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Direct Experimental Evidence for a Heterogeneous Reaction of Ozone with Bromide at the Air−Aqueous Interface

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Recent experimental and theoretical evidence has indicated an enhancement of the heavier halide ions at the air−aqueous interface, relative to their bulk concentrations. This, along with an order of magnitude discrepancy between measured and predicted Br_2 production in the reaction of ozone with deliquesced NaBr aerosol, has led to the suggestion that an interface reaction occurs between ozone and bromide. We have used harmine, a β-carboline alkaloid, as an interface-sensitive fluorescent pH probe in order to measure pH changes associated with the interfacial reaction of ozone and bromide. The rate of pH change depends upon the bulk bromide concentration in a way which is well described by a Langmuir−Hinshelwood kinetic model. In the presence of octanol at the interface, the rate of pH change tracks the octanol adsorption isotherm, as expected if octanol enhances the concentration of ozone at the surface.

Introduction

Sea salt aerosol is ubiquitous in the coastal and marine boundary layers. As such, there has been considerable effort directed toward understanding the chemistry that occurs in and on these aerosol particles.[1] Recent work of Finlayson-Pitts and co-workers,[2,3] as well as Frinak and Abbatt,[4] has examined molecular halogen formation resulting from reactions of halide ions in sea salt aerosol with various atmospheric oxidants. In a study by Hunt et al.,[2] the formation of molecular bromine from the reaction of gas-phase ozone with aqueous sodium bromide particles was investigated as a potentially important source of molecular bromine. It was found that the rate of production of Br_2 was faster by an order of magnitude than could be explained by a kinetics model using known gas-phase and aqueous chemistry alone. An interface reaction between Br^- and O_3 was proposed to explain this discrepancy, and indeed the inclusion of an interface reaction in this model was able to reconcile the difference in production rates. In a later study Thomas et al.[3] were able to show, using the Model of Aerosol, Gas and Interfacial Chemistry, that the interfacial reaction of bromide with ozone is expected to be the primary source of molecular bromine under dark conditions. This is a key result, as it could potentially represent the "missing" source of atomic bromine needed to initiate catalytic ozone destruction during "bromine explosion" events in the arctic spring, and could also represent an important sink of tropospheric ozone in the marine boundary layer.[5,6]

As early as 2000 Ghosal et al.[7] obtained experimental evidence showing significant segregation of bulk bromide ions to the surface of bromide-doped sodium chloride crystals, yielding a surface composition having an enrichment of bromide ions relative to the bulk. That study was motivated by the need to understand the source of gas-phase reactive bromine species causing tropospheric ozone depletion in the arctic at polar sunrise.[6] Since then there have been a number of additional studies examining the propensity toward surface enhancement of the larger, more polarizable halide ions, both in solid crystals and in aqueous solution.[8−15] These investigations have been carried out using a variety of experimental techniques, including atomic force microscopy,[9,11] electron spectroscopy,[8,11,13] electrospray ionization mass spectrometry,[10] and vibrational sum-frequency generation spectroscopy.[12,14,15] The results of second harmonic generation studies[16,17] have also been interpreted in terms of an enhancement of the polarizable thiocyanate and azide ions at the air−water interface.

While an enhancement of large, polarizable anions at the air−aqueous interface is observed or inferred in all of these studies, at this time there is no strong agreement regarding the magnitude of the enhancement of surface concentration relative to the bulk. What is clear from this work, however, is that the greatest enhancements among the halides are seen for the bromide and iodide ions. By contrast, a very recent study using X-ray reflectivity to probe concentrated aqueous salt solutions found little evidence to support a different halide composition between the surface and bulk, and indeed suggests a depletion of bromide at the surface of a 6 mol L^{-1} RbBr solution.[18] However, the authors note that due to a number of factors the confidence in this conclusion is at present lower than is desirable. Also, the study examined CsCl, LiBr, RbBr, RbCl, and $SrCl_2$, salts having limited atmospheric relevance, leaving the majority of experimental studies existing to date supporting the idea that bromide ions are enhanced at the air−aqueous interface. Much of the experimental work examining ions at the air−aqueous interface has been nicely summarized in a recent review by Petersen and Saykally.[19]

Surface enhancement of halides is also indicated by a variety of studies employing molecular dynamics simulations which use polarizable force fields to examine the behavior of halide ions in water slabs, modeled to simulate the extended air−aqueous interface.[14,15,20−23] Many of these studies have been summarized in a recent review by Jungwirth and Tobias,[24] who have been responsible for much of the molecular dynamics work. Generally speaking, the simulations have observed a

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surface enhancement of halide ions (except F^-), increasing in the order $Cl^- < Br^- < I^-$, consistent with the experimental studies. Based on the available experimental and theoretical studies, we may conclude that there is presently strong experimental and simulation-based evidence in the literature supporting the idea of a surface enrichment of the larger, more polarizable halide ions.

A separate molecular dynamics study by Vácha et al.[25] examined the adsorption of some atmospherically relevant gases, including ozone, at the air−water interface. The results of this study suggest that the concentration of ozone is enhanced at the water surface relative to its concentration in bulk water, a result supported by a later molecular dynamics study by Vieceli et al.[26] In our laboratory we have studied the reaction of ozone with anthracene adsorbed at the air−aqueous interface.[27,28] It was found that the reaction follows a Langmuir−Hinshelwood type mechanism, where O_3 initially adsorbs to the water surface, as suggested by the molecular dynamics simulations, and then proceeds to react with anthracene which is already present there. Of some relevance to the present work, it was found that the reaction rate increases when the surface is coated with a monolayer of 1-octanol.[27,28] These results were interpreted to arise from an increased partitioning of ozone to the octanol-coated interface, consistent with the molecular dynamics simulations of Tobias and co-workers, where it was found that the residence time of ozone at the air−water interface is increased in the presence of an organic coating.[29,30] A similar experimental result was observed by Raja and Valsaraj, who observed an enhancement of the reaction of ozone with naphthalene at the air−aqueous interface in the presence of fulvic acid, a surrogate for the surface-active organic component of aerosols.[31]

Organic films at the air−aqueous interface, and their effects on chemical and physical processes, have recently received a large amount of interest.[32] Atmospheric aerosols consist of as much as 50% organic compounds by mass,[33] made up at least in part of species which partition to the air−aqueous interface.[34,35] Additionally, the sea-surface microlayer has been shown to be enriched with a wide variety of organic substances, and marine aerosols are thus expected to have a similar composition.[36−39] Due to the likely ubiquitous nature of organic coatings on aerosols, an increase of ozone residence time at organic coated aerosol surfaces is thus a situation potentially very relevant to atmospheric chemistry, particularly in the marine boundary layer.

Finlayson-Pitts and co-workers proposed that an interface reaction between bromide anion and gas-phase ozone might proceed by the following mechanism:[3]

$$O_3(g) + Br^-(surf.) \rightarrow [O_3\cdots Br^-](surf.) \quad (1)$$

$$[O_3\cdots Br^-](surf.) \rightarrow O_3^-(aq) + {}^1/_2Br_2(g) \quad (2)$$

$$O_3^-(aq) \rightarrow O_2(g) + O^-(aq) \quad (3)$$

$$O^-(aq) + H_2O \rightarrow OH^-(aq) + OH(aq) \quad (4)$$

overall reaction:

$$O_3(g) + Br^-(surf.) + H_2O \rightarrow {}^1/_2Br_2(g) + O_2(g) + OH(aq) + OH^-(aq) \quad (5)$$

Here ozone and bromide form an initial interface complex in reaction 1, which then proceeds via some, as yet unknown, mechanism in reaction 2 to form molecular bromine. The results discussed above[25−28,31] also suggest that the first step in such a reaction would be the adsorption of ozone to the interface, followed by reaction between coadsorbed O_3 and Br^-. The O_3^- ion then formed decays to O_2 and O^- (reaction 3), which quickly reacts with water to form OH^- (reaction 4).[3] The overall reaction resulting from this sequence is given as reaction 5. Hydroxide formation during the interface reaction will lead to an increase in the pH there. Thus, if this mechanism holds, the presence of an interface reaction can be probed indirectly by measuring the associated change in surface pH. We have recently used this strategy to study the hydrolysis of acids and bases at the air−water interface.[40]

The reported surface enhancement of bromide ions combined with the surface adsorption behavior of ozone suggests that a heterogeneous surface reaction between these two species is possible at the air−aqueous interface. For reasons presented above, the presence of an organic coating at the interface is expected to enhance this surface reaction by increasing the ozone residence time at the interface. In the following we report results of experiments which used a glancing-angle laser-induced-fluorescence (LIF) technique to observe the pH change associated with the reaction of bromide with ozone at the air−aqueous interface. The results suggest that a surface reaction does indeed occur.

Experimental Section

In this work we have used the β-carboline alkaloid harmine (7-methoxy-1-methyl-9*H*-pyrido[3,4-*b*]indole) as an interface-sensitive pH probe. When excited at 337 nm, this species emits a broad fluorescence spectrum peaking at approximately 410 nm. The absorption spectrum of harmine in aqueous solution shifts to the blue as the pH of the solution is increased from neutral. Aqueous excitation and fluorescence spectra of harmine at two different pH values, as well as the structure of harmine, are displayed in Figure 1. These spectra are in good agreement with those measured previously by Dias et al.[41] Focusing on 337 nm in the absorption spectra, one sees from Figure 1a that a decrease in absorbance occurs as the pH is increased. This leads to a corresponding decrease in fluorescence intensity, and one can thus associate a decrease in harmine fluorescence intensity to an increase in solution pH. Unfortunately, unlike the case of acridine,[40] the ratio of intensities at different wavelengths cannot be related to a quantitative measure of pH using this indicator. Acridine could not be used in the present experiments due to its very efficient quenching by Br^-. Bromide was found to quench harmine fluorescence as well, but not so much that measurements could not be made.

Apparatus. The apparatus used for this work was a modification of that used previously in this laboratory to study the oxidation of anthracene by gas-phase ozone at the air−water interface,[27,28] and more recently to examine the suppression of aqueous surface hydrolysis reactions by short-chain organic amphiphiles.[40] It consists of a 250 mL three-neck round-bottom flask, with a quartz window mounted on either side, containing approximately 100 mL of solution. The 337 nm output of a Stanford Research Systems NL-100 pulsed N_2 laser is passed through the quartz window on the side of the flask, and impinges upon the aqueous surface at a glancing angle (roughly 72° from the surface normal), exciting fluorescence from species present there. This fluorescence is collected by a 7 mm diameter liquid light guide suspended approximately 1 cm above the sample surface, and then passed through a monochromator and detected by a photomultiplier tube, whose output is averaged over 64 laser shots by a Tektronix TDS-240 digital oscilloscope. The

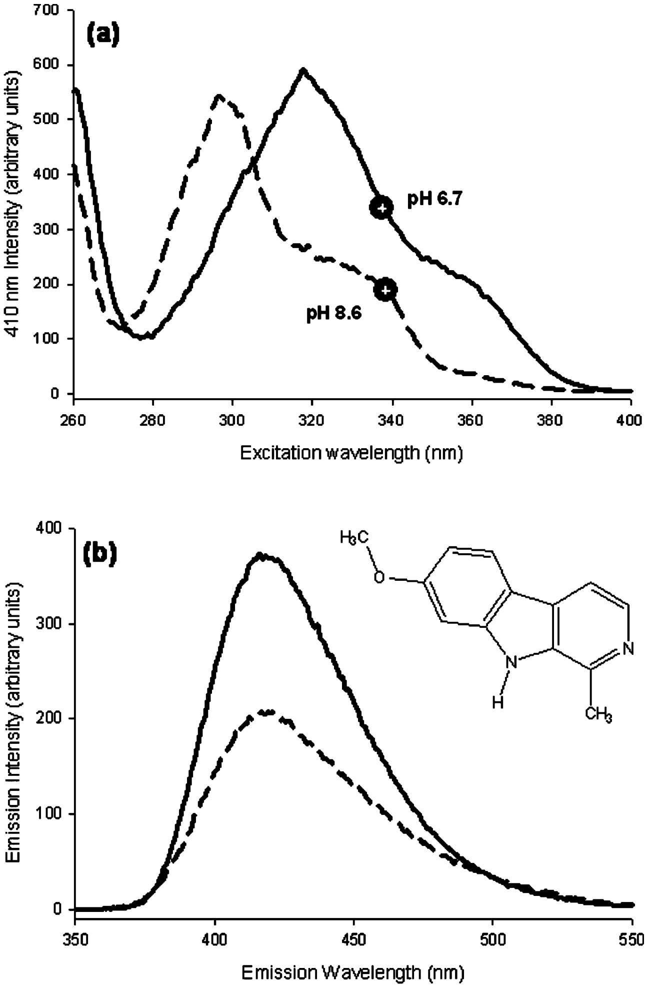

Figure 1. (a) Excitation (measured at 410 nm) and (b) fluorescence (excited at 337 nm) spectra of harmine at pH 6.7 (solid line) and pH 8.6 (dashed line). The large markers superimposed on the excitation spectra indicate the absorbance at 337 nm. The structure of harmine is shown superimposed on the fluorescence spectra.

resultant fluorescence decay is read from the oscilloscope by a custom LabVIEW program running on a PC, and a 40 ns “slice” around the peak of the decay curve was averaged and saved for later analysis. Ozone gas was generated by flowing 1 L min^{-1} high-purity oxygen gas through a Jelight Model 600 variable ozone generator, and its concentration was determined by measuring the attenuation of the output of a 254 nm mercury Pen-Ray lamp by the Hartley absorption band of ozone.

Sample Preparation. A saturated (approximately 3.31×10^{-5} mol L^{-1})[42] aqueous solution of harmine was prepared by adding an excess of solid harmine to 18 MΩ deionized water, and mixing over a period of at least 24 h with a magnetic stirrer to ensure complete dissolution up to the saturation point. Experimental samples were then prepared by dissolving sodium bromide salt in 18 MΩ deionized water and adding an appropriate amount of saturated harmine solution such that the harmine concentration was approximately 1.7×10^{-6} mol L^{-1}. Surface films of octanol were prepared by mixing a known amount of the alcohol into the previously prepared salt solution. The solution was then allowed to sit for at least 20 min to allow the octanol film to equilibrate on the surface prior to commencement of the run. Visual inspection of the solution confirmed that no “islands” of octanol had formed on the surface.

Reaction of Bromide and Ozone. For these experiments, harmine fluorescence was monitored at 410 nm, with one measurement being recorded every 10 s. A baseline was collected for the first 2.5 min of each run, at which point ozone at a concentration of 4.5×10^{15} molecules cm^{-3} was allowed to flow through the flask for approximately 2 s. The fluorescence intensity at 410 nm was monitored until some time beyond the point where a seemingly stable final intensity was reached.

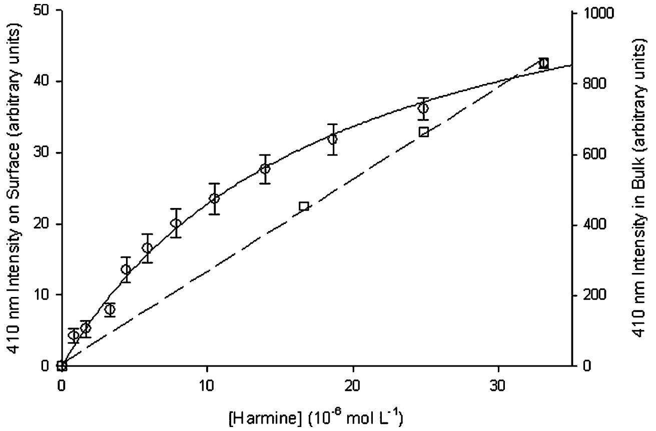

Figure 2. Fluorescence intensity of harmine measured at the air−aqueous interface as a function of its bulk concentration, shown as circles. Error bars show one standard deviation from the mean of three separate measurements. The solid line displays a fit to a Langmuir adsorption isotherm. Also displayed, as squares, are measurements of bulk harmine fluorescence as a function of concentration, with the dashed line displaying a linear fit to this data.

Harmine Adsorption Isotherm. To measure the propensity of harmine to partition to the air−aqueous interface, 100 mL of a saturated solution of harmine in 18 MΩ deionized water was placed in the three-neck round-bottom flask and the fluorescence intensity was measured at 410 nm. The harmine concentration in the flask was decreased by removing a known volume of solution with a volumetric pipet, and replacing it with an equal volume of 18 MΩ deionized water. The solution was then mixed well by repeatedly drawing up and expelling small portions with a Pasteur pipet. Care was taken not to disturb the position of the apparatus, in order to ensure that any decrease in measured intensity was only due to the decrease in harmine concentration. Harmine adsorption to the air−aqueous interface was also measured in the presence of a monolayer coating of 1-octanol. In this case removed solution was replaced with an equal volume of an aqueous solution of 1-octanol to maintain a constant concentration of the alcohol.

Chemicals. Harmine (98%, Aldrich), oxygen gas (Grade 4.4, BOC Scientific), sodium bromide (99%, ACP Chemicals), and 1-octanol (99%, Aldrich) were used as received, without any further purification.

Results and Discussion

In order for harmine to be useful as an indicator of interfacial pH, it must exhibit partitioning to the air−aqueous interface. The circles in Figure 2 display harmine fluorescence intensity measured at the water surface as a function of its bulk concentration. The solid line displays a fit of the data to a Langmuir adsorption isotherm, indicating that harmine partitions to the air−water interface. Fluorescence intensity was also measured in the bulk as a function of concentration, and the resulting data are shown in Figure 2 as the squares. Here the data is well-fit by a linear function, displayed on the plot as the dashed line, indicating that the curvature of the surface measurements is in fact due to partitioning of harmine to the air−aqueous interface, and not a result of the dimerization of

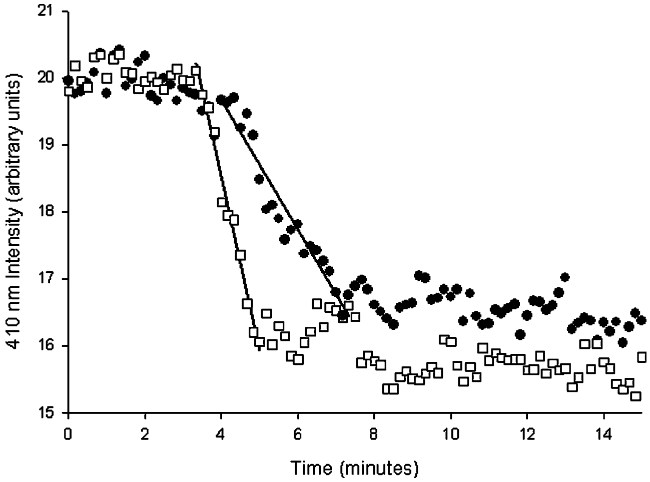

Figure 3. Results of a typical reactive experiment using a gas-phase ozone concentration of 4.5×10^{15} molecules cm^{-3} with both an uncoated (circles) and octanol-coated (squares) 2.5 mol L^{-1} NaBr solution. The slopes of the initial decrease in intensity are determined from the lines shown in the figure.

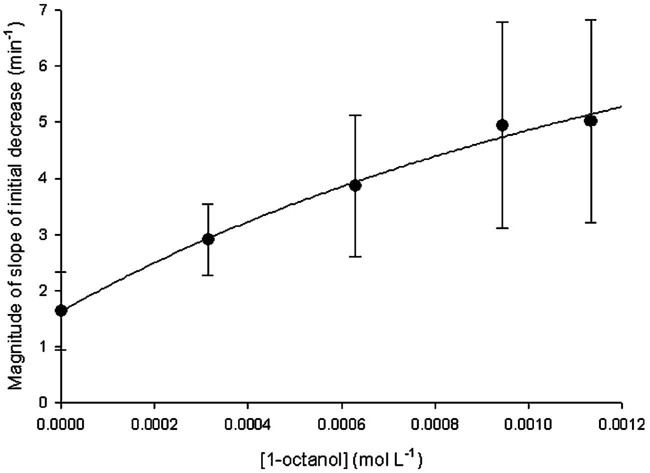

Figure 4. Magnitude of the slope of the initial fluorescence decrease as a function of 1-octanol concentration for a 2.5 mol L^{-1} NaBr solution. Error bars show one standard deviation from the mean of six separate measurements. The line displays a fit to the data, assuming a Langmuir adsorption isotherm.

harmine, or of an approach to its solubility limit. The presence of an octanol monolayer at the water surface had no effect on the harmine adsorption isotherm.

This strong partitioning of harmine to the air−aqueous interface is not surprising, given its chemical structure. Importantly, the observed Langmuir-type dependence of surface fluorescence intensity on bulk concentration also indicates that the source of the fluorescence measured in these experiments is the interface region and not the bulk solution. Similar measurements of harmine fluorescence as a function of bulk concentration were not undertaken in the presence of sodium bromide. However, due to a “salting-out” effect previously studied in this laboratory,[43] harmine is expected to partition somewhat more strongly to the surface of a sodium bromide solution relative to its partitioning in pure water.

In order for harmine to be a useful indicator of interfacial pH in these experiments, the presence of octanol must not influence its sensitivity. In a previous study of the surface hydrolysis reactions of some atmospherically relevant acids and bases,[40] acridine was used as an indicator of interfacial pH. In that study, the presence of octanol did not affect the sensitivity of acridine to the interfacial pH. Here we assume the same for harmine.

The result of a typical reactive experiment is shown in Figure 3, for a 2.5 mol L^{-1} NaBr substrate solution with both an uncoated and octanol-coated interface. In the uncoated case (shown by the circles in the figure), immediately following the introduction of ozone (at 2.5 min) into the flask, the fluorescence intensity decreased until a final stable intensity was reached. This observation indicates an increase in the surface region pH, consistent with the production of hydroxide ions from the reaction of bromide with ozone (reaction 5, above). Experiments performed with commercial sea salt in the place of NaBr showed no change in fluorescence intensity upon introduction of ozone, confirming that this observation is not due to a reaction of ozone with harmine.

As we noted in our previous work,[40] the time dependence of the pH change observed in the surface region in these experiments is necessarily complex, as it reflects gas-phase diffusion processes in addition to the interface reaction. Therefore, we cannot extract surface reaction kinetics directly from the time dependence of the fluorescence. However, when the experiment is repeated with a monolayer coating of 1-octanol (shown as squares in the figure), the rate of intensity decrease is significantly faster than it is in the uncoated case. The lines displayed in Figure 3 show linear fits to this decrease. The overall decrease in fluorescence intensity differs only slightly between the two cases, independent of octanol or salt concentration. Because the presence of an octanol monolayer at the surface has no effect on the gas-phase diffusion of ozone, the differences seen between the two cases shown in Figure 3 must arise from differences in the surface reaction.

Ozone is expected to exhibit a longer residence time at the air−aqueous interface in the presence of an organic coating[30] and thus enhance reaction rates there.[27] An increase in the rate of pH change in the presence of an octanol coating therefore provides strong support that an interfacial reaction between ozone and bromide takes place under these conditions. Since bromide is a strongly polarizable anion, it is possible that the presence of octanol may also enhance the partitioning of bromide to the interface. Such an enhancement, if it occurs, would also be expected to increase the rate of an interfacial reaction between ozone and bromide. There is no experimental or theoretical report of such an enhancement at this time, so this possibility remains speculative. Below, we examine more closely the initial pH increase as given by the slopes of the initial intensity decrease, as well as the overall change in pH over the course of the experiment, given qualitatively by the overall intensity decrease, as a function of the experimental parameters.

Relating the initial pH change to the surface component of a reaction suggests that the slope of the initial fluorescence decrease should depend on the surface concentration of octanol, because this concentration will affect the propensity of ozone to adsorb at the interface.[27−30] Indeed, the observed initial rate enhancement does depend strongly on the concentration of 1-octanol present in the sample. Figure 4 displays the magnitude of the slope of this initial intensity decrease, taken from linear fits to the data as shown in Figure 3, as a function of 1-octanol concentration for a 2.5 mol L^{-1} NaBr solution substrate. A strong correlation is observed, and at high octanol concentration, the dependence exhibits a “leveling off”, consistent with adsorption-like behavior.

With a monolayer of octanol present, the pH change rate is ∼3 times faster than for the uncoated surface. This factor is very similar to the rate enhancement observed for the hetero-

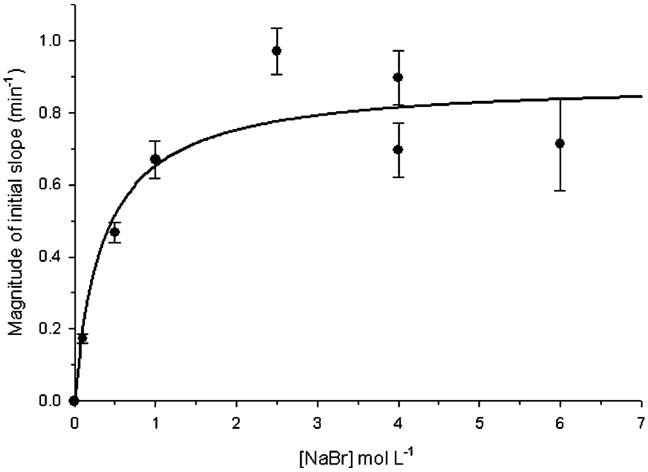

Figure 5. Initial rate of fluorescence decrease as a function of bromide concentration, for uncoated aqueous surfaces. The line displays a fit to the Langmuir−Hinshelwood interface reaction mechanism: rate = $A[Br^-(aq)]/(B + [Br^-(aq)])$, where $A = 0.89 \pm 0.08$ min^{-1} and $B = 0.36 \pm 0.18$ mol L^{-1}.

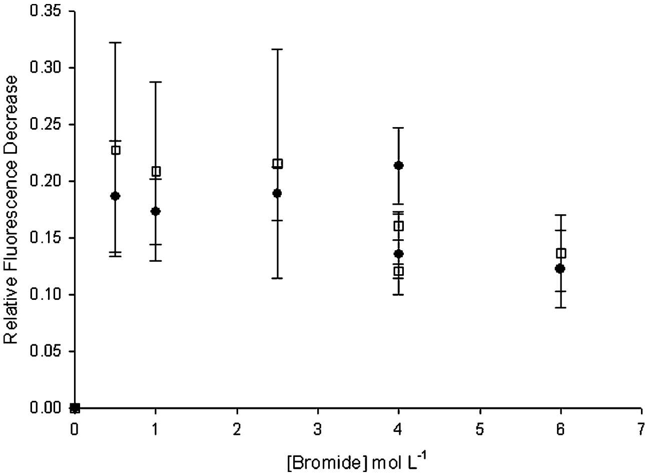

Figure 6. Overall fluorescence intensity decrease as a percentage of the original intensity, as a function of bulk bromide concentration, for uncoated (circles) and octanol-coated (squares) aqueous surfaces.

geneous reaction of gas-phase ozone with polycyclic aromatic hydrocarbons adsorbed at the water surface,[27,28] under low-ozone conditions with an octanol monolayer present. In that case, the low-ozone enhancement was attributed to better partitioning of the ozone to the octanol-coated surface; we conclude that a similar effect is operative here as well.

Due to an expected “salting-out” behavior, it is expected that octanol will be somewhat less soluble in the concentrated salt solutions employed in this study, and therefore its adsorption isotherm is expected to differ from that observed on salt-free aqueous surfaces.[43] Indeed, it was found to be more difficult to dissolve 1-octanol in solutions as bromide concentration increased, consistent with this expected “salting-out” effect. The line in Figure 4 displays a fit to the experimental data assuming Langmuir-type adsorption. This fit is marginally better statistically, with $R^2 = 0.992$, than a linear fit, which has an R^2 value of 0.976. This suggests that the experimental data could, in fact, display Langmuir type adsorption behavior, with an enhanced octanol surface concentration, consistent with the “salting-out” effect observed by Demou and Donaldson.[43] Direct measurement of an octanol adsorption isotherm on a salt solution substrate would help to clarify this point.

The results displayed in Figure 4 give clear evidence that the pH increase at the interface depends on the amount of ozone at the surface. A higher surface concentration of ozone (or bromide), induced by the presence of octanol, gives rise to a faster pH change—that is, a more rapid reaction at the interface. Figure 5 explores the effect of bulk bromide concentration on the rate of surface reaction in the absence of octanol. Here one sees an initial increase in rate with increasing $[Br^-]$, followed by a plateau above $[Br^-] \sim 2.5$ mol L^{-1}. Such behavior of reaction kinetics as a function of bulk reagent concentration is suggestive of a Langmuir−Hinshelwood mechanism, as we and others have seen previously for aqueous surface reactions.[27,28,44] In this mechanism, the reaction takes place in two dimensions, between reagents present at the interface. One or both of these surface reagents may exist in equilibrium with one of the bulk phases in contact with the interface. Our earlier work has shown that this is the case for ozone reacting with polycyclic aromatic hydrocarbons at the water surface:[27,28] the ozone surface concentration shows equilibrium partitioning behavior which is well described by a Langmuir adsorption isotherm. Because the interface reaction rate depends on the *surface* concentrations of the reagents, the observed dependence of kinetics on bulk concentration also follows a Langmuir form.

In the present case, bromide is thought to partition to the air−water interface.[8−15,20,21,23,24] The solid line in Figure 5 shows a fit to the kinetics data using a Langmuir−Hinshelwood form:[27,28]

$$\text{rate} = k[O_3(\text{surf.})][Br^-(\text{surf.})] \tag{6}$$

$$\text{rate} = k[O_3(\text{surf.})]\frac{[Br^-(aq)]}{(1/K_{\text{kin}}) + [Br^-(aq)]} \tag{7}$$

where K_{kin} represents the ratio of surface adsorption to desorption rate constants,[45] and the parameters are given in the Figure 5 caption. The fit is very good ($R^2 > 0.9$), indicating that bromide does indeed partition to the interface in the predicted manner, and that the reaction takes place in the interfacial region. From the B parameter given in the figure caption, we can estimate a kinetic partitioning constant of bromide to the air−aqueous interface of $K_{\text{kin}} = 2.78 \pm 0.93$ L mol^{-1}.

The relationship between bromide concentration and the overall fluorescence intensity decrease is explored in Figure 6, for both uncoated and octanol-coated samples. Because bromide is an efficient quencher of harmine fluorescence, the absolute changes in fluorescence intensity depend upon the bromide concentration. However, we observe that the “relative overall intensity decrease” on the *y*-axis, defined as the percentage decrease from the initial to final measured fluorescence intensity, has a value of 18 ± 5%, independent of the bromide concentration. This is consistent with the bromide concentration being far in excess of the ozone concentration for all the bromide concentrations used in this study. This leads to a situation where all the ozone is essentially “titrated”, and so the same overall change in pH (and hence fluorescence intensity) should be expected regardless of bromide concentration.

Conclusions and Atmospheric Implications

We have observed a pH increase at the air−water interface of NaBr solutions exposed to gas-phase ozone. The rate of pH increase depends on the *surface* concentration of ozone, as shown by the enhancement in the rate when octanol—known to enhance partitioning of ozone to the aqueous surface—is present. The rate of pH increase depends as well on the bromide concentration *at the surface*, as indicated by a Langmuir−

Hinshelwood type dependence of the rate on aqueous-phase bromide concentration.

These results provide direct experimental evidence that a surface reaction between ozone and bromide does occur. Assuming the partitioning constant presented above, for a seawater [Br^-] of 10^{-3} mol L^{-1} the surface bromide concentration is estimated to be about 10 times that of the bulk. The reacto-diffusive length parameter, $l = (D/k_1)^{1/2}$, where D represents the liquid-phase diffusion coefficient and k_1 gives the first-order rate coefficient, offers insight into the depth of penetration into solution before reaction takes place. Taking the aqueous-phase reaction rate constant of Hunt et al.[2] gives a reacto-diffusive length for the bulk reaction at this bromide concentration of ~50 μm. Given this short reacto-diffusive length, an enhancement in the surface concentration of bromide could give rise to a significant increase in the overall bromide oxidation rate, as inferred by Hunt et al.[2] This increase could be magnified by the presence of an organic film, which could increase the ozone surface concentration and perhaps that of bromide as well.

Given that the diameter of the round-bottom flask used in these experiments is ~7.5 cm, the surface volume contained within the ~50 μm reactodiffusive depth will contain on the order of ~10^{20} bromide ions at the molar concentrations used here. With only ~10^{17} molecules of ozone in total, under these high-bromide conditions the reaction will be confined to the surface region. The experiments described herein thus cannot address the issue of relative contributions of surface- and bulk-phase reactions under atmospheric conditions. Our results clearly demonstrate, however, that a surface reaction between ozone and bromide does occur.

The enhanced partitioning of ozone to octanol-coated surfaces may have further implications. Given that the sea-surface microlayer is enriched with organic species, and since atmospheric aerosols normally have at least some surface-active organic component, it might be that an organic enhanced surface reaction could be a contributor to the “bromine explosion” that often accompanies ozone depletion events in the arctic. Also, it has previously been suggested that the deposition of ozone to the sea surface involves a coupling of physical and chemical processes occurring at the ocean surface.[46] An enhanced surface reaction of ozone with bromide in the presence of an organic film, such as those found in the sea-surface microlayer, could certainly represent an important chemical enhancement of this process. Further work is required in order to quantitatively determine the kinetics of the surface reaction, in the presence and absence of an organic coating.

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