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Perchlorate Formation by Ozone Oxidation of Aqueous Chlorine/Oxy-Chlorine Species: Role of Cl_xO_y Radicals

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The environmental occurrence of perchlorate (ClO_4^-) can be related to either natural or anthropogenic sources. Recent studies highlighted the ubiquitous occurrence of natural ClO_4^- in the environment including wet deposition in the United States. Limited studies have investigated potential mechanisms responsible for natural ClO_4^- production in the environment. These studies have neither addressed the influence of relevant reaction conditions nor have they evaluated the rates of ClO_4^- production. The purpose of this study was to determine the comparative yields and rates of ClO_4^- production from O_3 mediated oxidation of Cl^- , OCl^- , ClO_2^- , ClO_3^- , and ClO_2 . The influence of reactant (O_3 and ClO_x^-) concentration and pH were evaluated. The comparative rate and efficiency of ClO_4^- production is generally greater for higher oxidation states of Cl (2.7 to 0.5% for $\text{ClO}_2^-/\text{ClO}_2$ and 0.02 to 0.005% for OCl^-/HOCl oxidation) with the notable exception of ClO_3^- which does not react with O_3 . The very slow rate of ClO_4^- production from Cl^- ($\sim 20 \times 10^{-9}$ mM min^{-1}) even at elevated O_3 and Cl^- concentrations implies negligible potential for anthropogenic ClO_4^- formation in process units of water/wastewater systems that use O_3 for treatment. Based on results of ClO_4^- formation from tested Cl species and available literature, we propose a potential formation pathway for ClO_4^- from Cl^- with emphasis on the role of ClO_2 and higher oxy-chlorine radicals/intermediates (e.g., Cl_2O_6) in its formation.

Introduction

Perchlorate (ClO_4^-), a known thyroid disruptor, occurs in surface and ground waters, soils, plants, and crops in the United States. Typically the occurrence of ClO_4^- in the

environment, especially at high concentrations, has been traced to anthropogenically produced or distributed sources. The Atacama Desert in Chile has long been known to contain large natural deposits of both common (e.g., NO_3^- , SO_4^{2-} , and Cl^-) and uncommon anions including ClO_4^- (1). The origin of NO_3^- , SO_4^{2-} , and ClO_4^- in these deposits has been attributed to atmospheric processes as evidenced by their substantial $\Delta^{17}\text{O}$ anomaly (2, 3). Recent studies have evaluated the occurrence of natural ClO_4^- unattributed to Atacama derived fertilizers; examples include the following: groundwater in Texas and New Mexico, subsoil in the desert regions of the Southwest, and wet deposition throughout the U.S. (4–8).

Perchlorate has been proposed as chlorine (Cl) sink in the stratosphere as it is not subject to photodecomposition or radical attack (9), and it has been measured at altitudes up to 19 km with maximum concentrations at higher altitudes (10). Laboratory studies have demonstrated ClO_4^- production for a variety of reactions. The ClO radical can react with sulfuric acid (H_2SO_4) to form small amounts of HClO_4 (11). Ozone (O_3) can oxidize aqueous Cl species (Cl^- , HOCl/OCl^- and ClO_2^-) and in dry systems containing sodium chloride (NaCl) to produce ClO_4^- as a minor product with the oxidation of ClO_2^- producing the highest yields of ClO_4^- (12). Photochemical mediated oxidation of HOCl/OCl^- and ClO_2^- but not Cl^- or ClO_3^- also form ClO_4^- , with similar yields (13, 14).

No studies have addressed the rate of ClO_4^- formation, the impact of potentially important environmental variables such as pH and O_3 concentration, or the potential for ClO_4^- formation from the oxidation of chlorine dioxide (ClO_2), a known constituent in the stratosphere. The objectives of the present study were to evaluate the rates of ClO_4^- production from the O_3 oxidation of chlorine and oxy-chlorine anions as well as ClO_2 and evaluate the effects of concentration of the reactants (starting Cl species and O_3) and pH. Our results allow the evaluation of the relevance of these reactions to both atmospheric production and potential formation in terrestrial O_3 disinfection systems and allow us to propose a mechanistic model of ClO_4^- formation.

Materials and Methods

Experimental Set-Up. Details of chemicals, reagents, and the apparatus used in the experiments are provided in the Supporting Information (SI). Experiments were conducted by bubbling O_3 through 0.5 L solutions (F1) of Cl^- , HOCl/OCl^- , ClO_2^- , or ClO_3^- (Figure S1, SI). Details of the experimental conditions are provided in Table 1. The concentrations of the reactant Cl species were chosen based on the yields from a previous study (12). Ozone was produced by passing pure oxygen (O_2 -purity >99.999%) through a corona discharge O_3 generator. The flow rate was maintained at 5 mL min^{-1} using a gas flow controller (Model GFC-17; Aalborg). ClO_2^- and ClO_3^- oxidation experiments used a single-setting portable O_3 generator (Model EOZ-300Y; Enaly Trade Company) and experiments involving Cl^- and OCl^-/HOCl an adjustable O_3 generator (Model OL80W, Ozone Services). The gas outlet of the flask was connected in series to a second flask (F2) containing 100 mM NaOH to trap any gaseous chlorine/oxy-chlorine species evolved from flask F1 (Figure S1, SI). Pure O_2 was bubbled through F1 and F2 for 1 h prior to ozonation to attain equilibrium conditions. Flasks F1 and F2 were sampled over time by removing 2 mL of solution through a Teflon valve (Figure S1, SI). The samples were analyzed for Cl^- , $\text{OCl}^-/\text{ClO}_2$, ClO_2^- , ClO_3^- , and ClO_4^- (see the SI). All experiments were performed in duplicate. The loss of solution volume in the flasks during the course

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TABLE 1. Matrix of Experiments Conducted Evaluating the Oxidation of Aqueous Chlorine Species in F1 by O₃^d

| experiment no. | initial conditions | | | O ₃ (g) concentration (mM) |
|----------------|-------------------------------|--------------------|------------------|---------------------------------------|
| | Cl species | concentration (mM) | pH | |
| 1. | ClO ₃ ⁻ | 12 | 8 | 0.5 |
| 2a. | ClO ₂ ⁻ | 1.2 | 9.2 | 0.5 |
| 2b. | | 12 | 9.3 | 0.5 |
| 3a. | OCI ⁻ | 1.7 | 9.5 | 0.7 |
| 3b. | | 17 | 9.5 | 0.7 |
| 3c. | HOCl | 1.7 | 5.6 ^a | 0.7 |
| 4a. | Cl ⁻ | 0.28 | 6.5 | 0.7 |
| 4b. | | 2.8 | 6.5 | 0.7 |
| 4c. | | 28 | 6.5 | 0.7 |
| 4d. | | 2.8 | 2.6 ^b | 0.7 |
| 4e. | | 2.8 | 9.3 ^a | 0.7 |
| 4f. | | 2.8 | 6.5 | 0.07 |
| 4 g. | | 2.8 | 6.5 | 3.1 |
| 5. | ClO ₂ (aq) | 0.11 | 4.5 ^c | 0.144 |

^a Buffered with phosphate buffer. ^b Buffered with HCl. ^c Represents the pH of O₃ (aq) to which ClO₂ (aq) (at pH 5.4) is added in minute quantities. ^d Ozone concentration was measured in the gas phase.

of the experiments due to sampling was less than 10%. All experiments (except ClO₂ oxidation as explained in the later section) were performed in the presence of laboratory light. Controls containing the aqueous chlorine species but not exposed to O₃ were analyzed, and there was less than a 10% change in initial concentration indicating minimal effect by laboratory light or O₂ exposure.

ClO₂ (aq) Oxidation. Aqueous ClO₂ (ClO₂ (aq)) was prepared using a modification of the process described by Furman and Margerum (15) (SI). Aqueous O₃ (O₃ (aq)) was prepared by bubbling a known concentration of O₃ (g) in DDI water (pH = 4.5) to produce a steady state concentration of O₃ (aq). The final O₃ (aq) concentration was 0.144 ± 0.013 mM, measured using UV absorption spectroscopy at 260 nm ($\epsilon = 3292 \pm 70 \text{ M}^{-1} \text{ cm}^{-1}$) (16). A 15-mL glass tube with a Teflon coated magnetic stirrer and glass stopper was filled with the O₃ (aq) solution to its maximum capacity followed immediately by a known volume of stock ClO₂ (aq). The molar ratio of initial O₃ (aq)/ClO₂ (aq) was ≥ 1 to ensure complete consumption of ClO₂. At the maximum ClO₂ (aq) concentration, the reaction was complete in only a few seconds as confirmed by measuring the solution absorbance at 359 nm. The solutions were stored in the refrigerator and analyzed for Cl⁻, ClO₂⁻, ClO₃⁻, and ClO₄⁻.

Results and Discussion

ClO₂⁻ Oxidation. Chlorate (ClO₃⁻) was found to be nonre-active even after 7 days of ozone exposure. Oxidation of ClO₂⁻ in F1 is divided into three time periods: Zones 1–3 (Figure 1a and 1b). The initial stage (Zone 1) is nonlinear, and in the final stage (Zone 3) ClO₂⁻ has essentially been completely oxidized. The rate of ClO₂⁻ oxidation was linear ($R^2 > 0.9$) (Zone 2) for both initial ClO₂⁻ concentrations indicating an apparent zero-order rate ($d\text{ClO}_2^-/dt = -k_{\text{ClO}_2^-}$) with respect to ClO₂⁻. This is expected given the large concentration of ClO₂⁻ and relatively low rate of O₃ addition (0.0025 mM min⁻¹). The lag phase in ClO₂⁻ oxidation observed at the start of ozonation (Zone 1) is likely due to a delay in achieving equilibrium of the injected O₃ with the solution. The rate of ClO₂⁻ oxidation is similar for both initial concentrations, with $k_{\text{ClO}_2^-} = 0.010 \pm 0.00003$ and $0.012 \pm 0.0002 \text{ mM min}^{-1}$ for 1.2 and 12 mM ClO₂⁻, respectively. ClO₂⁻ oxidation (Reaction 1 and 2, Table S1, SI) is known to be first-order with respect to ClO₂⁻ and O₃ (aq) with a very large second-order rate constant ($k \sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (17, 18). Therefore, the observed

pseudo- zero-order behavior of ClO₂⁻ oxidation is due to nonlimiting ClO₂⁻ concentration and constant O₃ (aq) concentration.

Production of ClO₃⁻ in F1 mimics the consumption of ClO₂⁻ (Figure 1a,b) with a similar production rate ($d\text{ClO}_3^-/dt = k_{\text{ClO}_3^-}$) as the oxidation rate of ClO₂⁻ in Zone 2 with $k_{\text{ClO}_3^-} = 0.0073 \pm 0.00025$ and $0.01 \pm 0.00007 \text{ mM min}^{-1}$ for 1.2 and 12 mM ClO₂⁻, respectively. There is no production of ClO₃⁻ once ClO₂⁻ is consumed as predicted by reactions 1–4 (Table S1, SI). Most studies indicate that the oxidation of ClO₂⁻ quantitatively produces ClO₃⁻ (17, 19). One study (20) has shown the formation of HOCl/OCI⁻ along with ClO₃⁻ from the reaction of OH/O⁻ radicals with ClO₂ (Reaction 5, Table S1, SI). Cl₂ and HOCl if produced would convert to OCI⁻ at the experimental pH ($\text{p}K_a$ of HOCl/OCI⁻ = 7.5 at 25 °C). OCI⁻ is known to react with O₃ to produce Cl⁻ and ClO₃⁻ (19) with Cl⁻ being the predominant product at pH = 9 (Figure S2, SI). A linear increase in Cl⁻ ($R^2 \sim 0.7$) was observed throughout the experiment resulting in a final molar Cl⁻ yield, $\Phi\text{Cl}^- = 14 \pm 1.4\%$, (where yield (ΦCl_x^-) = $[\text{ClO}_x^-]/[\text{ClO}_2^-]_0$) suggesting that OCI⁻ was produced from ClO₂⁻ oxidation, as neither ClO₃⁻ nor ClO₄⁻ are known to react with O₃ (second-order rate constants for ClO₃⁻ and ClO₄⁻, $k < 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) (19).

Total oxidants (OCI⁻ and ClO₂) were initially (Zone 1) below the detection limit (MDL for OCI⁻ = 0.06 mM and ClO₂ = 0.03 mM), rose to a nearly steady state value during Zone 2, and finally decreased to a negligible concentration in Zone 3 (Figure 1a,b). Ozone (O₃ (aq)) is not considered part of the total oxidant pool due to the high rate constant of O₃ with ClO₂⁻ combined with relatively low predicted equilibrium concentration of aqueous O₃ (0.09 mM) (21). This is experimentally supported by the absence of any measurable total oxidants ($[\text{OCI}^-] + [\text{ClO}_2] + [\text{O}_3 \text{ (aq)}] < 0.03 \text{ mM}$) at the end of both the 1.2 mM and 12 mM experiments. It was not possible to differentiate between ClO₂ and OCI⁻, and the ratio of these constituents may vary over time. A green/yellow gas, indicative of ClO₂ (presence of Cl₂ gas would be unlikely at the experimental pH ~ 9), was initially observed near the liquid bubble interface after starting the ozonation. However, the rate constant for the oxidation of ClO₂ with O₃ ($k = 1.05 \pm 0.10 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) (18) is an order of magnitude greater than that of OCI⁻ ($k = 95 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$) (19), and therefore OCI⁻ is likely the dominant species. This is supported by an increase in Cl⁻ and a decrease in OCI⁻ (Zone 3), while the increase in ClO₃⁻ and ClO₄⁻ is marginal (Figure 1a,b).

A full kinetic analysis of ClO₄⁻ production in F1 would require concentrations of O₃ and ClO₂ which could not be measured due to interferences. Unlike ClO₂⁻ and ClO₃⁻ the change in concentration of ClO₄⁻ clearly follows a nonlinear sigmoidal rate. The rate of ClO₄⁻ production is roughly linear in Zone 1 and increases with time in Zone 2 (Figure 1a,b). Essentially no change occurs in the concentration of ClO₄⁻ in Zone 3 corresponding to both complete oxidation of ClO₂⁻ and no production of ClO₃⁻. This negligible change combined with a substantially smaller yield (~0.005 to 0.02%) of ClO₄⁻ production (Figure 2a,b) from OCI⁻ oxidation indicates practically all ClO₄⁻ is produced due to oxidation of ClO₂⁻ (Figure 1a,b). The final yield of ClO₄⁻ (ΦClO_4^-) for the 1.2 and 12 mM experiments is 2.7% (±0.1) and 0.49% (±0.08), respectively, which is similar to the reported value in previous ClO₂⁻ oxidation experiments ($\Phi\text{ClO}_4^- = 4.0\%$ for 1.5 mM starting ClO₂⁻) (12).

There was a negligible increase in total Cl species ($\Phi\text{Cl}_T = 0.2 \pm 0.2\%$) in the trapping flask (F2) for the 1.2 mM ClO₂⁻ experiment that was accounted by the ClO₃⁻ and ClO₄⁻ produced ($\Phi\text{ClO}_3^- = 0.2 \pm 0.3\%$ and $\Phi\text{ClO}_4^- = 0.07 \pm 0.1\%$). The increase in the concentration of total Cl species in F2 was much greater for the higher initial ClO₂⁻ concentration (12 mM) with a $\Phi\text{Cl}_T = 1.93 \pm 1.5\%$ and peak $\Phi\text{ClO}_2^- = 1.4 \pm 0.2\%$ at $t \approx 800 \text{ min}$ (Figure S3, SI). The production of

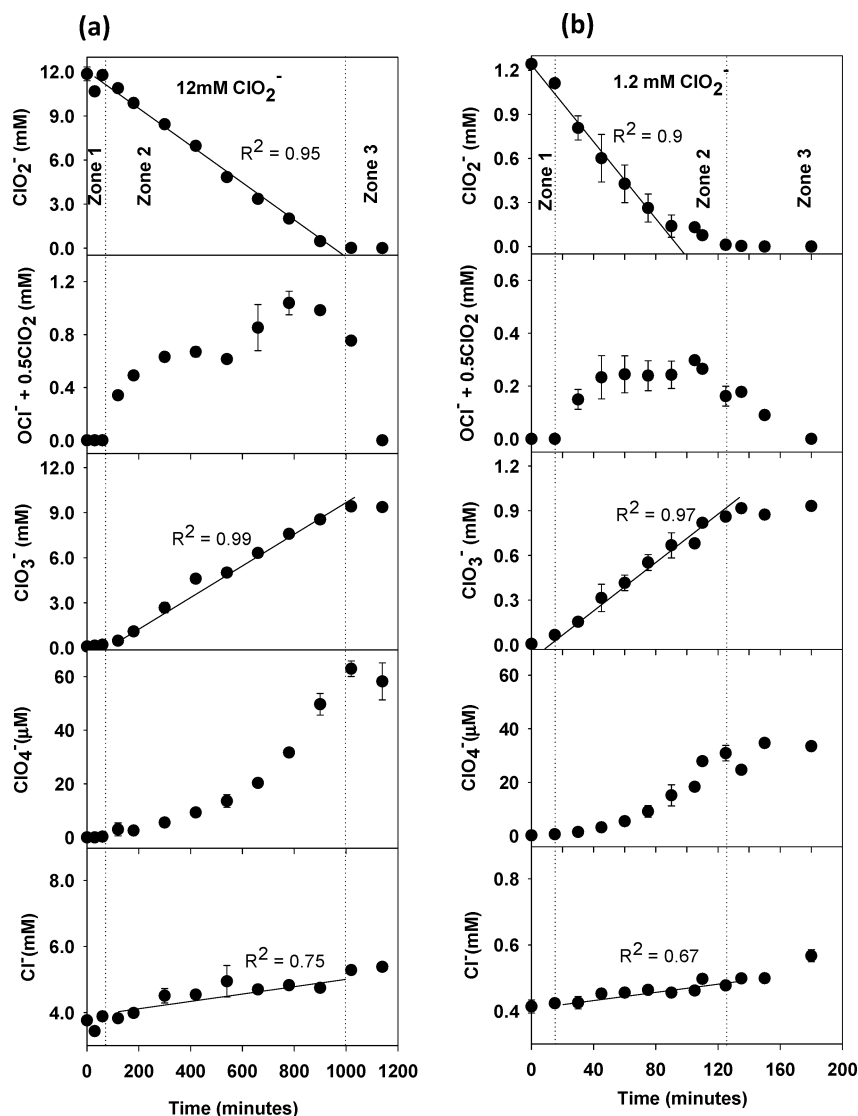


FIGURE 1. Production of total oxidants ($\text{OCl}^- + 0.5 \text{ClO}_2$), ClO_3^- , ClO_4^- , and Cl^- in F1 from the oxidation of (a) 12 mM and (b) 1.2 mM ClO_2^- , respectively, by O_3 . The starting pH of 12 mM and 1.2 mM ClO_2^- experiments are 9.3 and 9.2, respectively. All Cl species concentrations except that of ClO_4^- are expressed as mM ($1 \text{ mM} = 10^{-3} \text{ mol L}^{-1}$); ClO_4^- concentration is expressed as μM ($1 \mu\text{M} = 10^{-6} \text{ mol L}^{-1}$). Zone 2 represents the bulk of the ClO_2^- oxidation including ClO_3^- and ClO_4^- production, while Zones 1 and 3 represent the equilibration time for O_3 and consumption of total oxidants (predominantly as OCl^-), respectively. The consumption of ClO_2^- and production of ClO_3^- and Cl^- follows a nearly linear rate during much of the experiment (Zone 2) as shown by the solid lines.

ClO_2^- and ClO_3^- in F2 are likely due to the decomposition of ClO_2 stripped from F1 (Reaction 6, Table S1, SI). The sudden drop in ClO_2^- concentration after 800 min, followed by the sharp increase in both ClO_3^- and ClO_4^- , is likely due to O_3 breakthrough from F1 resulting in the oxidation of the accumulated ClO_2^- in F2 (Figure S3, SI).

HOCl/OCl⁻ Oxidation. ClO_4^- yield ($\Phi\text{ClO}_4^- = [\text{ClO}_4^-]/[\text{OCl}^-]_0$) in F1 was similar for the oxidation of 1.7 and 17 mM OCl^- , at pH ~ 10.0 ($\Phi\text{ClO}_4^- = 0.0211 \pm 0.0002$ and 0.0302 ± 0.0002 , respectively) (Figure 2a). Molar yield was at least an order of magnitude lower compared to the oxidation of ClO_2^- . Reducing the pH to 5.6 corresponding to the oxidation of HOCl ($\text{HOCl} = 98\%$ of Cl_2 at pH = 5.6) reduced the yield of ClO_4^- by an order of magnitude ($0.0051 \pm 0.0007\%$) (Figure 2b). A previous study did not observe significant ClO_4^- production from the oxidation of OCl^- (1.9 mM) by O_3 likely due to the presence of elevated ClO_4^- in the source HOCl/OCl⁻ (12). However, the preparation of HOCl/OCl⁻ from $\text{Ca}(\text{OCl})_2$ salt immediately prior to oxidation in this experiment minimized ClO_4^- in the controls, allowing the production of trace quantities of ClO_4^- to be evaluated.

The concentration of ClO_2^- in F1 was below the quantification limit ($[\text{ClO}_2^-]_t < 3 \times 10^{-3} \text{ mM}$) at all time points likely due to the high rate constant for the oxidation of ClO_2^- with respect to HOCl/OCl⁻ by O_3 (17, 19). The presence of ClO_2^- in F1 at concentrations equal to the quantification limit in the starting HOCl/OCl⁻ solutions could account for a maximum of 1.5, 2.1, and 8.6% of the ClO_4^- produced (assuming ΦClO_4^- for the ClO_2^- oxidation = 2.5%) from the oxidation of 17 mM OCl^- , 1.7 mM OCl^- , and 1.7 mM HOCl, respectively.

The reaction of OCl^- with O_3 produces Cl^- , ClO_2^- , and O_2 as primary products with ClO_2^- reacting further to produce ClO_3^- (Reactions 7 and 8, Table S1, SI). However, ClO_4^- is also shown as a minor product with yields 3 to 4 orders of magnitude below Cl^- and ClO_3^- . The molar yields of Cl^- in F1 were similar for the oxidation of 1.7 and 17 mM OCl^- ($\Phi\text{Cl}^- = 49 \pm 1$ and $42 \pm 4\%$, respectively), but the yields of ClO_3^- varied ($\Phi\text{ClO}_3^- = 12 \pm 3$ and $25 \pm 1\%$, respectively) (Figure S2, SI). Changing the dominant form to HOCl by lowering the pH did not impact the formation of Cl^- ($\Phi\text{Cl}^- = 42 \pm 6\%$), while the ClO_3^- yield ($\Phi\text{ClO}_3^- = 22 \pm 0.3\%$) was

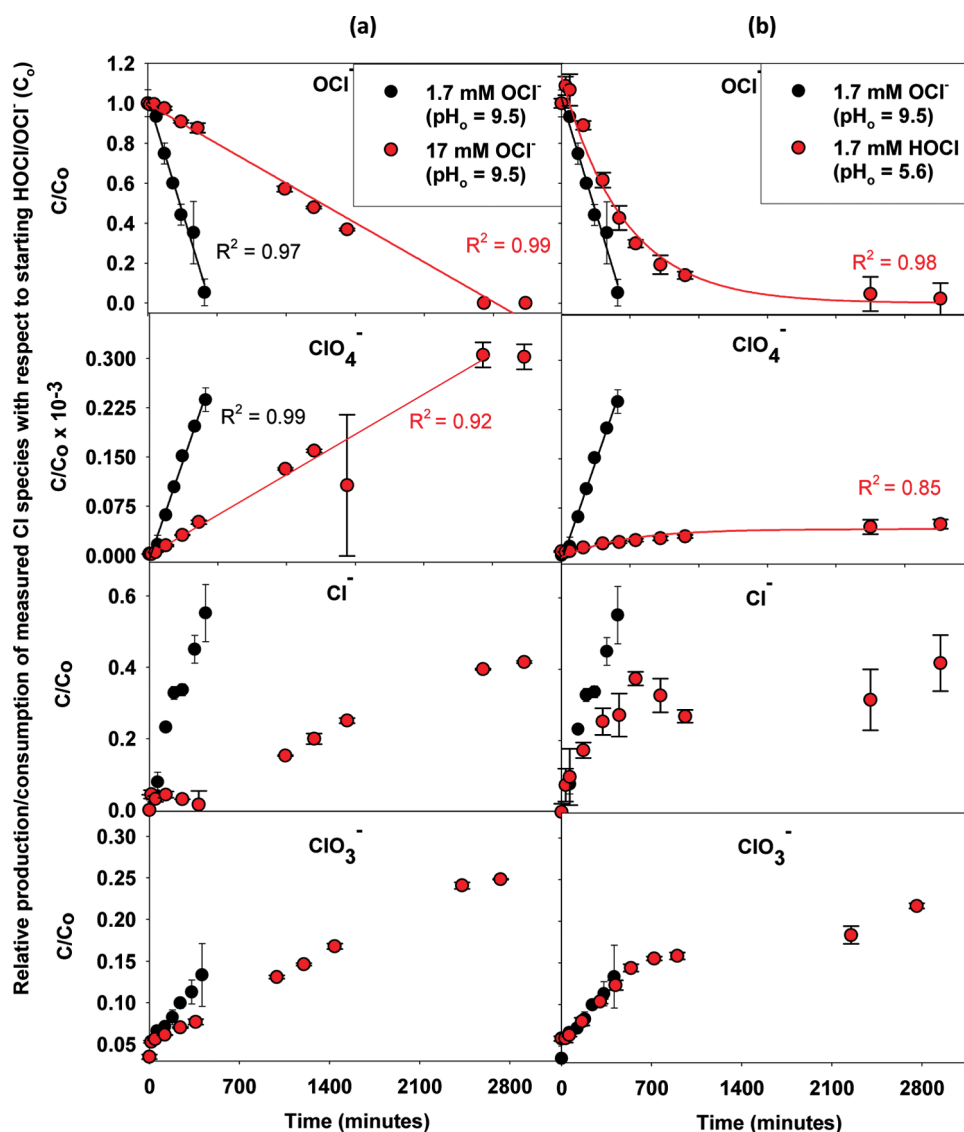


FIGURE 2. Oxidation of OCl^- by O_3 in F1 at (a) different initial OCl^- concentrations and varying initial pH (pH_0) showing the production of ClO_4^- , Cl^- , and ClO_3^- normalized to starting OCl^-/HOCl concentration (C/C_0). ClO_2^- is not shown as it was below the detection limit for all the experiments. The solid lines on the left (2a) are the modeled pseudo-zero-order consumption and production of OCl^- and ClO_4^- at two initial OCl^- concentrations. The solid curve (red) on the right (2b) is the modeled pseudo-first-order consumption and production of HOCl and ClO_4^- , respectively, for the oxidation of 1.7 mM HOCl .

intermediate to the oxidation of 17 and 1.7 mM OCl^- . Previous studies have shown that the yields of Cl^- and ClO_3^- ($\Phi_{\text{Cl}^-} = 77\%$ and $\Phi_{\text{ClO}_3^-} = 23\%$) from the aqueous oxidation of OCl^- is essentially independent of O_3 dose at pH 8 (22). The change in the molar ratios of Cl^- to ClO_3^- is possibly influenced by a lack of closure on the Cl mass balance. A deficit in the Cl mass balance (up to 35% of the total Cl species) was encountered that was unique to the experiments evaluating the oxidation of HOCl/OCl^- (Figure S2, SI). Separate experiments containing additional traps of NaOH and KI were provided in series after F1 to rule out the escape of volatile chlorine/chlorine-oxide compounds from the reaction flask (F1), but regardless there was no significant increase in total Cl for the combined traps. A small increase in ClO_4^- (~1–2% of the total ClO_4^- generated) did occur in F2, possibly because of the relatively high analytical sensitivity of ClO_4^- with respect to other oxy-chlorine species. The yield of ClO_3^- in the ozone oxidation of HOCl/OCl^- could be affected by changes in conditions such as pH and alkalinity, attributed to the presence of hydroxyl radicals increasing the formation of ClO_3^- (22).

The rate of OCl^- oxidation by O_3 was linear ($d\text{OCl}^-/dt = -k_{\text{OCl}^-}$) throughout the oxidation of both 1.7 mM and 17 mM initial OCl^- ($R^2 > 0.97$). Unlike the oxidation of ClO_2^- , the rate of OCl^- oxidation was not independent of the reactant concentration (Figure 2a). The rate of OCl^- consumption ($k_{\text{OCl}^-} = 0.0067 \pm 0.0006 \text{ mM min}^{-1}$) was higher for the oxidation of 17 mM OCl^- compared to 1.7 mM OCl^- ($k_{\text{OCl}^-} = 0.0039 \pm 0.0003 \text{ mM min}^{-1}$). Formation of ClO_4^- was also linear ($d\text{ClO}_4^-/dt = k_{\text{ClO}_4^-}$) with a similar proportional increase in rate for the oxidation of 1.7 and 17 mM OCl^- ($k_{\text{ClO}_4^-} = (9.2 \pm 0.2) \times 10^{-7}$ and $(20.8 \pm 0.2) \times 10^{-7} \text{ mM min}^{-1}$, $R^2 > 0.9$, respectively) (Figure 2a). In contrast to the oxidation of 1.7 mM OCl^- , the rate of 1.7 mM HOCl oxidation was nonlinear (Figure 2b). The rate of HOCl consumption was pseudo-first-order ($d\text{HOCl}/dt = -k_{\text{HOCl}}[\text{HOCl}]_t$) with respect to HOCl concentration with $k_{\text{HOCl}} = 0.0022 \pm 0.00003 \text{ min}^{-1}$ ($R^2 = 0.98$). ClO_4^- production was first-order ($d\text{ClO}_4^-/dt = k_{\text{ClO}_4^-}[\text{HOCl}]_t$) with respect to HOCl with $k_{\text{ClO}_4^-} = (9.5 \pm 1.2) \times 10^{-8} \text{ min}^{-1}$ ($R^2 = 0.85$), illustrating that ClO_4^- is formed by the oxidation of HOCl (Figure 2b). As mentioned, the production rate of ClO_4^- for the ClO_2^- oxidation experiments

TABLE 2. Consumption Rates of Cl⁻ and Production Rates of ClO₃⁻ and ClO₄⁻ from the Oxidation of Cl⁻ in F1^a

| initial conditions | | | mM min ⁻¹ | | | ending pH |
|--------------------------------------|-------------------------------------|-----|---------------------------------|--|--|-----------|
| [Cl ⁻] ₀ (mM) | [O ₃] ₀ (mM) | pH | k _{Cl⁻} | k _{ClO₄⁻} | k _{ClO₃⁻} | |
| 0.28 | 0.5 | 5.6 | (4.1 ± 0.14) × 10 ⁻⁶ | (2.9 ± 0.4) × 10 ⁻⁹ | (3.0 ± 0.03) × 10 ⁻⁶ | 4.4 ± 0.1 |
| 2.8 | 0.7 | 6.5 | (17 ± 1.3) × 10 ⁻⁶ | (5.3 ± 0.8) × 10 ⁻⁹ | (14 ± 0.01) × 10 ⁻⁶ | 4.7 ± 0.1 |
| 28 | 0.7 | 6.5 | (77 ± 9.4) × 10 ⁻⁶ | (24 ± 3.3) × 10 ⁻⁹ | (141 ± 5.7) × 10 ⁻⁶ | 5.6 ± 0.2 |
| 2.8 | 0.07 | 5.6 | (31 ± 14) × 10 ⁻⁶ | (0.8 ± 0.3) × 10 ⁻⁹ | (2.2 ± 0.5) × 10 ⁻⁶ | 4.0 ± 0.2 |
| 2.8 | 3.1 | 5.9 | (73 ± 9.8) × 10 ⁻⁶ | (21 ± 0.2) × 10 ⁻⁹ | (41 ± 0.9) × 10 ⁻⁶ | 3.9 ± 0.1 |
| 2.8 | 0.7 | 2.6 | (119 ± 4.9) × 10 ⁻⁶ | (4.0 ± 1.5) × 10 ⁻⁹ | (4.6 ± 0.2) × 10 ⁻⁶ | 2.8 ± 0.2 |
| 2.8 | 0.7 | 9.2 | (22 ± 5.4) × 10 ⁻⁶ | (0.9 ± 0.1) × 10 ⁻⁹ | (5.3 ± 0.9) × 10 ⁻⁶ | 8.7 ± 0.3 |

^a HOCl/OCl⁻ was not evaluated as it is an unstable intermediate subject to both production and consumption.

is sigmoidal and is attributed to higher chlorine oxide intermediates, possibly ClO₂. It is possible the large second-order rate constant for the ClO₂⁻ - O₃ reaction ($k = (4 \pm 1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) relative to that of the ClO₂-O₃ reaction ($k = 1050 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$) (18) results in the ClO₄⁻ formation rate being independent of the ClO₂⁻ consumption and governed by the aqueous concentration of ClO₄⁻ precursors (e.g., ClO₂) and O₃. The comparatively lower rate constant for the OCl⁻ and HOCl - O₃ reactions $95 \pm 12 \text{ M}^{-1} \text{ s}^{-1}$ and $\sim 0.002 \text{ M}^{-1} \text{ s}^{-1}$, respectively (19, 22), suggests negligible accumulation of ClO₄⁻ precursors and that ClO₄⁻ production is dependent on the consumption of HOCl/OCl⁻, supported by the close agreement of the ClO₄⁻ production and oxidation of HOCl/OCl⁻ rates.

Cl⁻ Oxidation. The impacts of initial Cl⁻ concentration, pH, and O₃ concentration on the production of ClO₄⁻ were systematically evaluated. Major products of the oxidation of Cl⁻ in F1 for all conditions were ClO₃⁻ and/or HOCl/OCl⁻ with the rate of ClO₄⁻ formation at least 3 orders of magnitude lower than the dominant product (Table 2). There was no measurable accumulation of ClO₂⁻ ($<3.0 \times 10^{-3} \text{ mM}$) similar to the oxidation of HOCl/OCl⁻. The slow second-order reaction rate constant for Cl⁻ oxidation by O₃ ($\approx 0.0002 \text{ M}^{-1} \text{ min}^{-1}$ (19)) resulted in the incomplete oxidation of Cl⁻ even at the lowest Cl⁻ concentration studied (0.28 mM), and a comparison of the final yields of the products is not possible. Instead, the rate of change of Cl species with time is used for comparison.

Impact of Cl⁻ Concentration. The Cl⁻ consumption rate was linear ($d\text{Cl}^-/dt = -k_{\text{Cl}^-}$) for all the conditions studied, $R^2 > 0.85$ (Table 2). The rate of Cl⁻ oxidation was proportional to starting Cl⁻ concentrations (Table 2 and Figure S4, SI). The formation rate of ClO₄⁻ was linear ($R^2 > 0.96$) and 2–3 orders of magnitude less than the Cl⁻ consumption rate. The ClO₄⁻ production rate ($d\text{ClO}_4^-/dt = k_{\text{ClO}_4^-}$) increased linearly ($k_{\text{ClO}_4^-}/[\text{Cl}^-]_0 = 0.75 \times 10^{-9} \text{ mM min}^{-1} \text{ Cl}_4^-/\text{mM-Cl}^-$, $R^2 = 0.995$) with respect to the initial Cl⁻ concentration (Table 2). Production of ClO₃⁻ is similarly linear ($R^2 > 0.97$) with a production rate ranging from $k_{\text{ClO}_3^-} = (3.01 \pm 0.03) \times 10^{-6}$ to $(141 \pm 6) \times 10^{-6} \text{ mM min}^{-1}$ identical in magnitude to that of Cl⁻ oxidation (Table 2). ClO₃⁻ accounts for most (>80%) of the product produced from Cl⁻ oxidation for any given time point. The HOCl/OCl⁻ concentration increased over the experimental time period for the oxidation of 2.8 and 28 mM Cl⁻ but remained below the minimum quantification limit (0.03 mM) for the oxidation of 0.28 mM Cl⁻ (Figure S4, SI). Total accumulation of HOCl/OCl⁻ was proportional to the initial Cl⁻ concentration but was always less than 25% of the total product Cl species.

The pH of the solution in F1 was not controlled and decreased during the experiment (Table 2), similar to previous studies (12). The cause of the pH drop is attributed to 1) generation of H⁺ ions during ClO₃⁻ and ClO₄⁻ formation from its conjugate acid ($\text{p}K_a = -1$ and < -7 respectively); 2) hydrolysis of Cl₂ (Reaction 9, Table S1, SI); and 3) the slow heterogeneous O₃ (g) attack on Teflon tubes generating small

amounts of acid gas (possibly F₂) which can hydrolyze in water to release H⁺ ($\text{p}K_a = 3.2$) (23). The increase in acidity based on the increase in the measured F⁻ concentration would result in a pH of about 4 at 12,000 min which would account for the observed decrease in pH.

Impact of O₃ (g) Concentration. The ozone concentrations in the O₃/O₂ mixtures were varied from 0.07 to 3.1 mM for a constant starting Cl⁻ concentration (2.8 mM). ClO₄⁻ formation for all O₃ exposures was linear ($R^2 > 0.9$), and the ClO₄⁻ production rate increased linearly ($k_{\text{ClO}_4^-}/[\text{O}_3]_0 = 6.6 \times 10^{-9} \text{ mM min}^{-1} \text{ ClO}_4^-/\text{mM-O}_3 \text{ (g)}$, $R^2 = 0.999$) with respect to O₃ (g) concentration (Table 2). Cl⁻ oxidation was linear ($R^2 > 0.78$) and the largest rate of Cl⁻ oxidation corresponded with the highest O₃ exposure (Table 2). The production of ClO₃⁻ was also generally linear ($R^2 > 0.9$). Accumulation of HOCl/OCl⁻ (assuming linearity) was higher for the 0.07 mM O₃ exposure (Figure S4, SI) representing the largest portion of the product Cl species (>85%), but the production rate of ClO₃⁻ and ClO₄⁻ was lower, indicating an O₃ (aq) limitation for further oxidation of HOCl/OCl⁻. The HOCl/OCl⁻ accumulation rate was comparable to the ClO₃⁻ production rate at the highest O₃ exposure (3.1 mM) implying the O₃ loading was sufficient to maintain the production and consumption of HOCl/OCl⁻ species to ClO₃⁻ and ClO₄⁻.

Impact of Starting pH. The impact of pH on ClO₄⁻ production from Cl⁻ (2.8 mM) oxidation by O₃ (0.7 mM) was evaluated at 3 pH ranges: 9.3 to 8.9 (HPO₄²⁻), 6.5 to 4.0 (unbuffered), and 2.5 to 2.6 (HCl), respectively (Table 2 and Figure S4, SI). The production rate ($k_{\text{ClO}_4^-} = (4.0 \pm 1.5) \times 10^{-9} \text{ mM min}^{-1}$) of ClO₄⁻ at a starting pH of 2.6 is similar to the unbuffered production rate of ($k_{\text{ClO}_4^-} = (5.3 \pm 0.8) \times 10^{-9} \text{ mM min}^{-1}$) at the same starting Cl⁻ concentration and O₃ exposure. A reduction in ClO₄⁻ production rate ($k_{\text{ClO}_4^-} = (0.94 \pm 0.06) \times 10^{-9} \text{ mM min}^{-1}$) occurred at a pH of 9.3. The rate of accumulation of HOCl/OCl⁻ was highest at pH 2.6 ($(7.6 \pm 0.01) \times 10^{-5} \text{ min}^{-1}$), representing the predominant product from the oxidation of Cl⁻ (>90%), whereas the concentration of HOCl/OCl⁻ was less than the detection limit for Cl⁻ oxidation at a pH of 9.3.

The role of pH in ClO₄⁻ production is influenced by numerous interdependent factors. The rate of Cl⁻ consumption is an inverse function of pH, with an increase in Cl⁻ consumption by an order of magnitude at very low pH (~ 2.5) concomitantly increasing the rate Cl₂/HOCl/OCl⁻ formation (Reactions 10 and 11, Table S1, SI). However, ClO₄⁻ production efficiency is much lower for the oxidation of HOCl (pH 4–7) relative to OCl⁻ as described previously. Further, at very low pHs (<4) the potential presence of ClO₂⁻ as HClO₂ ($\text{p}K_a = 2.0$) could increase the formation of reactive Cl species such as ClO₂ which can significantly contribute to ClO₄⁻ production (see ClO₂ oxidation).

ClO₂ (aq) Oxidation. As previously discussed, ClO₂ is likely a key intermediate in ClO₄⁻ formation from the oxidation by O₃ of aqueous chlorine/oxy-chlorine solutions. To evaluate its potential role, experiments were conducted using pure solutions of ClO₂ at a concentration of $0.11 \pm 0.03 \text{ mM}$ and

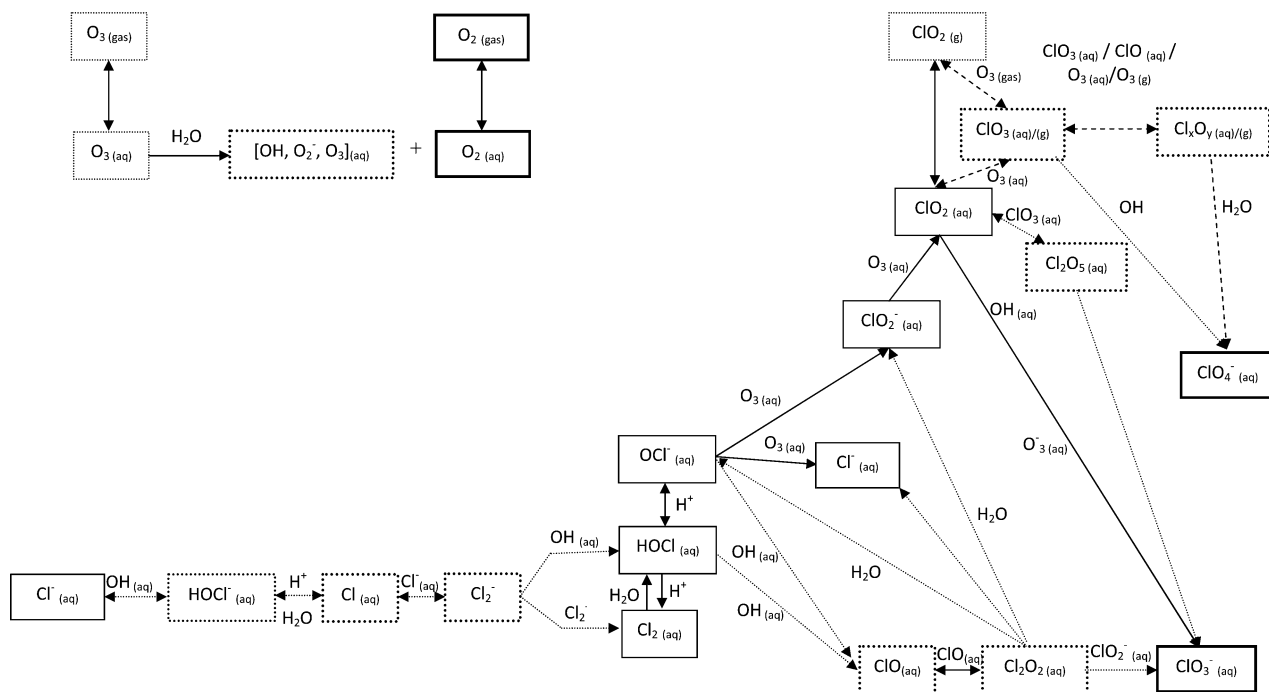


FIGURE 3. A schematic of the proposed mechanism for the formation of ClO_4^- from aqueous Cl^- species. The Cl^- species in the boxes with thick solid lines are the stable end products in the O_3 reaction of Cl^- , and the thin solid lines represent the intermediates that are well-known from the O_3 reactions of Cl^- species. The dashed boxes represent the intermediate species/radicals that are proposed to be involved in the Cl^- oxidation. The solid and dotted arrows are known, and speculated/proposed reactions (Reactions 1–11 and 20–29, Table S1, SI) from the literature, respectively. The dashed arrows represent reactions obtained from gas phase oxidation of oxy-chlorine radicals (Reactions 12–19, Table S1, SI).

an initial aqueous phase O_3 concentration of 0.14 ± 0.013 mM in closed flask batch experiments. Reaction of ClO_2 was fast (seconds for completion based on absorbance measurement at 360 nm), and ClO_3^- and ClO_4^- were the only products formed. The control solutions of ClO_2 and O_3 were stable and had negligible ClO_4^- and ClO_3^- . Chlorate accounted for almost 100% ($\pm 10\%$) of the initial ClO_2 with a ClO_4^- yield of $0.65 \pm 0.15\%$ comparable to the yields for the oxidation of ClO_2^- by O_3 .

Mechanistic Implications. Previous studies on the production of ClO_4^- from O_3 oxidation of HOCl/OCl^- were inconclusive possibly due to the presence of significant amounts of ClO_4^- in starting HOCl/OCl^- (12) and analytical limitations in measuring low levels of ClO_4^- (24). For this study O_3 oxidation of HOCl/OCl^- clearly results in the formation of ClO_4^- at concentrations significantly (5 to 100 times) higher than the experimental controls. A previous study of ClO_4^- production from oxidation of aqueous Cl^- and ClO_2^- suggested ClO_2^- is the most efficient precursor of ClO_4^- via aqueous phase ozonation and proposed the potential importance of ClO_2 and higher oxy-chlorine radicals (Cl_2O_6) in oxidation of ClO_2^- to ClO_4^- (12). Although our work did not identify the direct precursor for ClO_4^- formation, we experimentally show through aqueous oxidation of ClO_2 with O_3 that ClO_2 is involved in the formation of ClO_4^- and is likely the common intermediate in the formation of ClO_4^- from the ozonation of other oxy-chlorine anions. Possible direct precursors of ClO_4^- in the aqueous oxidation of Cl^- species with O_3 are proposed to be Cl_2O_4 , Cl_2O_6 , and Cl_2O_7 , all known to hydrolyze in water to produce ClO_4^- and ClO_3^- or ClO^- (Reactions 12–14, Table S1, SI). To our knowledge these higher chlorine oxide radicals have not been identified in aqueous phase solutions containing ClO_2 and O_3 , possibly due to rapid hydrolysis in the presence of water and thermal decomposition at low temperatures (25–28). Further, the concentrations of ClO_4^- precursors based on the final ClO_4^- concentrations are likely 2 to 4 orders of magnitude lower than the major end products thereby making them difficult

to determine. Proposed reactions (Reactions 15–18, Table S1, SI) leading to the formation of ClO_4^- precursors are obtained from the available literature on gas phase reactions of ClO_2 and O_3 (25–28) where they are well characterized.

Results of this work in conjunction with previous studies involving oxidation of oxy-chlorine compounds leads to the following potential pathway for ClO_4^- production (Figure 3). The oxidation of the lower chlorine/oxy-chlorine species to other stable end products (Cl^- and ClO_3^-) are described in previous literature (Reactions 1–11, Table S1, SI). Oxidation of ClO_2 by O_3 leading to the formation of ClO_4^- precursors could involve the formation of ClO_3 radical analogous to proposed gas phase reactions of ClO_2 . Evidence of ClO_3 in the gas phase has been tentative (27) with occurrences in aqueous phase demonstrated by pulse radiolysis and laser photolysis studies of aqueous ClO_3^- salts (29, 30).

The rate of ClO_4^- production depends on the nature of the starting Cl^- species with the lowest rate for the oxidation of Cl^- with progressively higher rates for HOCl , OCl^- and ClO_2^- . Efficiency of ClO_4^- production is generally greater for higher oxidation states of Cl in agreement with previous O_3 and UV oxidation studies of aqueous ClO_x^- species (12–14). These observations are consistent with the proposed mechanistic pathway for ClO_4^- formation. The slow rate of ClO_4^- formation (Table 2) from Cl^- under all conditions examined indicates negligible potential for anthropogenic ClO_4^- production from the ozone treatment of water and wastewater systems containing Cl^- as the predominant Cl species. However, the presence of ClO_2^- or OCl^- could potentially contribute to significant ClO_4^- production in O_3 treated waters. Evidence for the involvement of atmospheric O_3 mediated processes in the formation of natural ClO_4^- based on its stable oxygen isotope anomaly ($\Delta^{17}\text{O}$) (3) implies that the mechanism of natural ClO_4^- formation may be similar to the proposed pathway in our study. The observations of ClO_2 in the polar stratosphere with elevated concentrations in the presence of heterogeneous surfaces such as polar stratospheric clouds (PSCs) (31) and sulfate aerosols from

major volcanic eruptions (32) combined with the present insight into the ClO_4^- formation pathway, supports the potential for stratospheric ClO_4^- production. Previous studies speculated the possible role of higher oxidation states of chlorine (e.g., Cl_2O_4 , Cl_2O_6 , and Cl_2O_7) in $\text{Cl}-\text{O}_3$ chemistry of the upper atmosphere especially the polar stratosphere (33). If unequivocal evidence is obtained on the presence of ClO_4^- in the stratosphere, this proposed mechanism may be useful in evaluating the role of higher chlorine oxides in complex atmospheric photochemistry.

Acknowledgments

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Supporting Information Available

Text, Table S1, and Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Ericksen, G. E. *Geology and origin of the Chilean nitrate deposits*; U.S. Geological Survey, Prof. Paper 1188, 1981; 37p.
- Michalski, G.; Böhlke, J. K.; Thiemens, M. Long-term atmospheric deposition as the source of nitrate and other salts in the Atacama desert, Chile: New evidence from mass-independent oxygen isotopic composition. *Geochim. Cosmochim. Acta* **2004**, *68*, 4023–4038.
- Bao, H.; Gu, B. Natural perchlorate has a unique oxygen isotope signature. *Environ. Sci. Technol.* **2004**, *38*, 5073–5077.
- Rajagopalan, S.; Anderson, T. A.; Fahlquist, L.; Rainwater, K. A.; Ridley, M.; Jackson, A. W. Widespread presence of naturally occurring perchlorate in High Plains of Texas and New Mexico. *Environ. Sci. Technol.* **2006**, *40*, 3156–3162.
- Rao, B.; Anderson, T. A.; Orris, G. J.; Rainwater, K. A.; Rajagopalan, S.; Sandvig, R. M.; Scanlon, B. R.; Stonestrom, D. A.; Walvoord, M. A.; Jackson, W. A. Widespread natural perchlorate in unsaturated zones of the Southwest United States. *Environ. Sci. Technol.* **2007**, *41*, 4522–4528.
- Orris, G. J.; Harvey, G. J.; Tsui, D. T.; Eldridge, J. E. *Preliminary analyses for perchlorate in selected natural materials and their derivative products*; USGS Open File Report 03-314; USGS, U.S. Government Printing Office: Washington, DC, 2003.
- Plummer, L. N.; Böhlke, J. K.; Doughten, M. W. Perchlorate in pleistocene and holocene groundwater in North-Central New Mexico. *Environ. Sci. Technol.* **2005**, *39*, 4586–4593.
- Rajagopalan, S.; Anderson, T.; Cox, S.; Harvey, G.; Cheng, Q. Perchlorate in wet deposition across North America. *Environ. Sci. Technol.* **2009**, *43*, 616–622.
- Simonatis, C.; Hecklen, J. Perchloric acid: A possible sink for stratospheric chlorine. *Plant. Space. Sci.* **1975**, *23*, 1567–1569.
- Murphy, D. M.; Thomson, D. S. Halogen ions and NO^+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere. *Geophys. Res. Lett.* **2000**, *27*, 3217–3220.
- Jaegle, L.; Yung, Y. L.; Toon, G. C.; Sen, B.; Blavier, J. Balloon observations of organic and inorganic chlorine in the stratosphere: The role of HClO_4 production on sulfate aerosols. *Geophys. Res. Lett.* **1996**, *23*, 1749–1752.
- Kang, N.; Jackson, W. A.; Dasgupta, P. K.; Anderson, T. A. Perchlorate production by ozone oxidation of chloride in aqueous and dry systems. *Sci. Total Environ.* **2008**, *405*, 301–309.
- Kang, N.; Anderson, T. A.; Jackson, W. A. Photochemical formation of perchlorate from aqueous oxychlorine anions. *Anal. Chim. Acta* **2006**, *567*, 48–56.
- Kang, N.; Anderson, T. A.; Rao, B.; Jackson, W. A. Characteristics of perchlorate formation via photodissociation of aqueous chlorite. *Environ. Chem.* **2009**, *6*, 53.
- Furman, C. S.; Margerum, D. W. Mechanism of chlorine dioxide and chlorate ion formation from the reaction of hypobromous acid and chlorite ion. *Inorg. Chem.* **1998**, *37*, 4321–4327.
- Hart, E. J.; Sehested, K.; Holeman, J. Molar absorptivities of ultraviolet and visible bands of ozone in aqueous solutions. *Anal. Chem.* **1983**, *55*, 46–49.
- Nicoson, J. S.; Wang, L.; Becker, R. H.; Hartz, K. E. H.; Muller, C. E.; Margerum, D. W. Kinetics and mechanisms of the ozone/bromite and ozone/chlorite reactions. *Inorg. Chem.* **2002**, *41* (11), 2975–2980.
- Klänning, U. K.; Sehested, K.; Holeman, J. Standard Gibbs energy of formation of the hydroxyl radical in aqueous solution. Rate constants for the reaction $\text{ClO}_2^- + \text{O}_3 \leftrightarrow \text{O}_3^- + \text{ClO}_2$. *J. Phys. Chem.* **1985**, *89*, 760–763.
- Hoigné, J.; Bader, H.; Haag, W. R.; Staehelin, J. Rate constants of direct reactions of ozone with organic and inorganic compounds in water-III. Inorganic compounds and Radicals. *Water Res.* **1985**, *19* (8), 993–1004.
- Klänning, U. K.; Sehested, K. The primary process $\text{ClO}_3^- (+ h\nu) \leftrightarrow \text{ClO}^- + \text{O}_2$ in the photolysis of aqueous ClO_3^- solutions. *J. Phys. Chem.* **1991**, *95*, 740–743.
- Horváth, M.; Bilitzky, L.; Huttner, J. *Ozone*; Elsevier: New York, 1985.
- Siddiqui, M. S. Chlorine-ozone interactions: Formation of chlorate. *Water Res.* **1996**, *30* (9), 2160–2170.
- Obvintseva, L. A.; Chibirova, F. K.; Kazakov, S. A.; Avetisov, A. K.; Srobkova, M. V.; Finogenova, N. V. Semiconductor sensors application for definition of factor of ozone heterogenous destruction on Teflon surface. *Sensors* **2003**, *3*, 504–508.
- Haag, W. R.; Hoigné, J. Ozonation of water containing chlorine or chloramines: Reaction products and kinetics. *Water Res.* **1983**, *17* (10), 1397–1402.
- Jansen, M.; Schatte, G.; Tobais, K. M.; Willner, H. Properties of dichlorine hexaoxide in the gas phase and in low-temperature matrices. *Inorg. Chem.* **1988**, *27*, 1703–1706.
- Quiroga, S. L.; Perissinotti, L. J. Reduced mechanism for the 366 nm chlorine dioxide photodecomposition in N_2 -saturated aqueous solutions. *J. Photochem. Photobiol., A* **2005**, *171*, 59–67.
- Green, T. J.; Islam, M.; Canosa-Mas, C.; Marston, G.; Wayne, R. P. Higher oxides of chlorine: absorption cross-section of Cl_2O_6 and Cl_2O_4 , the decomposition of Cl_2O_6 , and the reactions of OClO with O and O_3 . *J. Photochem. Photobiol., A* **2004**, *162*, 353–370.
- Wiberg, N.; Eagleson, M.; Aylett, B. J., Eds. *Inorg. Chem.*, 1st ed.; Academic Press: New York, 2001.
- Domae, M.; Katsumura, Y.; Jiang, P.; Nagaishi, R.; Hasegawa, C.; Ishigure, K.; Yoshida, Y. Observation of ClO_3 radical in aqueous chlorate solution by pulse radiolysis. *J. Phys. Chem.* **1994**, *98*, 190–192.
- Zuo, Z.; Katsumura, Y.; Ueda, K.; Ishigure, K. Laser photolysis study on reactions of sulfate radical and nitrate radical with chlorate ion in aqueous solutions. Formation and reduction potential of ClO_3^\bullet radical. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (4), 533–536.
- Solomon, S.; Mount, G. H.; Sanders, R. W.; Jakoubek, R. O.; Schmeltekopf, A. L. Observations of the nighttime abundance of OClO in the winter stratosphere above Thule, Greenland. *Science* **1988**, *242* (4878), 550–555.
- Solomon, S.; Sanders, R. W.; Garcia, R. R.; Keys, J. G. Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mount Pinatubo. *Nature* **1993**, *363*, 245–248.
- Parthiban, S.; Raghunandan, B. N.; Sumathi, R. Ab initio study of the molecular structure and vibrational spectra of dichlorine hexoxide and its significance to stratospheric ozone depletion. *Chem. Phys.* **1995**, *199*, 183–193.

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