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Authors

Foster, Krishna L
Caldwell, Tracy E
Benter, Thorsten
et al.

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Techniques for quantifying gaseous HOCl using atmospheric pressure ionization mass spectrometry

Krishna L. Foster, Tracy E. Caldwell,[†] Thorsten Benter,^{*} Sarka Langer,[‡] John C. Hemminger and Barbara J. Finlayson-Pitts^{*}

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

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HOCl is speculated to be an important intermediate in mid-latitude marine boundary layer chemistry and at high latitudes in spring-time when surface-level O₃ depletion occurs. However, techniques do not currently exist to measure HOCl in the troposphere. We demonstrate that atmospheric pressure ionization mass spectrometry (API-MS) is a highly sensitive and selective technique which has promise for HOCl measurements both in laboratory systems and in field studies. While HOCl can be measured as the (HOCl·O₂)[−] adduct with air as the chemical ionization (CI) reagent gas, the intensity of this adduct is sensitive to the presence of acids and to the amount of water vapor, complicating its use for quantitative measurements. However, the addition of bromoform vapor to the corona discharge region forms bromide ions that attach to HOCl and allow its detection *via* the (HOCl·Br)[−] adduct. The ion–molecule chemistry associated with the use of air or bromoform as the CI reagent gas is discussed, with particular emphasis on the effects of relative humidity and gas phase acid concentrations. HOCl is quantified by measuring the amount of Cl₂ formed by its heterogeneous reaction with condensed-phase HCl/H₂O. Detection limits are ~3 parts per billion (ppb) using air as the CI reagent gas and ~0.9 ppb using bromoform. The atmospheric implications of this work are discussed.

I. Introduction

There is increasing evidence for a contribution of reactive halogens to the chemistry of the troposphere. For example, rapid ozone depletion has been observed in the Arctic at polar sunrise and attributed to the chain reaction of bromine atoms in the gas phase with ozone.¹ The chain destruction must involve continuing activation of additional bromine from sea salt at the surface,^{2,3} and there is evidence for simultaneous activation of chlorine as well.⁴ While the details of the mechanism are not established experimentally, modeling studies^{5,6} carried out for mid-latitude regions suggest that intermediates such as HOCl are central to this chemistry. For example, HOCl is known from laboratory studies to react with chloride and bromide ions in the condensed phase, generating Cl₂ and BrCl, respectively.^{7,8} In addition, HOCl and HOBr have been proposed,⁶ based on laboratory kinetic studies,^{9,10} to play an important role in the oxidation of S(IV) in aerosol particles.

In mid-latitudes, generation of photochemically labile halogen compounds such as ClNO₂, Cl₂, HOCl, Br₂, HOBr and BrCl is expected to occur *via* a number of well-known reactions of NaCl, NaBr and other components of sea salt.¹¹ Despite the interest in such chemistry, to date, only Cl₂, which has been measured at concentrations up to 150 ppt,¹² has been specifically identified in the marine boundary layer. Mist chamber studies have measured similar levels of unspiciated chlorine in the marine boundary layer.^{13,14} The measured chlorine was not HCl, a less reactive chlorine compound than those listed

above. Additionally, unspiciated photochemically active chlorine and bromine gas phase compounds have been identified in the Arctic by photolyzing air samples and trapping the halogen atoms by reaction with propene.^{15,16}

Developing a detailed understanding of halogen chemistry in the troposphere requires a combination of laboratory, model and field studies in which all halogen species are identified and measured. Field and laboratory studies require sampling from pressures of ~1 atm, and detection at the sub-ppb level. A promising technique is that of atmospheric pressure ionization mass spectrometry (API-MS), which has been used in the past to measure a variety of inorganics, including Cl₂, and organic gases in air.¹⁷ This technique produces ions in air at atmospheric pressure using a corona discharge. If another chemical ionization (CI) reagent gas is not added, the main components in air serve as the primary CI reagent gas. A series of ions are generated that undergo a variety of ion–molecule reactions.¹⁸ These reactions include ion formation from the trace species of interest, allowing their detection and measurement. In the case of Cl₂, for example, air was used as the CI reagent gas, O₂[−] reagent ions were formed in the discharge, and electron transfer from O₂[−] to Cl₂ formed Cl₂[−], which allowed the detection of Cl₂ down to ~16 ppt in the field.¹² While the application of API-MS to the detection of trace species is thus very promising, the complexity of the ionization processes within the corona discharge and their subsequent ion–molecule chemistry, render a challenge for the interpretation of spectra and quantification of trace gases.

We show here that API-MS is a useful technique for detecting and measuring HOCl down to less than 1 ppb sampled directly from 1 atm of air. The relevant ion–molecule chemistry involved using air as the CI reagent gas is addressed, as are the implications for detecting acids using this technique. The implications for elucidating the role of HOCl in tropospheric chemistry are discussed.

[†] NASA Johnson Space Center, Mail Code CB, Houston, TX 77058, USA.

[‡] University of Göteborg, Department of Chemistry, Section for Inorganic Chemistry, S-412 96 Göteborg, Sweden; also at SP Swedish National Testing and Research Institute, Box 857, S-501 15 Borås, Sweden.

II. Experimental

II.A. Atmospheric pressure ionization mass spectrometry

The API-MS (Perkin-Elmer Sciex, Model 300) is a tandem quadrupole instrument. The advantage of sampling directly at atmospheric pressure into the ion source is of particular interest for atmospheric applications. API-MS monitoring techniques employed in this study include single quadrupole (Q1), MS/MS product, and multiple reaction monitoring (MRM) experiments. Q1 scans use a single quadrupole to monitor ions in a selected mass-to-charge range. This monitoring technique is particularly useful for an initial identification of compounds in complex reaction systems. Further identification of the observed Q1 signals is achieved using MS/MS product scans. These scans use the first quadrupole to select an ion of interest. Subsequent collisionally activated dissociation (CAD), using N₂ gas in an RF-only quadrupole located between the first and second mass filters, leads to production of daughter (product) ions. The second quadrupole scans a range of masses to identify the fragment ions associated with the parent ion selected using Q1. This permits great specificity in the identification of various compounds. The MS-MS capabilities of the instrument are also very useful for accurate quantification. In multiple reaction monitoring (MRM), a parent ion selected in the first quadrupole is coupled with a chosen daughter ion in the second quadrupole to create a unique parent/daughter ion pair whose signal intensity is followed.

The API-MS gas inlet is constructed from two concentric glass tubes. Samples from Teflon reaction chambers were introduced to the API-MS through the outer gas inlet tube (id = 18 mm) at a flow rate of $\approx 1 \text{ L min}^{-1}$. In one set of experiments, bromoform, CHBr₃, was used as the CI reagent gas providing bromide ions. CHBr₃ was introduced to the API-MS through the inner gas inlet tube (id = 4 mm). In the experiments described here, collapsible 35–55 L Teflon reaction chambers were used, resulting in a constant sampling pressure of 1 atm. For the HOCl calibration experiments, a U-tube with a bypass described in more detail below was located immediately in front of the API-MS inlet.

The CI reagent gases used in this study were Ultra-Zero air (99.9%, Oxygen Service Co.) and bromoform (96%, Aldrich). The manufacturer reported specifications for the Ultra-Zero air are: total hydrocarbons <0.1 ppm, CO <0.5 ppm, CO₂ <0.5 ppm and H₂O <2.0 ppm. To generate air with higher percent relative humidities (% RH), a Teflon reaction chamber was prepared by bubbling Ultra-Zero air through room temperature Nanopure water (Barnstead, $\rho > 18 \text{ M}\Omega$). The % RH in the chamber at room temperature was measured with a humidity and temperature transmitter (Vaisala). Ultra-Zero air was bubbled through bromoform held at room temperature at a flow rate of 0.1 L min^{-1} and directed through the inner gas inlet tube to bath the corona discharge in bromoform vapor.

II.B. Electron impact ionization time of flight mass spectrometry

For comparison to the API-MS experiments, and to confirm the quantification of HOCl by heterogeneous titration with HCl, some experiments were also carried out using a Bruker TOF1 (time of flight) mass spectrometer equipped with a pulsed inlet described in more detail elsewhere.^{19,20} Briefly, HOCl in air or N₂ was sampled from a 50 L collapsible Teflon reaction chamber into the differentially pumped low pressure ion source ($p < 10^{-6}$ mbar) of the TOF-MS. The individual gas pulses into the differentially pumped low pressure ionization region of the EI-MS were < 500 μs . Ionization by electron impact (EI) at 70 eV occurred at a 20 Hz repetition rate and a duty cycle of 4.5 μs . Typically, 100 mass spectra were co-added prior to signal integration in selected

areas. HOCl was monitored following the parent ion signals at $m/z = 52$ and 54.

II.C. Preparation of HOCl

HOCl in solution was synthesized by adding sodium hypochlorite, NaOCl (10–13% available chlorine, Aldrich), dropwise to a slurry composed of 40 g anhydrous magnesium sulfate, MgSO₄ (certified anhydrous, Fisher), dissolved in 100 mL of Nanopure water). Vacuum distillation was used to purify the HOCl solution. The solution was stored in the dark at 273 K and used within 15 days of synthesis.

Common impurities in HOCl samples prepared by this method include HCl, Cl₂O and Cl₂. Electron impact ionization mass spectrometry was used to show that HOCl samples prepared by this method have <1% impurities from both HCl and Cl₂O.²⁰ To remove excess Cl₂ prior to each use, Zero air was vigorously bubbled through the HOCl solution for several minutes at room temperature. HOCl samples were introduced into a 35 L Teflon reaction chamber by bubbling Zero air through the HOCl solution immediately after removal of Cl₂ vapor. HOCl dilution was achieved by adding dry Ultra-Zero air to the Teflon reaction chamber.

II.D. Quantification of HOCl

Numerous studies have shown HOCl reacts with condensed HCl/H₂O to produce Cl₂ rapidly:^{21–24}

In this study, HOCl was titrated with HCl and the calibrated Cl₂ titration product was used to determine the concentration of HOCl. This method has been used successfully with EI-MS detection of the Cl₂ in the past,²⁰ and the results were confirmed using an independent method: photolysis of the HOCl and trapping of the generated Cl atoms with propene to form chloroacetone.²⁰ We report here the first such measurement using API-MS.

Thin layers of dilute 20 wt.% HCl in H₂O solutions were frozen in a glass U-tube (id = 8 mm) and submerged in a 243 K cooling bath (MGW Lauda Brinkmann, Model RC 6 with Ultra-Therm SK Frigor coolant). For titration, the HOCl was passed through the U-tube containing the HCl/H₂O solution and the Cl₂ product was monitored by API-MS. Cl₂ is calibrated with known concentrations prepared in a 55 L Teflon reaction chamber. The Cl₂ source gas (Matheson, 99.5% as a 1% mixture in N₂) is stored in a dark 5 L glass bulb. Samples were prepared by dilution with Zero air. Cl₂ concentrations were calibrated in the range 250–1500 ppb. The U-tube had a bypass which permitted HOCl to be monitored directly as well.

Cl₂ calibrations were performed using MRM and both air and bromoform CI reagent gases. To simulate conditions of the HOCl titration experiments, the Cl₂ was directed over the 243 K HCl/H₂O solution in the U-tube. The ion pair at 72/35 was used to monitor Cl₂ when air was used as the CI reagent gas. The most intense Cl₂[−] ion pair, 70/35, could not be used because HCl vapor forms the (HCl·O₂)[−] adduct with signals at $m/z = 68, 70$ (see below). With bromoform as the CI reagent gas, the (Cl₂·Br)[−] adduct was calibrated using the MRM ion pair at 149/79. Plots of the Cl₂ MRM signals against Cl₂ concentration were linear with a 2 σ error in the slope of $\leq 12\%$.

III. Results and discussion

III.A. Comparison of EI- and API-mass spectra using air as the CI reagent gas

Fig. 1a shows a typical EI-MS of ~ 100 ppm HOCl sampled from a Teflon reaction chamber. Strong positive ion parent

Fig. 1 Mass spectra of HOCl using (a) electron impact time of flight ionization and (b) atmospheric pressure ionization with air at the Cl reagent gas. The HOCl concentrations were ~ 100 ppm in (a) and ~ 50 ppm in (b). Note that the axis in (a) is in time and that in (b) in m/z .

peaks at $m/z = 52$ and 54 are observed, as well as weaker signals at $m/z = 51$ and 53 . The latter are primarily due to fragmentation of the HOCl^+ , with a possible contribution from low level impurities of Cl_2O . Based on the Cl_2O^+ parent peaks at $m/z = 86$, 88 and 90 , the Cl_2O impurity is estimated to be $< 1\%$.²⁰

In contrast, the API-MS of HOCl shows insignificant peak intensities for the parent masses ($m/z = 52$, 54). Fig. 1b shows a typical API-MS of ~ 50 ppm HOCl in the same mass region. For this application of API-MS, negative ions are monitored as opposed to the positive ions observed in EI-MS discussed above. Only fragment peaks at $m/z = 51$ and 53 (OCl^-) are seen, suggesting that electron transfer to HOCl to produce HOCl^- in the corona discharge at these HOCl concentrations is not a major ionization process. As discussed below, acid-base reactions are the dominant pathway for HOCl ionization.

III.B. Effects of relative humidity and acids on the air Cl reagent gas in API-MS

The Q1 spectra in Fig. 2 show which ions are produced in the ionization region when dry (Fig. 2a) or humid (Fig. 2b) air is introduced into the corona discharge. The dominant peaks in Fig. 2a are $m/z = 32$, 46 , 48 , 60 , 61 , 62 and 77 . These peaks have been previously assigned to O_2^- , NO_2^- , O_3^- , CO_3^- , $(\text{CO}_2 \cdot \text{OH})^-$, NO_3^- and $(\text{CO}_3 \cdot \text{OH})^-$, respectively.¹⁸ Peaks

Fig. 2 Q1 scans of (a) dry air, (b) humid air (84% RH) and (c) dry air with HCl vapor (~ 300 ppm).

due to CO_2 and water fragments arise from background gases in the Teflon reaction chamber and API-MS ion source chamber.

Fig. 2b is a Q1 scan of humidified air (84% RH). A comparison between Fig. 2a and 2b shows that the signal intensity of O_3^- at $m/z = 48$ is much higher in humid air than in dry air, as opposed to the CO_3^- signal at $m/z = 60$ which is lower. An explanation for the above observations follows. Water reacts with electrons in a corona discharge forming OH^- (although not necessarily in a single step):²⁵

There are also other sources of OH^- in the corona discharge such as²⁶

OH^- has a smaller electron affinity than O_3 (1.8 eV for OH and 2.1 eV for O_3)²⁷ and can transfer an electron:

This is consistent with the observed increase in the O_3^- ion in humid air. Ozone ions react with CO_2 to produce CO_3^- :

Hence, one might expect a higher signal intensity for CO_3^- ($m/z = 60$) in humid air than in dry air. However, the rate constant of reaction (5) is affected by water vapor, decreasing from $5.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for O_3^- to $< 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ when O_3^- has two waters of hydration attached.²⁸ The decrease in the rate of reaction

(5) in the presence of water is consistent with the observed decrease in CO_3^- when the concentration of water vapor in air is increased.

To examine the effect of acids on the ionization processes and species, HCl vapor was added to dry air (Fig. 2c). In this experiment, three drops of HCl (37.4%) are placed in the U-tube, and cooled to 273 K. The vapor pressure of HCl over a 38% solution at 273 K is 8.4 kPa, while H_2O vapor is only 0.070 kPa.²⁹ After further dilution, the concentration of HCl vapor in Fig. 2c is estimated to be ~ 300 ppm.

There is a dramatic change in the mass spectrum observed in air when these high HCl concentrations are added to air. Comparing Fig. 2b and 2c, signals at $m/z = 32$ (O_2^-), 46 (NO_2^-) and 48 (O_3^-) disappear and that at $m/z = 60$ (CO_3^-) becomes much smaller. Only that at $m/z = 62$ (NO_3^-) is not dramatically affected. This is understandable in terms of acid–base reactions, since HCl is a strong acid and will proton transfer to O^- and OH^- (which are below the mass range of the API-MS), O_2^- , NO_2^- and CO_3^- . The gas-phase acidities of acids increase with decreasing acid dissociation energies, ΔH_{acid} .^{30,31} Because the ΔH_{acid} for $\text{HO}_2 = 1476 \pm 9$ kJ mol⁻¹, is greater than the ΔH_{acid} for $\text{HCl} = 1395 \pm 1$ kJ mol⁻¹, HCl is expected to proton transfer to O_2^- :

Proton transfer from HCl to NO_3^- , however, is not expected due to a lower ΔH_{acid} for HNO_3 ($\Delta H_{\text{acid}} = 1358 \pm 1$ kJ mol⁻¹).

In short, acids are observed to proton transfer to OH^- as well as to species whose neutrals are weaker acids, such as HO_2 and HONO in the negative ion mode of API-MS. As a result, peaks due to O_2^- and NO_2^- decrease. This leads to reduced O_3^- , since it is formed by electron transfer from OH^- , reaction (4), and to reduced CO_3^- since it is formed at least in part from electron transfer from O_3^- , reaction (5). The complete removal of ions such as O_2^- , NO_2^- and O_3^- can occur in the presence of high concentrations of acids, as evidenced by the disappearance of the peaks at $m/z = 32$, 46 and 48 (Fig. 2c). Such acid–base chemistry suggests that care must be taken to maintain constant ionization conditions in the ion source when using API-MS for quantitative measurements.

While parent peaks were not observed for HCl at $m/z = 36$ and 38, which would have been consistent with simple electron capture or transfer, ion–neutral adduct formation between HCl and reactant ions in air is evident in the observed peaks $m/z = 68$ and 70 assigned to $(\text{HCl} \cdot \text{O}_2)^-$, and $m/z = 98$, 100 assigned to $(\text{HCl} \cdot \text{NO}_3)^-$. Small pairs of peaks at 81, 83 and 82, 84 as well as 85, 87 are assigned to the $(\text{NO}_2 \cdot \text{Cl})^-$, $(\text{NO}_2 \cdot \text{HCl})^-$ and $(\text{H}_2\text{O} \cdot \text{O}_2 \cdot \text{OH})^-$ adducts. (Note that these assignments represent the stoichiometry and not necessarily the structure of the adduct.) Product scans were used to confirm these identifications. Thus, Cl^- was the primary daughter ion from the $m/z = 68$ and 70 parents and NO_3^- was the major daughter ion from $m/z = 98$ and 100. Evidence for the $(\text{HCl} \cdot \text{NO}_3)^-$ adduct in the stratosphere further supports the assignment of the peaks at $m/z = 98$ and 100.³²

The relative peak intensities based on the natural isotopic abundance of $m/z = 71$, 73, 75 and $m/z = 97$ and 99 in Fig. 2c suggests adducts of neutrals with Cl^- are responsible for these peaks. Based on the 3 : 1 natural isotope abundance of ^{35}Cl and ^{37}Cl , an ion containing one chlorine atom should appear as two peaks separated by 2 u with relative peak intensities of 3 : 1. Likewise, an ion with two chlorine atoms should have 3 peaks, each separated by 2 u, with relative peak intensities of 9 : 6 : 1. The $m/z = 71$, 73 and 75 are thus assigned to $(\text{HCl} \cdot \text{Cl})^-$ adducts and those at $m/z = 97$ and 99 to $(\text{HCl} \cdot \text{CO}_2 \cdot \text{OH})^-$ adducts. Product scans confirmed these assignments. Thus, the major daughter ion for $m/z = 71$, 73

and 75 was Cl^- and those for $m/z = 97$ and 99 were Cl^- , $(\text{HCl} \cdot \text{OH})^-$ and $(\text{CO}_2 \cdot \text{OH})^-$.

Because HOCl is also an acid, it might be expected to have similar effects as HCl on the ionizing species in air. Fig. 3a presents Q1 scans of air containing dilute HOCl . Reductions in the major air ion peaks are seen, but they are not completely eliminated since the acid concentrations are much smaller than for HCl in Fig. 2c. A number of new peaks are observed after HOCl is added to the air, including peaks at $m/z = (35, 37)$, (51, 53), (84, 86), (87, 89, 91), (95, 97), (103, 105 and 107). Only small parent peaks are observed at $m/z = 52$ and 54. The dominant non-background peaks in Fig. 3a can be assigned to HOCl –ion adducts. Thus, the reagent ions O_2^- , Cl^- and ClO^- bind to HOCl to form the adducts $(\text{HOCl} \cdot \text{O}_2)^-$ ($m/z = 84, 86$), $(\text{HOCl} \cdot \text{Cl})^-$ ($m/z = 87, 89, 91$) and $(\text{HOCl} \cdot \text{OCl})^-$ ($m/z = 103, 105, 107$), respectively. The peaks at $m/z = 95$ and 97 can be assigned to $(\text{CO}_2 \cdot \text{OCl})^-$ adducts.

A comparison of the relative acid dissociation energies show that both HCl and HO_2 are stronger acids than HOCl and hence proton transfer from HOCl to Cl^- and O_2^- should not occur. Rather, as seen in Fig. 3a, adduct formation occurs between HOCl and Cl^- or O_2^- . However, since HOCl is a stronger acid than H_2O ($\Delta H_{\text{acid}} = 1635$ kJ mol⁻¹), OH^- deprotonates HOCl , resulting in OCl^- which is observed alone and as the $(\text{HOCl} \cdot \text{OCl})^-$ adduct in Fig. 3a.

III.C. Quantifying HOCl using air as a Cl reagent gas

Fig. 3b shows the Q1 spectrum obtained following titration with HCl. Here HOCl is diverted through the glass U-tube containing dilute HCl at 243 K. A drop in peak intensity is observed for those masses assigned to HOCl while new peaks at $m/z = 70$, 72 and 74 appear due to Cl_2 formation.

MRM data were used to quantify reactants and products in the HOCl titration experiment. The MRM data from a typical HOCl titration experiment are shown in Fig. 4 as a comparison of signal intensities of specific ion pairs during the titration. The ion pair 84/35 assigned to the $(\text{HO}^{35}\text{Cl} \cdot \text{O}_2)^-$ adduct in the first Q1 quadrupole and the ^{35}Cl daughter ion at $m/z = 35$ in the second, is shown by the heavy solid line (a), in Fig. 4. The ion pair 72/35 for Cl_2 monitored simultaneously, is shown as the dashed line (b). Other ion pairs were also monitored, including 87/35 $(\text{HO}^{35}\text{Cl} \cdot ^{35}\text{Cl})^-$ and 103/51

Fig. 3 Q1 scans of (a) air containing ~ 700 ppb HOCl and (b) products of an HOCl reaction with HCl using air as the Cl reagent gas.

Fig. 4 MRM data from a heterogeneous HOCl titration experiment using air as the CI reagent gas. The MRM signals for (a) $(\text{HOCl}\cdot\text{O}_2)^-$ measured at 84/35, and (b) Cl_2^- measured at 72/35 are shown as the heavy solid line and the dashed line, respectively.

$(\text{HO}^{35}\text{Cl}\cdot^{35}\text{ClO})^-$; maximum and minimum intensities of these signals showed the same behavior as the 84/35 ion pair during the titrations.

Between 0 and 100 s, HOCl was delivered directly to the API-MS through the bypass, giving a strong 84/35 signal due to the $(\text{HOCl}\cdot\text{O}_2)^-$ adduct. A small signal for the 72/35 ion pair is detected which is due to small amounts of impurity Cl_2 in the HOCl. When the HOCl is diverted over the HCl solution in the U-tube, a rapid drop in the 84/35 signal and concurrent rise in the 72/35 signal is observed. Less than 15% of the 84/35 signal intensity remains. This trend in signal strength continues as the HOCl flow is cycled between the U-tube containing HCl and the bypass.

The HOCl concentrations ranging from 0–500 ppb determined from the Cl_2 produced on reaction with HCl, are plotted as a function of the average $m/z = 84/35$ signal intensity in Fig. 5. Because there were small amounts of impurity Cl_2 present initially in the HOCl, the difference between the signals after the flow was diverted through the U-tube and the initial background was taken as the initial HOCl concentration. The relationship between HOCl concentration determined by the HCl titration and the $(\text{HOCl}\cdot\text{O}_2)^-$ adduct signal intensity is linear in this range. This is important in light of the effects H_2O vapor and acids can have on reactant ions in air. However, signals at higher HOCl concentrations became non-linear, indicating that the reagent O_2^- ion in the

Fig. 5 HOCl concentration (ppb) vs. average $(\text{HOCl}\cdot\text{O}_2)^-$ MRM signal intensity at 84/35. Error bars are $\pm 2\sigma$.

corona discharge was depleted by the addition of these higher concentrations of acid as discussed in Section III.B.

III.D. Quantifying HOCl using bromoform as the CI reagent gas

Because of the effects of water vapor and acids on ions in the air reagent gas, it is desirable to have other CI reagent gases which are not sensitive to these effects. Electron affinity is a physical property that can be used to determine if API-MS sensitivity to HOCl can be enhanced by monitoring an ion–HOCl adduct other than $(\text{HOCl}\cdot\text{O}_2)^-$. The bromine atom has a higher electron affinity than O_2 , and can be readily generated in the corona discharge. This could potentially result in an enhanced API-MS sensitivity for HOCl by monitoring $(\text{HOCl}\cdot\text{Br})^-$ rather than $(\text{HOCl}\cdot\text{O}_2)^-$. A similar approach has been used to measure HONO, for example, by the addition of CCl_4 to the source region in order to form the $(\text{HONO}\cdot\text{Cl})^-$ adduct.³³

Relative gas phase acidities also support adduct formation between Br^- and HOCl. Hydrobromic acid ($\Delta H_{\text{acid}} = 1354 \text{ kJ mol}^{-1}$) has a lower dissociation energy than HOCl ($\Delta H_{\text{acid}} = 1502 \text{ kJ mol}^{-1}$) so that proton transfer from HOCl to Br^- is not expected. In short, both gas phase acidity and electron affinity arguments indicate Br^- is potentially well suited as a reactant ion for the detection of HOCl.

Fig. 6a shows the Q1 spectrum for air with bromoform vapor added to the corona discharge. The dominant reagent ion is Br^- at $m/z = 79$ and 81. The molecular bromine anion, Br_2^- , also appears in the spectra at $m/z = 158, 160$ and 162. Only the air peaks attributable to CO_3^- ($m/z = 60$) and NO_3^- ($m/z = 62$) are present.

Fig. 6 Q1 scans of (a) bromoform in air, (b) with 340 ppb added HOCl and (c) products of a heterogeneous HOCl reaction with HCl using bromoform as the CI reagent gas.

Fig. 6b shows the ionization of HOCl using the bromoform CI reagent gas. The intensities of $m/z = 79$ and 81 resulting from Br^- are still very large after the addition of dilute HOCl, indicating Br^- reactant ions are still abundant. Thus, unlike reactant ions in the air ion source, depletion of the reactant ions is not of concern under these conditions. Peaks observed for HOCl ionization in air assigned to Cl^- , $(\text{HOCl}\cdot\text{O}_2)^-$, $(\text{HOCl}\cdot\text{Cl})^-$ and $(\text{HOCl}\cdot\text{OCl})^-$ are still present in the bromoform ion source. A new series of peaks, $m/z = 131$, 133 and 135 appear in Fig. 6b, which have been assigned to $(\text{HOCl}\cdot\text{Br})^-$ adducts.²⁰ The small amounts of chlorine impurities in the HOCl sample take a new form as well. In addition to small Cl_2^- peaks at $m/z = 70$, 72 and 74 , a new series of peaks at $m/z = 149$, 151 and 153 due to $(\text{Cl}_2\cdot\text{Br})^-$ adducts also appear.

Fig. 6c is the Q1 scan of HOCl titrated by HCl using the bromoform CI reagent gas. The HOCl peaks have been almost completely eliminated, as expected. Concurrently, Cl_2^- and $(\text{Cl}_2\cdot\text{Br})^-$ intensities have increased, confirming the production of Cl_2^- .

MRM data using Br^- reactant ions are shown in Fig. 7. The ion pair $131/79$ from the $(\text{HOCl}\cdot\text{Br})^-$ adduct is shown as a heavy solid line (a) and the ion pair $149/35$ assigned to $(^{35,35}\text{Cl}_2\cdot^{79}\text{Br})^{35}\text{Cl}^-$ as the dashed line (b). The experiment in Fig. 4 in which $(\text{HOCl}\cdot\text{O}_2)^-$ was monitored used the same HOCl sample as this one; note the intensity of this bromide ion adduct is much greater than that due to $(\text{HOCl}\cdot\text{O}_2)^-$. As expected, when the HOCl is diverted through the U-tube containing HCl, the HOCl signal drops sharply while Cl_2 rises simultaneously. The signals return to their original intensities when the above procedure is repeated. Less than 13% of the signal intensity in the ion pair $131/79$ remains after reaction with HCl.

Fig. 8 shows a plot of the HOCl concentrations derived from the Cl_2 product as a function of HOCl MRM signals using the parent/daughter ion pair $131/79$ assigned to the $(\text{HO}^{35}\text{Cl}\cdot^{79}\text{Br})^-$ adduct. The plot is linear over HOCl concentrations from 4–960 ppb.

A comparison of the air and bromoform ion sources shows that the HOCl concentrations derived using both techniques are in excellent agreement. Thus, a correlation plot of HOCl concentration derived using air in the ion source region *vs.* the HOCl concentration using bromoform from five experiments where identical HOCl samples were used for both ion sources has a slope of 1.04 ± 0.25 (2σ) and an intercept of 22 ± 40 (2σ). Additionally, note that the signal intensities for

Fig. 7 MRM signals for an HOCl titration experiment using bromoform as the CI reagent gas. The MRM signals for (a) $(\text{HOCl}\cdot\text{Br})^-$ measured as $131/79$ and (b) $(\text{Cl}_2\cdot\text{Br})^-$ measured as $149/35$ are shown by the heavy solid and dashed line, respectively.

Fig. 8 HOCl concentration (ppb) *vs.* average $(\text{HOCl}\cdot\text{Br})^-$ MRM signal intensity at $131/79$ using bromoform as the CI reagent gas. Error bars are $\pm 2\sigma$.

$(\text{HOCl}\cdot\text{Br})^-$ in Fig. 8 are about an order of magnitude greater than those for HOCl samples monitored with $(\text{HOCl}\cdot\text{O}_2)^-$ in Fig. 5. The enhanced sensitivity of $(\text{HOCl}\cdot\text{Br})^-$ relative to $(\text{HOCl}\cdot\text{O}_2)^-$ results in an enhanced signal-to-noise ratio for the former. Additionally, higher concentrations of HOCl, ranging from 500–1000 ppb, that could not be quantified in air due to changes in O_2^- were successfully quantified with bromoform as the CI reagent gas.

IV. Atmospheric implications

Both air and bromoform can be used as CI reagent gases for the detection of HOCl. However, in the case of air, care must be taken to control water vapor and acid concentrations which can change the CI reagent ions both during measurements and calibrations. In addition, depletion of ions such as O_2^- which form the adducts must be carefully avoided. While this may not be a severe problem in atmospheric air measurements, it can be at the higher acid concentrations found in many laboratory systems.

Alternative CI reagent gases such as bromoform can be used in place of air. The principle advantages of bromoform are its relative immunity to changes in gas phase water and acids and the excellent sensitivity of API-MS to $(\text{HOCl}\cdot\text{Br})^-$. Additionally, the flux of bromoform to the ionization chamber of the API-MS can be controlled by varying the flow rate of air and the temperature through the bromoform bubbler. Of course, the use of bromoform adds complexity to a field apparatus. The use of bromoform as the CI reagent gas also precludes the simultaneous measurement of gaseous bromine species such as Br_2 .

The estimated HOCl detection limit for the air and bromoform CI reagent gases are 3 ppb and 0.9 ppb, respectively. Although no measurements of HOCl have been made in the troposphere to date, modeling studies^{5,6,12} predict peak concentrations in the marine boundary layer may be in the range of a few to hundreds of ppt. The detection limits measured here suggest that with further work to improve the sensitivity, identification of HOCl in the troposphere may be possible under some conditions through the use of bromoform to form the bromide ion adduct. For example, the dwell time on each peak measured here was 0.5 s; if this were increased to 50 s an order of magnitude increase in sensitivity could in principle be obtained.

V. Summary

It is clear that the quantitative application of API-MS to the detection and measurement of trace gases in air requires a

thorough understanding of the ion–molecule chemistry in the source region. However, with such understanding, API-MS is an extremely powerful tool for the detection and measurement of many species in ambient air which are difficult to measure by other techniques. For example, we have shown here that HOCl can be successfully quantified by measuring Cl_2 produced in the titration of HOCl with HCl in the negative ion mode using either air or bromoform as CI reagent gases. HOCl concentrations ranging from 4–500 ppb are readily measured using air, and higher concentrations, up to 960 ppb, could be measured using the bromoform CI reagent gas. Detection limits are ~ 3 ppb using air as the CI reagent gas and the $(\text{HOCl}\cdot\text{O}_2)^-$ adduct, and ~ 0.9 ppb using bromoform and the $(\text{HOCl}\cdot\text{Br})^-$ adduct. The latter approach is preferred both from the point of view of sensitivity and because the use of air to generate the O_2^- adduct is limited by perturbations of the ion source region by water vapor and acids. These studies suggest that if a further increase in the sensitivity of approximately an order of magnitude or more can be attained, it may be possible to measure HOCl in the marine boundary layer using these techniques.

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