Br^- occurring in Cl^- reagents to enable halogen radical formation must be considered, as previously demonstrated for UV/oxidant AOPs.[67,68] Furthermore, the unique role of Br^- must be accounted for when translating prior studies on plasma treatment in Cl^--only solutions[45,54−56] to more complex chemistries occurring in brines, as well as other halide-containing solutions (i.e., blood serum)[158] exposed to plasma.[159]

Whereas the degradation of organic compounds in halide-containing solutions during UV/oxidant AOP treatment is

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

typically attributable to their reactions with halogen radicals,[67,68,142] the plasma system is unique because organic compounds are primarily degraded due to reactions with hypohalous acids, which are generated by the recombination of halogen radicals.[66] A possible cause for this difference is that the generation of radical species during plasma treatment primarily occurs at the plasma−water interface,[8] potentially leading to localized regions of high radical concentrations that accelerate the recombination reactions. Beyond determining the kinetics of compound degradation, the formation of hypohalous acids during plasma treatment is relevant if applications of plasma for disinfection[160−163] are expanded to systems wherein halides are present. In addition, the formation of hypohalous acids potentially leads to the generation of halogenated byproducts,[164,165] though these byproducts may also undergo dehalogenation by reductive species[31−33] generated by plasma.

By elucidating the distinct roles of both radicals and hypohalous acids in organic contaminant degradation during plasma treatment of halide-containing waters, our work also informs a more accurate consideration of the impact of other brine constituents on these reactions. Only constituents with known reactions with radicals and/or hypohalous acids (i.e., carbonates and organic matter, as opposed to SO_4^{2-} and NO_3^-) suppressed contaminant degradation. The ability of carbonates to prevent hypohalous acid formation by scavenging halogen radicals[68] appeared to dominate over the potential for $CO_3^{\bullet-}$ to itself contribute to contaminant degradation,[157,166] resulting in slower degradation rates. Hypohalous acids formed during plasma treatment may also be less susceptible to scavenging by organic matter than radicals (Table S5),[64,75,125] contributing to smaller reductions in contaminant degradation than reported in UV/oxidant AOPs.[64]

Our results also impact approaches that enable plasma systems to be compared to other technologies for brine treatment. A typical basis for comparison is energy consumption, which has been quantified as the electrical energy required per order of magnitude compound degradation (E_{EO}) using pseudo-first-order rate constants.[167] In the presence of ClO_4^-, we calculated the E_{EO} of probe compounds based on their pseudo-first-order degradation rate constants (Figure 1a). Using the total power output (i.e., 15 W) and the solution volume (i.e., 0.05 L), the E_{EO} for probe compounds ranged from 950 to 1,070 kWh/m^3 per order, which was within the same order of magnitude as previously reported E_{EO} for pharmaceutical degradation during plasma treatment (i.e., 10^3−10^4 kWh/m^3).[44] However, our results demonstrate that this approach is unsuitable as a basis to compare plasma technologies, both among different plasma reactors and to other treatment technologies, e.g., UV/oxidant AOPs, for brine treatment due to the impact of halides on the reaction order. Instead, energy cost calculations for brine treatment by plasma must account for complexities arising from the nonsteady-state concentrations of hypohalous acids generated during plasma exposure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c07162.

Chemical sources, brine constituents, compound selection, analytical methods, supporting results, and data analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Kimberly M. Parker − *Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States;* orcid.org/0000-0002-5380-8893; Phone: 314-935-3461; Email: kmparker@wustl.edu

Authors

Moshan Chen − *Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States;* orcid.org/0000-0002-7393-6921

Dillon Moher − *Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States;* orcid.org/0000-0002-3123-4518

Jacqueline Rogers − *Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States;* orcid.org/0000-0003-3367-4039

Shurik Yatom − *Princeton Plasma Physics Laboratory, Princeton University, Princeton, New Jersey 08540, United States*

Elijah Thimsen − *Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.3c07162

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the U.S. National Science Foundation (ECO−CBET 2033714) and Princeton Collaborative Research Facility (pcrf.princeton.edu), which is supported by the U.S. Department of Energy (DOE) under Contract No. DE-AC02-09CH11466. We thank Dr. Trey Oldham and Dr. Xiaoshuang Chen for training in plasma operation, Dr. Daniel Giammar for providing some chemicals, Dr. Yinjie Tang and Dr. Marcus Foston for access to the UV−vis spectrophotometer and conductivity meter, respectively, and Brent Dummitt for making the custom glass vessel. We thank the Institute of Materials Science and Engineering at Washington University in St. Louis for the use of the material characterization facility.

■ REFERENCES

(1) Rezaei, F.; Vanraes, P.; Nikiforov, A.; Morent, R.; De Geyter, N. Applications of Plasma-Liquid Systems: A Review. *Materials.* **2019**, *12* (17), 2751.

(2) Foster, J. E. Plasma-Based Water Purification: Challenges and Prospects for the Future. *Phys. Plasmas* **2017**, *24* (5), No. 055501.

(3) Wang, X.; Zhou, M.; Jin, X. Application of Glow Discharge Plasma for Wastewater Treatment. *Electrochim. Acta* **2012**, *83*, 501−512.

(4) Zeghioud, H.; Nguyen-Tri, P.; Khezami, L.; Amrane, A.; Assadi, A. A. Review on Discharge Plasma for Water Treatment: Mechanism,

Reactor Geometries, Active Species and Combined Processes. *J. Water Process Eng.* **2020**, *38*, No. 101664.
(5) Foster, J.; Sommers, B. S.; Gucker, S. N.; Blankson, I. M.; Adamovsky, G. Perspectives on the Interaction of Plasmas with Liquid Water for Water Purification. *IEEE Trans. Plasma Sci.* **2012**, *40* (5), 1311−1323.
(6) Sharma, A. K.; Josephson, G. B.; Camaioni, D. M.; Goheen, S. C. Destruction of Pentachlorophenol Using Glow Discharge Plasma Process. *Environ. Sci. Technol.* **2000**, *34* (11), 2267−2272.
(7) Stratton, G. R.; Dai, F.; Bellona, C. L.; Holsen, T. M.; Dickenson, E. R. V.; Mededovic Thagard, S. Plasma-Based Water Treatment: Efficient Transformation of Perfluoroalkyl Substances in Prepared Solutions and Contaminated Groundwater. *Environ. Sci. Technol.* **2017**, *51* (3), 1643−1648.
(8) Bruggeman, P. J.; Kushner, M. J.; Locke, B. R.; Gardeniers, J. G. E.; Graham, W. G.; Graves, D. B.; Hofman-Caris, R. C. H. M.; Maric, D.; Reid, J. P.; Ceriani, E.; Fernandez Rivas, D.; Foster, J. E.; Garrick, S. C.; Gorbanev, Y.; Hamaguchi, S.; Iza, F.; Jablonowski, H.; Klimova, E.; Kolb, J.; Krcma, F.; Lukes, P.; MacHala, Z.; Marinov, I.; Mariotti, D.; Mededovic Thagard, S.; Minakata, D.; Neyts, E. C.; Pawlat, J.; Petrovic, Z. L.; Pflieger, R.; Reuter, S.; Schram, D. C.; Schröter, S.; Shiraiwa, M.; Tarabová, B.; Tsai, P. A.; Verlet, J. R.R.; Von Woedtke, T.; Wilson, K. R.; Yasui, K.; Zvereva, G. Plasma-Liquid Interactions: A Review and Roadmap. *Plasma Sources Sci. Technol.* **2016**, *25* (5), No. 053002.
(9) Tachibana, K.; Nakamura, T. Comparative Study of Discharge Schemes for Production Rates and Ratios of Reactive Oxygen and Nitrogen Species in Plasma Activated Water. *J. Phys. D. Appl. Phys.* **2019**, *52* (38), 385202.
(10) Zhang, X.; Zhou, R.; Bazaka, K.; Liu, Y.; Zhou, R.; Chen, G.; Chen, Z.; Liu, Q.; Yang, S.; Ostrikov, K. Quantification of Plasma Produced OH Radical Density for Water Sterilization. *Plasma Process. Polym.* **2018**, *15* (6), 1700241.
(11) Franclemont, J.; Fan, X.; Thagard, S. M. Physicochemical Mechanisms of Plasma-Liquid Interactions within Plasma Channels in Liquid. *Appl. Phys.* **2015**, *48* (42), No. 424004.
(12) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals ($^{\bullet}OH/^{\bullet}O^{-}$) in Aqueous Solutions. *J. Phys. Chem. Ref. Data* **1988**, *17* (2), 513−886.
(13) Wardenier, N.; Gorbanev, Y.; Van Moer, I.; Nikiforov, A.; Van Hulle, S. W. H.; Surmont, P.; Lynen, F.; Leys, C.; Bogaerts, A.; Vanraes, P. Removal of Alachlor in Water by Non-Thermal Plasma: Reactive Species and Pathways in Batch and Continuous Process. *Water Res.* **2019**, *161*, 549−559.
(14) Magureanu, M.; Bradu, C.; Parvulescu, V. I. Plasma Processes for the Treatment of Water Contaminated with Harmful Organic Compounds. *Appl. Phys.* **2018**, *51* (31), 313002.
(15) Sarangapani, C.; Misra, N. N.; Milosavljevic, V.; Bourke, P.; O'Regan, F.; Cullen, P. J. Pesticide Degradation in Water Using Atmospheric Air Cold Plasma. *J. Water Process Eng.* **2016**, *9*, 225−232.
(16) Banaschik, R.; Jablonowski, H.; Bednarski, P. J.; Kolb, J. F. Degradation and Intermediates of Diclofenac as Instructive Example for Decomposition of Recalcitrant Pharmaceuticals by Hydroxyl Radicals Generated with Pulsed Corona Plasma in Water. *J. Hazard. Mater.* **2018**, *342*, 651−660.
(17) Magureanu, M.; Piroi, D.; Mandache, N. B.; David, V.; Medvedovici, A.; Bradu, C.; Parvulescu, V. I. Degradation of Antibiotics in Water by Non-Thermal Plasma Treatment. *Water Res.* **2011**, *45* (11), 3407−3416.
(18) Wang, R.; Wang, T.; Qu, G.; Zhang, Y.; Guo, X.; Jia, H.; Zhu, L. Insights into the Underlying Mechanisms for Integrated Inactivation of *A. Spiroides* and Depression of Disinfection Byproducts by Plasma Oxidation. *Water Res.* **2021**, *196*, No. 117027.
(19) Xin, Q.; Zhang, Y.; Wu, K. Degradation of Microcystin-LR by Gas-Liquid Interfacial Discharge Plasma. *Plasma Sci. Technol.* **2013**, *15* (12), 1221−1225.
(20) Zhang, H.; Huang, Q.; Ke, Z.; Yang, L.; Wang, X.; Yu, Z. Degradation of Microcystin-LR in Water by Glow Discharge Plasma Oxidation at the Gas-Solution Interface and Its Safety Evaluation. *Water Res.* **2012**, *46* (19), 6554−6562.
(21) Rumbach, P.; Bartels, D. M.; Sankaran, R. M.; Go, D. B. The Solvation of Electrons by an Atmospheric-Pressure Plasma. *Nat. Commun.* **2015**, *6*, 7248.
(22) Richmonds, C.; Witzke, M.; Bartling, B.; Lee, S. W.; Wainright, J.; Liu, C.; Sankaran, R. M. Electron-Transfer Reactions at the Plasma A Liquid Interface. *J. Am. Chem. Soc.* **2011**, *133* (44), 17582−17585.
(23) Ilich, P. P.; McCormick, K. R.; Atkins, A. D.; Mell, G. J.; Flaherty, T. J.; Bruck, M. J.; Goodrich, H. A.; Hefel, A. L.; Juranić, N.; Seleem, S. Solvated Electrons in Organic Chemistry Laboratory. *J. Chem. Educ.* **2010**, *87* (4), 419−422.
(24) Abel, B.; Buck, U.; Sobolewski, A. L.; Domcke, W. On the Nature and Signatures of the Solvated Electron in Water. *Phys. Chem. Chem. Phys.* **2012**, *14* (1), 22−34.
(25) Neta, P. Reactions of Hydrogen Atoms in Aqeuous Solutions. *Chem. Rev.* **1972**, *75* (5), 533−543.
(26) Mededovic Thagard, S.; Stratton, G. R.; Dai, F.; Bellona, C. L.; Holsen, T. M.; Bohl, D. G.; Paek, E.; Dickenson, E. R. V. Plasma-Based Water Treatment: Development of a General Mechanistic Model to Estimate the Treatability of Different Types of Contaminants. *Appl. Phys.* **2017**, *50* (1), No. 014003.
(27) Gao, X.; Wang, X.; Ma, J.; Liu, Y. Potential and Mechanism of Disinfection By-products Removal in Drinking Water by Bubbling Corona Discharge. *Water Res.* **2023**, *245*, No. 120624.
(28) Zhao, Y.; Zhang, C.; Chu, L.; Zhou, Q.; Huang, B.; Ji, R.; Zhou, X.; Zhang, Y. Hydrated Electron Based Photochemical Processes for Water Treatment. *Water Res.* **2022**, *225*, No. 119212.
(29) Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J. Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. *Environ. Sci. Technol.* **2019**, *53* (7), 3718−3728.
(30) Singh, R. K.; Multari, N.; Nau-Hix, C.; Anderson, R. H.; Richardson, S. D.; Holsen, T. M.; Mededovic Thagard, S. Rapid Removal of Poly- and Perfluorinated Compounds from Investigation-Derived Waste (IDW) in a Pilot-Scale Plasma Reactor. *Environ. Sci. Technol.* **2019**, *53* (19), 11375−11382.
(31) Li, X.; Fang, J.; Liu, G.; Zhang, S.; Pan, B.; Ma, J. Kinetics and Efficiency of the Hydrated Electron-Induced Dehalogenation by the Sulfite/UV Process. *Water Res.* **2014**, *62* (2), 220−228.
(32) Wu, Z.; Shang, C.; Wang, D.; Zheng, S.; Wang, Y.; Fang, J. Rapid Degradation of Dichloroacetonitrile by Hydrated Electron (e_{aq}^{-}) Produced in Vacuum Ultraviolet Photolysis. *Chemosphere* **2020**, *256*, No. 126994.
(33) Cole, S. K.; Cooper, W. J.; Fox, R. V.; Gardinali, P. R.; Mezyk, S. P.; Mincher, B. J.; O'Shea, K. E. Free Radical Chemistry of Disinfection Byproducts. 2. Rate Constants and Degradation Mechanisms of Trichloronitromethane (Chloropicrin). *Environ. Sci. Technol.* **2007**, *41* (3), 863−869.
(34) Liu, Z.; Haddad, M.; Sauvé, S.; Barbeau, B. Alleviating the Burden of Ion Exchange Brine in Water Treatment: From Operational Strategies to Brine Management. *Water Res.* **2021**, *205*, No. 117728.
(35) Singh, R. K.; Multari, N.; Nau-Hix, C.; Woodard, S.; Nickelsen, M.; Mededovic Thagard, S.; Holsen, T. M. Removal of Poly- And Per-Fluorinated Compounds from Ion Exchange Regenerant Still Bottom Samples in a Plasma Reactor. *Environ. Sci. Technol.* **2020**, *54* (21), 13973−13980.
(36) Giwa, A.; Dufour, V.; Al Marzooqi, F.; Al Kaabi, M.; Hasan, S. W. Brine Management Methods: Recent Innovations and Current Status. *Desalination* **2017**, *407*, 1−23.
(37) Tow, E. W.; Ersan, M. S.; Kum, S.; Lee, T.; Speth, T. F.; Owen, C.; Bellona, C.; Nadagouda, M. N.; Mikelonis, A. M.; Westerhoff, P.; Myrose, C.; Frenkel, V. S.; deSilva, V.; Walker, W. S.; Safulko, A. K.; Ladner, D. A. Managing and Treating Per-and Polyfluoroalkyl

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

Substances (PFAS) in Membrane Concentrates. *AWWA Water Sci.* **2021**, *3* (5), e1233.
(38) Azerrad, S. P.; Lütke Eversloh, C.; Gilboa, M.; Schulz, M.; Ternes, T.; Dosoretz, C. G. Identification of Transformation Products during Advanced Oxidation of Diatrizoate: Effect of Water Matrix and Oxidation Process. *Water Res.* **2016**, *103*, 424−434.
(39) Jose, J.; Philip, L. Continuous Flow Pulsed Power Plasma Reactor for the Treatment of Aqueous Solution Containing Volatile Organic Compounds and Real Pharmaceutical Wastewater. *J. Environ. Manage.* **2021**, *286*, No. 112202.
(40) Manakhov, A.; Orlov, M.; Grokhovsky, V.; Alghunaimi, F. I.; Ayirala, S. Functionalized Nanomembranes and Plasma Technologies for Produced Water Treatment a Review. *Polymers.* **2022**, *14* (9), 1785.
(41) Sun, M.; Lowry, G. V.; Gregory, K. B. Selective Oxidation of Bromide in Wastewater Brines from Hydraulic Fracturing. *Water Res.* **2013**, *47* (11), 3723−3731.
(42) Singh, R. K.; Brown, E.; Mededovic Thagard, S.; Holsen, T. M. Treatment of PFAS-Containing Landfill Leachate Using an Enhanced Contact Plasma Reactor. *J. Hazard. Mater.* **2021**, *408*, No. 124452.
(43) Sathiyaraj, G.; Chellappan Ravindran, K.; Hussain Malik, Z. Physico-Chemical Characteristics of Textile Effluent Collected from Erode, Pallipalayam and Bhavani Polluted Regions, Tamilnadu. *India. J. Ecobiotechnology* **2017**, *9*, 1−4.
(44) Rodriguez, E. E.; Tarpeh, W. A.; Wigginton, K. R.; Love, N. G. Application of Plasma for the Removal of Pharmaceuticals in Synthetic Urine. *Environ. Sci. Water Res. Technol.* **2022**, *8* (3), 523−533.
(45) Nau-Hix, C.; Holsen, T. M.; Thagard, S. M. Influence of Solution Electrical Conductivity and Ionic Composition on the Performance of a Gas-Liquid Pulsed Spark Discharge Reactor for Water Treatment. *J. Appl. Phys.* **2021**, *130* (12), 123301.
(46) Li, Z.; Lyu, X.; Gao, B.; Xu, H.; Wu, J.; Sun, Y. Effects of Ionic Strength and Cation Type on the Transport of Perfluorooctanoic Acid (PFOA) in Unsaturated Sand Porous Media. *J. Hazard. Mater.* **2021**, *403*, No. 123688.
(47) Lyu, Y.; Brusseau, M. L. The Influence of Solution Chemistry on Air-Water Interfacial Adsorption and Transport of PFOA in Unsaturated Porous Media. *Sci. Total Environ.* **2020**, *713*, No. 136744.
(48) Le, S. T.; Gao, Y.; Kibbey, T. C. G.; Glamore, W. C.; O'Carroll, D. M. Predicting the Impact of Salt Mixtures on the Air-Water Interfacial Behavior of PFAS. *Sci. Total Environ.* **2022**, *819*, No. 151987.
(49) Shih, K. Y.; Locke, B. R. Optical and Electrical Diagnostics of the Effects of Conductivity on Liquid Phase Electrical Discharge. *IEEE Trans. Plasma Sci.* **2011**, *39* (3), 883−892.
(50) Thagard, S. M.; Takashima, K.; Mizuno, A. Chemistry of the Positive and Negative Electrical Discharges Formed in Liquid Water and above a Gas-Liquid Surface. *Plasma Chem. Plasma Process.* **2009**, *29* (6), 455−473.
(51) El-Tayeb, A.; El-Shazly, A. H.; Elkady, M. F. Investigation the Influence of Different Salts on the Degradation of Organic Dyes Using Non-Thermal Plasma. *Energies* **2016**, *9* (11), 874.
(52) Zhu, D.; Sun, Z.; Zhang, H.; Zhang, A.; Zhang, Y.; Miruka, A. C.; Zhu, L.; Li, R.; Guo, Y.; Liu, Y. Reactive Nitrogen Species Generated by Gas−Liquid Dielectric Barrier Discharge for Efficient Degradation of Perfluorooctanoic Acid from Water. *Environ. Sci. Technol.* **2022**, *56* (1), 349−360.
(53) Yi, R.; Yi, C.; Du, D.; Zhang, Q.; Yu, H.; Yang, L. Research on Quinoline Degradation in Drinking Water by a Large Volume Strong Ionization Dielectric Barrier Discharge Reaction System. *Plasma Sci. Technol.* **2021**, *23* (8), No. 085505.
(54) Haghighat, G.; Sohrabi, A.; Shaibani, P. M.; Van Neste, C. W.; Naicker, S.; Thundat, T. The Role of Chloride Ions in Plasma-Activated Water Treatment Processes. *Environ. Sci. Water Res. Technol.* **2017**, *3* (1), 156−168.
(55) Wang, L. Aqueous Organic Dye Discoloration Induced by Contact Glow Discharge Electrolysis. *J. Hazard. Mater.* **2009**, *171* (1−3), 577−581.
(56) Wang, L.; Jiang, X.; Liu, Y. Degradation of Bisphenol A and Formation of Hydrogen Peroxide Induced by Glow Discharge Plasma in Aqueous Solutions. *J. Hazard. Mater.* **2008**, *154* (1−3), 1106−1114.
(57) Jirásek, V.; Lukeš, P. Formation of Reactive Chlorine Species in Saline Solution Treated by Non-Equilibrium Atmospheric Pressure He/O_2 Plasma Jet. *Plasma Sources Sci. Technol.* **2019**, *28* (3), No. 035015.
(58) Jirásek, V.; Lukeš, P. Competitive Reactions in Cl^- Solutions Treated by Plasma-Supplied O Atoms. *J. Phys. D. Appl. Phys.* **2020**, *53*, 505206.
(59) Gorbanev, Y.; Van Der Paal, J.; Van Boxem, W.; Dewilde, S.; Bogaerts, A. Reaction of Chloride Anion with Atomic Oxygen in Aqueous Solutions: Can Cold Plasma Help in Chemistry Research? *Phys. Chem. Chem. Phys.* **2019**, *21* (8), 4117−4121.
(60) Wu, D.; Wong, D.; Di Bartolo, B. Evolution of Cl_2^- in Aqueous NaCl Solutions. *J. Photochem.* **1980**, *14* (4), 303−310.
(61) Yu, X. Y.; Bao, Z. C.; Barker, J. R. Free Radical Reactions Involving $Cl^•$, $Cl_2^{•-}$, and $SO_4^{•-}$ in the 248 nm Photolysis of Aqueous Solutions Containing $S_2O_8^{2-}$ and Cl^-. *J. Phys. Chem. A* **2004**, *108* (2), 295−308.
(62) Deborde, M.; von Gunten, U. Reactions of Chlorine with Inorganic and Organic Compounds during Water Treatment-Kinetics and Mechanisms: A Critical Review. *Water Res.* **2008**, *42* (1−2), 13−51.
(63) Magazinovic, R. S.; Nicholson, B. C.; Mulcahy, D. E.; Davey, D. E. Bromide Levels in Natural Waters: Its Relationship to Levels of Both Chloride and Total Dissolved Solids and the Implications for Water Treatment. *Chemosphere* **2004**, *57* (4), 329−335.
(64) Yang, Y.; Pignatello, J. J.; Ma, J.; Mitch, W. A. Effect of Matrix Components on UV/H_2O_2 and UV/$S_2O_8^{2-}$ Advanced Oxidation Processes for Trace Organic Degradation in Reverse Osmosis Brines from Municipal Wastewater Reuse Facilities. *Water Res.* **2016**, *89*, 192−200.
(65) Justo, A.; González, O.; Aceña, J.; Pérez, S.; Barceló, D.; Sans, C.; Esplugas, S. Pharmaceuticals and Organic Pollution Mitigation in Reclamation Osmosis Brines by UV/H_2O_2 and Ozone. *J. Hazard. Mater.* **2013**, *263*, 268−274.
(66) Zhang, K.; Parker, K. M. Halogen Radical Oxidants in Natural and Engineered Aquatic Systems. *Environ. Sci. Technol.* **2018**, *52* (17), 9579−9594.
(67) Grebel, J. E.; Pignatello, J. J.; Mitch, W. A. Effect of Halide Ions and Carbonates on Organic Contaminant Degradation by Hydroxyl Radical-Based Advanced Oxidation Processes in Saline Waters. *Environ. Sci. Technol.* **2010**, *44* (17), 6822−6828.
(68) Yang, Y.; Pignatello, J. J.; Ma, J.; Mitch, W. A. Comparison of Halide Impacts on the Efficiency of Contaminant Degradation by Sulfate and Hydroxyl Radical-Based Advanced Oxidation Processes (AOPs). *Environ. Sci. Technol.* **2014**, *48* (4), 2344−2351.
(69) Jayson, G. G.; Parsons, B. J.; Swallow, A. J. Some Simple, Highly Reactive, Inorganic Chlorine Derivatives in Aqueous Solution. Their Formation Using Pulses of Radiation and Their Role in the Mechanism of the Fricke Dosimeter. *J. Chem. Soc. Faraday Trans* **1973**, *69* (9), 1597−1607.
(70) Kläning, U. K.; Wolff, T. Laser Flash Photolysis of HClO, ClO^-, HBrO, and BrO^- in Aqueous Solution. Reactions of Cl- and Br-Atoms. *Berichte der Bunsengesellschaft für Phys. Chemie* **1985**, *89* (3), 243−245.
(71) Grigorev, A. E.; Makarov, I. E.; Pikaev, A. K. Formation of Cl_2^- in the Bulk Solution during the Radiolysis of Concentrated Aqueous Solution of Chlorides. *High Energy Chem.* **1987**, *21*, 99−102.
(72) Zehavi, D.; Rabani, J. The Oxidation of Aqueous Bromide Ions by Hydroxyl Radicals. A Pulse Radiolytic Investigation. *J. Phys. Chem.* **1972**, *76* (3), 312−319.
(73) Merényi, G.; Lind, J. Reaction Mechanism of Hydrogen Abstraction by the Bromine Atom in Water. *J. Am. Chem. Soc.* **1994**, *116* (17), 7872−7876.
(74) Matthew, B. M.; Anastasio, C. A Chemical Probe Technique for the Determination of Reactive Halogen Species in Aqueous Solution:

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

Part 1 - Bromide Solutions. *Atmos. Chem. Phys.* **2006**, *6* (9), 2423−2437.
(75) Westerhoff, P.; Chao, P.; Mash, H. Reactivity of Natural Organic Matter with Aqueous Chlorine and Bromine. *Water Res.* **2004**, *38* (6), 1502−1513.
(76) Ershov, B. G. Kinetics, Mechanism and Intermediates of Some Radiation-Induced Reactions in Aqueous Solutions. *Russ. Chem. Rev.* **2004**, *73* (1), 101−113.
(77) Heeb, M. B.; Criquet, J.; Zimmermann-Steffens, S. G.; Von Gunten, U. Oxidative Treatment of Bromide-Containing Waters: Formation of Bromine and Its Reactions with Inorganic and Organic Compounds - A Critical Review. *Water Res.* **2014**, *48* (1), 15−42.
(78) Wagner, I.; Karthaeuser, J.; Strehlow, H. On the Decay of the Dichloride Anion Cl_2^- in Aqueous Solution. *Berichte der Bunsengesellschaft für Phys. Chemie* **1986**, *90* (10), 861−867.
(79) Wagner, I.; Strehlow, H. On the Flash Photolysis of Bromide Ions in Aqueous Solutions. *Berichte der Bunsengesellschaft für Phys. Chemie* **1987**, *91* (12), 1317−1321.
(80) Wong, D.; Di Bartolo, B. Evolution of the Dihalide Ion Br_2^- in Aqueous Solutions. *J. Photochem.* **1975**, *4* (4), 249−268.
(81) Feng, Y.; Smith, D. W.; Bolton, J. R. Photolysis of Aqueous Free Chlorine Species (HOCl and OCl^-) with 254 nm Ultraviolet Light. *J. Environ. Eng. Sci.* **2007**, *6* (3), 277−284.
(82) Troy, R. C.; Margerum, D. W. Non-Metal Redox Kinetics: Hypobromite and Hypobromous Acid Reactions with Iodide and with Sulfite and the Hydrolysis of Bromosulfate. *Environ. Sci. Technol.* **1991**, *30* (18), 3538−3543.
(83) Moravej, M.; Yang, X.; Nowling, G. R.; Chang, J. P.; Hicks, R. F.; Babayan, S. E. Physics of High-Pressure Helium and Argon Radio-Frequency Plasmas. *J. Appl. Phys.* **2004**, *96* (12), 7011−7017.
(84) Sun, B.; Sato, M.; Sid Clements, J. Optical Study of Active Species Produced by a Pulsed Streamer Corona Discharge in Water. *J. Electrostat.* **1997**, *39* (3), 189−202.
(85) Rumbach, P.; Bartels, D. M.; Sankaran, R. M.; Go, D. B. The Effect of Air on Solvated Electron Chemistry at a Plasma/Liquid Interface. *J. Phys. D. Appl. Phys.* **2015**, *48* (42), No. 424001.
(86) Clifford, D.; Liu, X. Biological Denitrification of Spent Regenerant Brine Using a Sequencing Batch Reactor. *Water Res.* **1993**, *27* (9), 1477−1484.
(87) Haddad, M.; Bazinet, L.; Barbeau, B. Eco-Efficient Treatment of Ion Exchange Spent Brine via Electrodialysis to Recover NaCl and Minimize Waste Disposal. *Sci. Total Environ.* **2019**, *690*, 400−409.
(88) Haddad, M.; Bazinet, L.; Barbeau, B. Towards Water, Sodium Chloride and Natural Organic Matter Recovery from Ion Exchange Spent Brine. *Membranes* **2021**, *11* (4), 262.
(89) Hiremath, T.; Roberts, D. J.; Lin, X.; Clifford, D. A.; Gillogly, T. E. T.; Lehman, S. G. Biological Treatment of Perchlorate in Spent ISEP Ion-Exchange Brine. *Environ. Eng. Sci.* **2006**, *23* (6), 1009−1016.
(90) Homan, N. P.; Green, P. G.; Young, T. M. Evaluating Ferrous Chloride for Removal of Chromium From Ion-Exchange Waste Brines. *J. Am. Water Works Assoc.* **2018**, *110* (4), E43−E54.
(91) Hutchison, J. M.; Zilles, J. L. Biocatalytic Removal of Perchlorate and Nitrate in Ion-Exchange Waste Brine. *Environ. Sci. Water Res. Technol.* **2018**, *4* (8), 1181−1189.
(92) Korak, J. A.; Huggins, R. G.; Arias-Paić, M. S. Nanofiltration to Improve Process Efficiency of Hexavalent Chromium Treatment Using Ion Exchange. *J. Am. Water Works Assoc.* **2018**, *110* (6), E13−E26.
(93) Leong, J.; Tan, J.; Heitz, A.; Ladewig, B. P. Performance of a Vibratory Shear Membrane Filtration System during the Treatment of Magnetic Ion Exchange Process Concentrate. *Desalination* **2015**, *365*, 196−203.
(94) Liu, J.; Choe, J. K.; Sasnow, Z.; Werth, C. J.; Strathmann, T. J. Application of a Re-Pd Bimetallic Catalyst for Treatment of Perchlorate in Waste Ion-Exchange Regenerant Brine. *Water Res.* **2013**, *47* (1), 91−101.
(95) McAdam, E. J.; Judd, S. J. Biological Treatment of Ion-Exchange Brine Regenerant for Re-Use: A Review. *Sep. Purif. Technol.* **2008**, *62* (2), 264−272.
(96) Pakzadeh, B.; Batista, J. R. Chromium Removal from Ion-Exchange Waste Brines with Calcium Polysulfide. *Water Res.* **2011**, *45* (10), 3055−3064.
(97) Plummer, S.; Gorman, C.; Henrie, T.; Shimabuku, K.; Thompson, R.; Seidel, C. Optimization of Strong-Base Anion Exchange O&M Costs for Hexavalent Chromium Treatment. *Water Res.* **2018**, *139*, 420−433.
(98) Schaefer, C. E.; Tran, D.; Fang, Y.; Choi, Y. J.; Higgins, C. P.; Strathmann, T. J. Electrochemical Treatment of Poly- and Perfluoroalkyl Substances in Brines. *Environ. Sci. Water Res. Technol.* **2020**, *6* (10), 2704−2712.
(99) Vaudevire, E.; Radmanesh, F.; Kolkman, A.; Vughs, D.; Cornelissen, E.; Post, J.; van der Meer, W. Fate and Removal of Trace Pollutants from an Anion Exchange Spent Brine during the Recovery Process of Natural Organic Matter and Salts. *Water Res.* **2019**, *154*, 34−44.
(100) Yang, T.; Doudrick, K.; Westerhoff, P. Photocatalytic Reduction of Nitrate Using Titanium Dioxide for Regeneration of Ion Exchange Brine. *Water Res.* **2013**, *47* (3), 1299−1307.
(101) Hajbi, F.; Hammi, H.; M'Nif, A. Reuse of RO Desalination Plant Reject Brine. *J. Phase Equilibria Diffus.* **2010**, *31* (4), 341−347.
(102) Ji, X.; Curcio, E.; Al Obaidani, S.; Di Profio, G.; Fontananova, E.; Drioli, E. Membrane Distillation-Crystallization of Seawater Reverse Osmosis Brines. *Sep. Purif. Technol.* **2010**, *71* (1), 76−82.
(103) Lior, N.; Kim, D. Quantitative Sustainability Analysis of Water Desalination − A Didactic Example for Reverse Osmosis. *Desalination* **2018**, *431*, 157−170.
(104) Opong, R. W.; Nsiah-Baafi, E.; Andrews, A.; Koomson, B. Preliminary Study on the Use of Reverse Osmosis Brine and Mine Tailings as Cement Paste Mixtures for Mine Backfilling Application. *Water. Air. Soil Pollut.* **2022**, *233* (12), 1−15.
(105) Walker, W. S.; Kim, Y.; Lawler, D. F. Treatment of Model Inland Brackish Groundwater Reverse Osmosis Concentrate with Electrodialysis - Part II: Sensitivity to Voltage Application and Membranes. *Desalination* **2014**, *345*, 128−135.
(106) Eeso, K. *Non-Thermal Plasma Degradation of Per- and Polyfluoroalkyl Substances from Landfill Leachate*. Ph.D. Dissertation, The Florida State University, Tallahassee, FL, 2022. https://diginole.lib.fsu.edu/islandora/object/fsu:802711/datastream/PDF/view (accessed 2023−08−28).
(107) Ma, X.; Li, M.; Feng, C.; He, Z. Electrochemical Nitrate Removal with Simultaneous Magnesium Recovery from a Mimicked RO Brine Assisted by in Situ Chloride Ions. *J. Hazard. Mater.* **2020**, *388*, No. 122085.
(108) An, B.; Steinwinder, T. R.; Zhao, D. Selective Removal of Arsenate from Drinking Water Using a Polymeric Ligand Exchanger. *Water Res.* **2005**, *39* (20), 4993−5004.
(109) An, B.; Liang, Q.; Zhao, D. Removal of Arsenic(V) from Spent Ion Exchange Brine Using a New Class of Starch-Bridged Magnetite Nanoparticles. *Water Res.* **2011**, *45* (5), 1961−1972.
(110) Arias-Paić, M. S.; Korak, J. A. Forward Osmosis for Ion Exchange Waste Brine Management. *Environ. Sci. Technol. Lett.* **2020**, *7* (2), 111−117.
(111) Bergquist, A. M.; Choe, J. K.; Strathmann, T. J.; Werth, C. J. Evaluation of a Hybrid Ion Exchange-Catalyst Treatment Technology for Nitrate Removal from Drinking Water. *Water Res.* **2016**, *96*, 177−187.
(112) Jones, D. R. Improved Spectrophotometric Method for the Determination of Low Levels of Bromide. *Anal. Chim. Acta* **1993**, *271* (2), 315−321.
(113) De Geyter, N.; Morent, R.; Leys, C.; Gengembre, L.; Payen, E. Treatment of Polymer Films with a Dielectric Barrier Discharge in Air, Helium and Argon at Medium Pressure. *Surf. Coat. Technol.* **2007**, *201* (16−17), 7066−7075.
(114) Jiang, J.; Han, J.; Zhang, X. Nonhalogenated Aromatic DBPs in Drinking Water Chlorination: A Gap between NOM and

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

Halogenated Aromatic DBPs. *Environ. Sci. Technol.* **2020**, *54* (3), 1646−1656.
(115) Hasegawa, K.; Neta, P. Rate Constants and Mechanisms of Reaction of Chloride (Cl_2^-) Radicals. *J. Phys. Chem.* **1978**, *82* (8), 854−857.
(116) Lei, Y.; Lei, X.; Yu, Y.; Li, K.; Li, Z.; Cheng, S.; Ouyang, G.; Yang, X. Rate Constants and Mechanisms for Reactions of Bromine Radicals with Trace Organic Contaminants. *Environ. Sci. Technol.* **2021**, *55* (15), 10502−10513.
(117) Kemsley, K.; Moore, J. S.; Phillip, G. O.; Sosnowski, A. Reaction of Radical Probes with Substituted Phenols as Models for the Investigation of Tyrosine in Aldolase and Chemically Modified Aldolase. *Acta Vitaminol. Enzym.* **1974**, *28* (6), 263−267.
(118) Lei, Y.; Cheng, S.; Luo, N.; Yang, X.; An, T. Rate Constants and Mechanisms of the Reactions of $Cl^•$ and $Cl_2^{•-}$ with Trace Organic Contaminants. *Environ. Sci. Technol.* **2019**, *53* (19), 11170−11182.
(119) Barazesh, J. M.; Prasse, C.; Sedlak, D. L. Electrochemical Transformation of Trace Organic Contaminants in the Presence of Halide and Carbonate Ions. *Environ. Sci. Technol.* **2016**, *50* (18), 10143−10152.
(120) Mertens, R.; von Sonntag, C. Photolysis (λ=254 nm) of Tetrachloroethene in Aqueous Solutions. *J. Photochem. Photobiol. A Chem.* **1995**, *85* (1−2), 1−9.
(121) Huie, R. E.; Clifton, C. L.; Neta, P. Electron Trasnfer Reaction Rates and Equilibria of the Carbonate and Sulfate Radical Anions. *Radiat. Phys. Chem. Int. J. Radiat. Appl. lnstrum., Part C* **1991**, *38* (5), 477−481.
(122) Jiang, P.-Y.; Katsumura, Y.; Nagaishi, R.; Domae, M.; Ishikawa, K.; Ishigure, K.; Yoshia, Y. Pulse Radiolysis Study of Concentrated Sulfuric Acid Solutions. *J. Chem. Soc. Faraday Trans.* **1992**, *88* (22), 1653−1658.
(123) Katsumura, Y.; Jiang, P. Y.; Nagaishi, R.; Oishi, T.; Ishigure, K.; Yoshida, Y. Pulse Radiolysis Study of Aqueous Nitric Acid Solutions. Formation Mechanism, Yield, and Reactivity of NO_3 Radical. *J. Phys. Chem.* **1991**, *95* (11), 4435−4439.
(124) Buxton, G. V.; Elliot, A. J. Rate Constant for Reaction of Hydroxyl Radicals with Bicarbonate Ions. *Int. J. Radiat. Appl. Instrumentation. Part* **1986**, *27* (3), 241−243.
(125) Westerhoff, P.; Mezyk, S. P.; Cooper, W. J.; Minakata, D. Electron Pulse Radiolysis Determination of Hydroxyl Radical Rate Constants with Suwannee River Fulvic Acid and Other Dissolved Organic Matter Isolates. *Environ. Sci. Technol.* **2007**, *41* (13), 4640−4646.
(126) Chen, R.; Avotinsh, Y.; Freeman, G. R. Solvent Effects on Reactivity of Solvated Electrons with Ions in Isobutanol/Water Mixed Solvents. *Can. J. Chem.* **1994**, *72* (4), 1083−1093.
(127) Thomas, J. K.; Gordon, S.; Hart, E. J. The Rates of Reaction of the Hydrated Electron in Aqueous Inorganic Solutions. *J. Phys. Chem.* **1964**, *68* (6), 1524−1527.
(128) Nash, K.; Mulac, W.; Noon, M.; Fried, S.; Sullivan, J. C. Pulse Radiolysis Studies of U(VI) Complexes in Aqueous Media. *J. Inorg. Nucl. Chem.* **1981**, *43* (5), 897−899.
(129) Huang, Y. C.; Rao, A.; Huang, S. J.; Chang, C. Y.; Drechsler, M.; Knaus, J.; Chan, J. C. C.; Raiteri, P.; Gale, J. D.; Gebauer, D. Uncovering the Role of Bicarbonate in Calcium Carbonate Formation at Near-Neutral pH. *Angew. Chemie - Int. Ed.* **2021**, *60* (30), 16707−16713.
(130) Van Driessche, A. E. S.; Stawski, T. M.; Kellermeier, M. Calcium Sulfate Precipitation Pathways in Natural and Engineered Environments. *Chem. Geol.* **2019**, *530*, No. 119274.
(131) Case, D. H.; Wang, F.; Giammar, D. E. Precipitation of Magnesium Carbonates as a Function of Temperature, Solution Composition, and Presence of a Silicate Mineral Substrate. *Environ. Eng. Sci.* **2011**, *28* (12), 881−889.
(132) American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*; 1998.
(133) Pearse, R. W. B.; Gaydon, A. G. *The Identification of Molecular Spectra*; London Chapman & Hall LTD, 1941.
(134) National Institute of Standards and Technology. *Atomic Spectra Database Lines Data* https://physics.nist.gov/PhysRefData/ASD/lines_form.html (accessed 2023−07−23).
(135) Hong, Y. J.; Nam, C. J.; Song, K. B.; Cho, G. S.; Uhm, H. S.; Choi, D. I.; Choi, E. H. Measurement of Hydroxyl Radical Density Generated from the Atmospheric Pressure Bioplasma Jet. *J. Instrum.* **2012**, *7* (3), C03046.
(136) Zhang, D. J.; Cai, Y.; Chen, M. L.; Yu, Y. L.; Wang, J. H. Dielectric Barrier Discharge-Optical Emission Spectrometry for the Simultaneous Determination of Halogens. *J. Anal. At. Spectrom.* **2016**, *31* (2), 398−405.
(137) Ashton, L.; Buxton, G. V.; Stuart, C. R. Temperature Dependence of the Rate of Reaction of OH with Some Aromatic Compounds in Aqueous Solution Evidence for the Formation of a π-Complex Intermediate? *J. Chem. Soc. Faraday Trans.* **1995**, *91* (11), 1631−1633.
(138) Anderson, R. F.; Patel, K. B.; Stratford, M. R. L. Radical Spectra and Product Distribution Following Electrophilic Attack by the $OH^•$ Radical on 4-Hydroxybenzoic Acid and Subsequent Oxidation. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1987**, *83* (10), 3177−3187.
(139) Anbar, M.; Alfassi, Z. B.; Bregman-Reisler, H. Hydrated Electron Reactions in View of Their Temperature Dependence. *J. Am. Chem. Soc.* **1967**, *89* (5), 1263−1264.
(140) Neta, P.; Schuler, R. H. Effect of Ionic Dissociation of Organic Compounds on Their Rate of Reaction with Hydrogen Atoms. *J. Phys. Chem.* **1972**, *76* (19), 2673−2679.
(141) Neta, P.; Dorfman, L. M. Pulse-Radiolysis Studies. XIV. Rate Constants for the Reactions of Hydrogen Atoms with Aromatic Compounds in Aqueous Solution. *J. Phys. Chem.* **1969**, *73* (2), 413−417.
(142) Li, Y.; Song, W.; Fu, W.; Tsang, D. C. W.; Yang, X. The Roles of Halides in the Acetaminophen Degradation by UV/H_2O_2 Treatment: Kinetics, Mechanisms, and Products Analysis. *Chem. Eng. J.* **2015**, *271*, 214−222.
(143) Rebenne, L. M.; Gonzalez, A. C.; Olson, T. M. Aqueous Chlorination Kinetics and Mechanism of Substituted Dihydroxybenzenes. *Environ. Sci. Technol.* **1996**, *30* (7), 2235−2242.
(144) Korshin, G. V. Chlorine Based Oxidants for Water Purification and Disinfection. *In Aquatic Redox Chemistry* **2011**, *1071*, 223−245.
(145) Sivey, J. D.; Bickley, M. A.; Victor, D. A. Contributions of BrCl, Br_2, BrOCl, Br_2O, and HOBr to Regiospecific Bromination Rates of Anisole and Bromoanisoles in Aqueous Solution. *Environ. Sci. Technol.* **2015**, *49* (8), 4937−4945.
(146) Liu, T.; Xiao, S.; Li, N.; Chen, J.; Xu, Y.; Yin, W.; Zhou, X.; Huang, C. H.; Zhang, Y. Selective Transformation of Micropollutants in Saline Wastewater by Peracetic Acid: The Overlooked Brominating Agents. *Environ. Sci. Technol.* **2023**, *57* (47), 18940−18949.
(147) Perlmutter-Hayman, B.; Weissmann, Y. The Oxidation of 2-Propanol by Bromine and by Hypobromous Acid in Aqueous Solution. *J. Am. Chem. Soc.* **1969**, *91* (3), 668−672.
(148) Zhang, B.; Fang, Z.; Wang, S.; Shi, X.; Guo, B.; Gao, J.; Wang, D.; Zong, W. Effect of Bromide on Molecular Transformation of Dissolved Effluent Organic Matter during Ozonation, UV/H_2O_2, UV/Persulfate, and UV/Chlorine Treatments. *Sci. Total Environ.* **2022**, *811*, No. 152328.
(149) Shu, Z.; Wang, J.; Liu, H.; Liu, C. Improvement of Bromide Ions on the Degradation of Sulfamerazine by Horseradish Peroxidase-H_2O_2 System and Its Interaction Mechanisms. *Chem. Eng. J.* **2022**, *428*, No. 131132.
(150) Oum, K. W.; Lakin, M. J.; DeHaan, D. O.; Brauers, T.; Finlayson-Pitts, B. J. Formation of Molecular Chlorine from the Photolysis of Ozone and Aqueous Sea-Salt Particles. *Science.* **1998**, *279* (5347), 74−77.
(151) George, I. J.; Abbatt, J. P. D. Heterogeneous Oxidation of Atmospheric Aerosol Particles by Gas-Phase Radicals. *Nat. Chem.* **2010**, *2* (9), 713−722.

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152

(152) Enami, S.; Hoffmann, M. R.; Colussi, A. J. Halogen Radical Chemistry at Aqueous Interfaces. *J. Phys. Chem. A* **2016**, *120* (31), 6242−6248.
(153) Amphlett, C. B.; Adams, G. E.; Michael, B. D. Pulse Radiolysis Studies of Deaerated Aqueous Salicylate Solutions. *In Radiation Chemistry* **1968**, *81*, 231−250.
(154) Bisby, R. H.; Tabassum, N. Properties of the Radicals Formed by One-Electron Oxidation of Acetaminophen-A Pulse Radiolysis Study. *Biochem. Pharmacol.* **1988**, *37* (14), 2731−2738.
(155) Mezyk, S. P.; Neubauer, T. J.; Cooper, W. J.; Peller, J. R. Free-Radical-Induced Oxidative and Reductive Degradation of Sulfa Drugs in Water: Absolute Kinetics and Efficiencies of Hydroxyl Radical and Hydrated Electron Reactions. *J. Phys. Chem. A* **2007**, *111* (37), 9019−9024.
(156) Prutz, W. A.; Land, E. J. Chemiluminescent Reactions after Pulse Radiolysis of Aqeuous Dye Solutions. Absolute Yields. *J. Phys. Chem.* **1974**, *78* (13), 1251−1253.
(157) Wojnárovits, L.; Tóth, T.; Takács, E. Rate Constants of Carbonate Radical Anion Reactions with Molecules of Environmental Interest in Aqueous Solution: A Review. *Sci. Total Environ.* **2020**, *717*. 137219.
(158) Olszowy, H. A.; Rossiter, J.; Hegarty, J.; Geoghegan, P.; Haswell-Elkins, M. Background Levels of Bromide in Human Blood. *J. Anal. Toxicol.* **1998**, *22* (3), 225−230.
(159) Kaushik, N.; Lee, S. J.; Choi, T. G.; Baik, K. Y.; Uhm, H. S.; Kim, C. H.; Kaushik, N. K.; Choi, E. H. Non-Thermal Plasma with 2-Deoxy-D-Glucose Synergistically Induces Cell Death by Targeting Glycolysis in Blood Cancer Cells. *Sci. Rep.* **2015**, *5*, 1−11.
(160) Scholtz, V.; Pazlarova, J.; Souskova, H.; Khun, J.; Julak, J. Nonthermal Plasma - A Tool for Decontamination and Disinfection. *Biotechnol. Adv.* **2015**, *33* (6), 1108−1119.
(161) Guesmi, A.; Cherif, M. M.; Baaloudj, O.; Kenfoud, H.; Badawi, A. K.; Elfalleh, W.; Hamadi, N. B.; Khezami, L.; Assadi, A. A. Disinfection of Corona and Myriad Viruses in Water by Non-Thermal Plasma: A Review. *Environ. Sci. Pollut. Res.* **2022**, *29* (37), 55321−55335.
(162) Patange, A.; Boehm, D.; Giltrap, M.; Lu, P.; Cullen, P. J.; Bourke, P. Assessment of the Disinfection Capacity and Eco-Toxicological Impact of Atmospheric Cold Plasma for Treatment of Food Industry Effluents. *Sci. Total Environ.* **2018**, *631*−*632*, 298−307.
(163) Kondeti, V. S. S. K.; Phan, C. Q.; Wende, K.; Jablonowski, H.; Gangal, U.; Granick, J. L.; Hunter, R. C.; Bruggeman, P. J. Long-Lived and Short-Lived Reactive Species Produced by a Cold Atmospheric Pressure Plasma Jet for the Inactivation of *Pseudomonas Aeruginosa* and *Staphylococcus Aureus*. *Free Radic. Biol. Med.* **2018**, *124*, 275−287.
(164) Hua, G.; Reckhow, D. A. Comparison of Disinfection Byproduct Formation from Chlorine and Alternative Disinfectants. *Water Res.* **2007**, *41* (8), 1667−1678.
(165) Hua, G.; Reckhow, D. A. Evaluation of Bromine Substitution Factors of DBPs during Chlorination and Chloramination. *Water Res.* **2012**, *46* (13), 4208−4216.
(166) Canonica, S.; Kohn, T.; Mac, M.; Real, F. J.; Wirz, J.; von Gunten, U. Photosensitizer Method to Determine Rate Constants for the Reaction of Carbonate Radical with Organic Compounds. *Environ. Sci. Technol.* **2005**, *39* (23), 9182−9188.
(167) Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. A. Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Technologies for Both Electric- and Solar-Driven Systems. *Pure Appl. Chem.* **2001**, *73* (4), 627−637.

https://doi.org/10.1021/acs.est.3c07162
Environ. Sci. Technol. 2024, 58, 5139−5152