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Direct Observation of the Kinetics of an Atmospherically Important Reaction at the Air−Aqueous Interface

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Many atmospherically important chemical processes are believed to occur at the interface between the air and aqueous phases. We report the first direct measurement of the kinetics of a reaction between a gas-phase species (ozone) and a compound (anthracene) adsorbed at the air−water interface. The reaction was studied at the "clean" air−water interface and also at an interface consisting of approximately one monolayer of 1-octanol. In both instances, the reaction was seen to follow a Langmuir−Hinshelwood mechanism, in which ozone first adsorbs to the surface and then reacts with adsorbed anthracene. Using typical atmospheric ozone concentrations, a reactive uptake coefficient of approximately 6×10^{-8} at the air−water interface may be estimated; this value increases by about a factor of 5 when the water surface is coated by a monolayer of 1-octanol.

Introduction

The importance of heterogeneous chemical processes in the atmosphere is now well established.[1] Processes such as stratospheric ozone depletion, acid rain formation, the growth of cloud condensation nuclei, and secondary organic aerosol formation are only a few of those which involve interactions between trace atmospheric gases and atmospheric condensed phase material. Laboratory experiments to date have concentrated largely on transformations taking place in aqueous solution, although there is a growing interest in reactions occurring on soot, mineral dust, and salt surfaces. Only a handful of studies have been reported on chemical reactions[2] taking place at the air−water interface.

In groundbreaking work, Wadia et al.[3] observed in real time the gas-phase products of the reaction of ozone with an unsaturated phospholipid adsorbed in a film at the air−water interface. There is a growing body of evidence, from both field studies[4−6] and laboratory measurements,[7,8] that such organic and bio-organic films may coat atmospheric aerosol particles. In ref 3, a full kinetic study was not performed, but the time required for complete reaction suggested a rate that was faster at the interface than in the gas phase. A very recent paper by George and co-workers[9] reports a measurement of the rate coefficient for reaction of the Cl_2^- radical anion with ethanol at the air−water interface; again, this rate coefficient is larger than the corresponding value in solution. These studies suggest that chemical reactions of atmospheric (and potentially biological) importance could occur more rapidly than expected at the air−aqueous interface. This conclusion is consistent with the results of reactive uptake measurements of OH and O_3 by organic aerosols,[10−12] films,[13,14] and organized monolayers.[15]

There have been no direct measurements to date of the kinetics of atmospheric gas-aqueous surface reactions. In the following, we present our direct measurements of the kinetics of the reaction between gas-phase ozone and anthracene adsorbed at the air−aqueous surface. Anthracene is a three ring member of a class of compounds called polycyclic aromatic hydrocarbons (PAHs), which consist of three or more fused aromatic rings. These compounds may be released into the environment during combustion of fossil fuels and biomass burning.[1] They react with atmospheric oxidants, such as OH radicals, ozone, and NO_3, yielding degradation products which are often more carcinogenic and mutagenic than the parent compounds.[16] Reaction with ozone, while slower than the reaction with OH, may become important at night when OH concentrations are low. The kinetics of the reaction between gaseous ozone and several PAHs (though not anthracene), both in the gas phase and adsorbed on various solid surfaces, have been studied by a number of researchers.[1,17−20]

The reactive uptake coefficient of ozone is estimated for pure water and for an aqueous solution with a monolayer surface coverage of 1-octanol. We use 1-octanol as a proxy for the partially oxidized compounds which are expected to coat atmospheric aqueous aerosols.[7] Such coatings are implicated in enhanced uptake of organic compounds in rain and fog waters[21−23] as well as altering the reactive uptake of N_2O_5[24] and the mass accommodation coefficient of H_2SO_4.[25] Our recent work on solution−interface partitioning[26] and mass accommodation coefficients[27] of PAHs has explored and quantified these effects.

Experimental Methods

The work described here used an apparatus and methods modified slightly from those described in our work on partitioning[26] and uptake[27] of PAHs to the air−aqueous interface. Experiments were performed in a darkened 250 mL, three-necked round-bottom Pyrex flask containing approximately 100 mL of either 18 MΩ deionized water or a 2.5×10^{-3} mol L^{-1} aqueous solution of 1-octanol. This concentration gives rise to about one monolayer of 1-octanol at the interface, as estimated from the results of Lin et al.,[28] which are illustrated in Figure 1. Anthracene (98% purity) was introduced at its room temperature vapor pressure (8×10^{-4} Pa) in a stream of N_2 (1.2 L min^{-1}), which entered one of the side necks of the flask and

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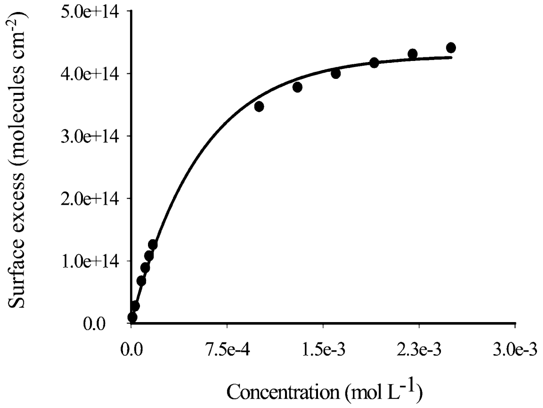

Figure 1. Surface excess of 1-octanol in aqueous solution as a function of its bulk concentration (constructed from surface tension data in ref 28). The line shows a fit to the Langmuir adsorption equation.

exited through the other. A switching valve on the entrance neck allowed the N_2/anthracene stream to be replaced with a stream of (99.996%) O_2. Ozone could be generated in this stream using a variable ozone generator (model 600, Jelight Company). Concentrations of ozone in the reaction flask could be varied over the range 10^{14} to 10^{16} molecules cm^{-3}, as determined by absorbance spectroscopy using the Hartley band absorption of ozone.

Anthracene at the aqueous surface was excited at 355 nm by the frequency-tripled output of a pulsed (10 μJ per 5 ns pulse) Nd:YAG laser operating at 10 Hz. The laser beam impinged on the sample at an angle of approximately 85° to the surface normal such that it made a glancing reflection at the surface of the solution. Fluorescence from anthracene was collected perpendicular to the liquid surface through the central neck of the sample flask using a 7 mm diameter fiber optic bundle. The fluorescence was imaged into a monochromator set to pass the wavelength 402 ± 2 nm, and it was detected by a photomultiplier. The detected signal was sent to a digital oscilloscope and computer for analysis. The fluorescence intensity was recorded at a 5 ns delay time following the laser pulse every 15−60 s over the course of the experiment.

In our work on the partitioning of PAHs to the air−aqueous interface[26] and uptake to the aqueous surface,[27] we give evidence supporting our assertion that the fluorescence signal observed in these experiments arises from surface-bound species. Both the wavelength-resolved fluorescence spectra and the fluorescence lifetimes of pyrene at the interface show significant differences from those measured in bulk phases, and both depend as well on the degree of coverage of the aqueous surface by 1-octanol or hexanoic acid (i.e. submonolayer, monolayer, or multilayer).[26] The fluorescence intensity measured at the surface of aqueous solutions of anthracene shows a dependence on the bulk solution concentration that is well fit by a Langmuir adsorption isotherm, indicating that it is the *surface* concentration which is measured.[27] Finally, the time dependence of the fluorescence intensity we observe following exposure of the aqueous surface to anthracene or pyrene indicates that uptake is not to the solution but to the surface (initially, at least) alone.[27]

Gas-phase anthracene was introduced into the darkened reaction cell over a time of 20−30 min while its surface concentration on an aqueous substrate was followed using the glancing-angle laser-induced fluorescence method. As discussed in ref 27 and illustrated in Figure 2, this exposure time results in a surface concentration of anthracene which is somewhat less than its saturated value. The left-hand portion of Figure 3 shows the increase in fluorescence intensity with time, as in Figure 2,

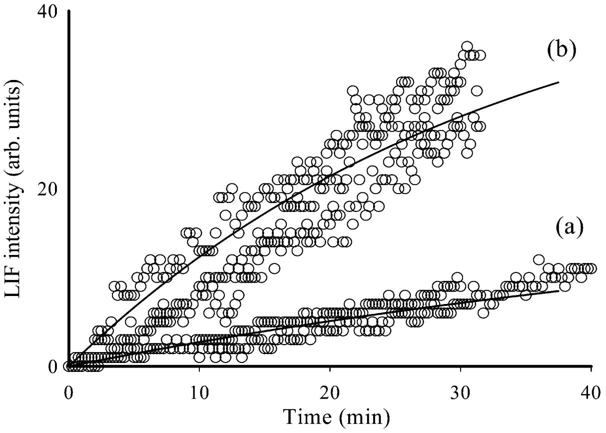

Figure 2. Anthracene fluorescence intensity as a function of time following exposure of the surface to anthracene vapor at (a) the clean air−water interface and (b) the surface of a 2.5 × 10^{-3} M aqueous solution of 1-octanol. The solid lines show exponential fits to the time-dependent uptake. See ref 27 for full details.

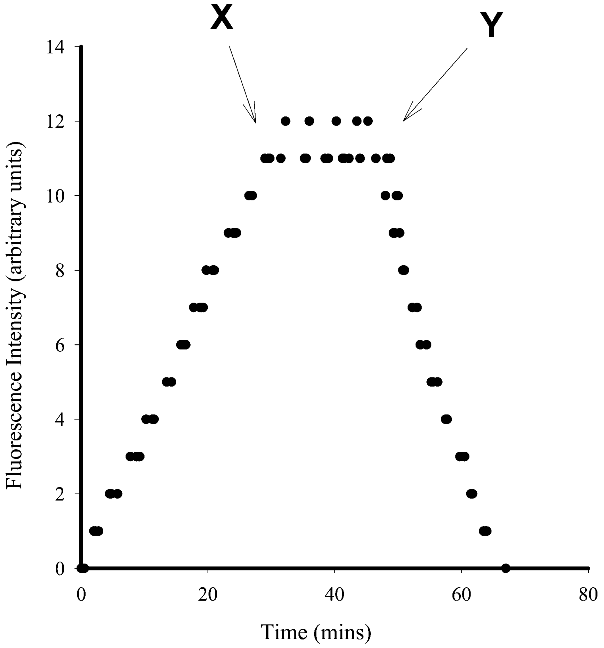

Figure 3. Anthracene fluorescence intensity as a function of time showing the various steps in a single experimental run including uptake of anthracene to the air−pure water interface (0−X), anthracene supply switched off and ozone-free O_2 supply turned on (X−Y), and ozone generator turned on (at point Y). The signal-to-noise ratio is indicated by the scatter in the points.

indicating the uptake of anthracene to the surface. The anthracene flow was switched off at the time labeled "X" in Figure 3, and an identical flow of oxygen was introduced through the reaction cell with the ozone generator off. No change in the anthracene fluorescence intensity was observed during the approximately 20 min these conditions existed. (Separate experiments were done to establish a half-life of approximately 2 h for the anthracene fluorescence from the water surface to be eliminated under these conditions.) After this time, the ozone generator was turned on (at point "Y") and an immediate decrease in fluorescence intensity was measured. A pen-ray lamp−photodiode ozone monitor, situated perpendicular to the laser beam axis, was used to confirm that the ozone concentration remained constant during this time, ensuring pseudo-first-order kinetics. Switching off the ozone generator halted the decrease in fluorescence intensity, while the ozone concentration

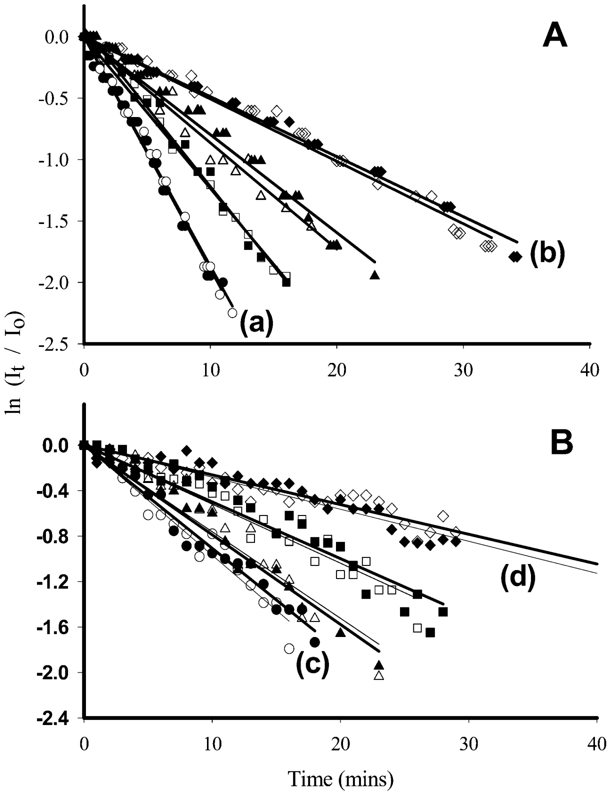

Figure 4. Representative anthracene decays observed for (A) an uncoated water surface at ozone concentration ranging from (a) 8.4 × 10^{15} to (b) 6.8 × 10^{14} molecules cm^{-3} and for (B) a 2.5 × 10^{-3} M aqueous solution of 1-octanol at O_3 concentrations of (c) 6.8 × 10^{14} to (d) 1.2 × 10^{14} molecules cm^{-3}.

in the cell decreased to zero within 5−7 min. This procedure was repeated several times for each gas-phase ozone concentration over a 2 order-of-magnitude range of $[O_3(g)]$.

Results and Discussion

The observed decays in the surface anthracene concentration all showed single exponential behavior. Figure 4 illustrates representative plots of $\ln(I_t/I_0)$ (proportional to $\ln\{[\text{anthracene}]_t/[\text{anthracene}]_0\}$) versus time at different ozone concentrations for anthracene adsorbed at the clean (A) and 1-octanol coated (B) water surfaces. The linearity of the plots indicates that the reaction is first-order with respect to anthracene. The slopes of the linear least-squares fits of the plots were used to determine pseudo-first-order rate coefficients, k_{obs}, from

$$\ln\left(\frac{[\mathrm{An}]_t}{[\mathrm{An}]_0}\right) \propto \ln\left(\frac{I_t}{I_0}\right) = -k_{\mathrm{obs}}t \qquad (1)$$

Because the ozone concentration is constant, k_{obs} is actually the product of a second-order rate coefficient, k^{II}, and the ozone concentration. In Figure 5 the values of k_{obs} extracted from analysis of the decay curves are plotted against $[O_3(g)]$ for both the "clean" and coated water surfaces. The dependence of k_{obs} on $[O_3(g)]$ is clearly nonlinear, implying an indirect reaction mechanism. A direct (Eley-Rideal)[29] mechanism, in which a gas-phase ozone molecule collides with an adsorbed anthracene molecule and undergoes a chemical reaction, would give rise to a linear dependence of k_{obs} on the gas-phase ozone concentration. Such a mechanism has been determined for several reactions that involve a reagent adsorbed on a solid surface (for recent work, see refs 30 and 31), including atmospherically important systems.[32]

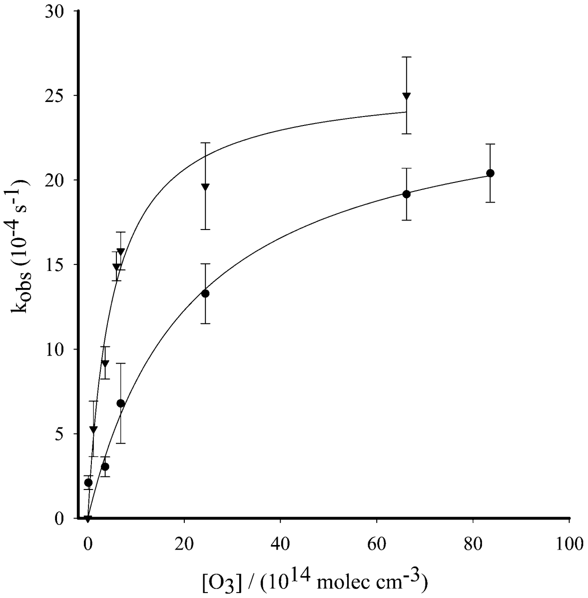

Figure 5. Pseudo-first-order anthracene decay rate coefficients (k_{obs}) as a function of gas-phase ozone concentration for the 2.5 × 10^{-3} M 1-octanol aqueous solution (inverted triangles) and uncoated water (circles). The curves are nonlinear least-squares fits of eq 3. The error bars represent one standard deviation about the mean of at least 3 measurements (coated surface) and at least 5 measurements (uncoated surface).

A second possible mechanism involves uptake of ozone into solution, followed by reaction of dissolved ozone with adsorbed anthracene. To ensure that this was not taking place, we performed one set of experiments using a 0.2 mol L^{-1} solution of Na_2SO_3, rather than pure water. The sulfite anion, SO_3^{2-}, reacts with dissolved O_3 at close to the diffusion limit, with a room-temperature rate coefficient of about 1.5 × 10^9 L mol^{-1} s^{-1}.[33] If dissolved ozone was responsible for the observed reaction, a decrease in the rate would be observed, due to the (much) reduced $[O_3(aq)]$. Under these conditions, we observed no significant difference in the rate of loss of adsorbed anthracene compared to the pure water case. We conclude that the reaction does not involve dissolved ozone. One may also estimate the reactive uptake coefficient for ozone into solution due to reaction with dissolved anthracene, (vide infra) compared to that expected for the sulfite reaction, and arrive at the same conclusion.

The shapes of the plots shown in Figure 5 suggest a third possibility. The Langmuir−Hinshelwood mechanism[29] for surface reactions posits that reaction occurs between coadsorbed species, in which one reactant is more strongly adsorbed and the other is in rapid equilibrium between bulk and surface phases. Assuming Langmuir adsorption behavior of ozone on the aqueous surface, the surface concentration of ozone is given by

$$[O_3(\mathrm{surf})] = \frac{N^{\mathrm{surf}}[O_3(g)]}{B + [O_3(g)]} \qquad (2)$$

where N^{surf} is the maximum number of surface sites available to ozone, and B represents a ratio of desorption/adsorption rate coefficients involving both bulk phases.[34] In the limit of little or no ozone dissolution in the aqueous phase, B approximates the inverse of the gas−surface partition coefficient.[34] The dependence of k_{obs} on the gas-phase ozone concentration then becomes

$$k_{\mathrm{obs}} = \frac{k^{\mathrm{II}}N^{\mathrm{surf}}[\mathrm{O_3(g)}]}{B + [\mathrm{O_3(g)}]} \tag{3}$$

The data shown in Figure 5 were fit to this general form, taking $A = k^{\mathrm{II}}N^{\mathrm{surf}}$ as a single parameter. The lines in the figure illustrate the resulting fits, using parameters listed in Table 1. The fit is excellent for both the clean water and 1-octanol-coated surfaces, strongly implying that the Langmuir−Hinshelwood mechanism operates for this reaction in both cases.

Poschl et al.[17] have recently reported that the reaction of gas-phase ozone with benzo[*a*]pyrene (BaP) adsorbed on soot displays a very similar dependence of k_{obs} on the gas-phase ozone concentration. In that work the adsorption parameters of ozone onto soot were measured independently of reaction, confirming that ozone adsorption follows a Langmuir isotherm. To our knowledge, there is no report of ozone adsorption onto aqueous surfaces. In fact, the present measurement represents, to our knowledge, the first direct experimental determination of the kinetics and mechanism of *any* atmospheric gas−aqueous surface reaction, although such reactions have been inferred from previous kinetic results.[35]

Several interesting conclusions may be drawn from the results shown in Figure 5 and Table 1. First, the parameter representing $k^{\mathrm{II}}N^{\mathrm{surf}}$ is the same, within experimental uncertainty, for both the clean water and 1-octanol-coated water surfaces. Either the bimolecular surface reaction coefficients are different in the two cases, and, coincidentally, the values of N^{surf} differ in the opposite manner, or both N^{surf} and k^{II} are essentially the same for the two interfaces. If the latter conclusion is true, assuming a value of N^{surf} of 10^{14} cm^{-2} gives a surface reaction coefficient of 2.6×10^{-17} cm^2 molecule^{-1} s^{-1}, identical to that derived for the ozone + BaP reaction on a soot substrate.[17]

The *B* parameter in the Langmuir−Hinshelwood fits relates the ratio of surface desorption to adsorption from *both* bulk phases.[34] The values given in Table 1 are about a factor of 4 smaller for the 1-octanol-coated surface than for clean water. This suggests either a more facile uptake of ozone from the gas phase for the 1-octanol-coated surface or a smaller rate of its loss to the bulk phases (or both). We note in this regard that Poschl et al.[17] report a significant adsorption enthalpy for ozone on soot, between 80 and 90 kJ mol^{-1}. Although the adsorption enthalpy of ozone to the water surface is not known, it is probably not greatly different from the binding energy of the ozone−water complex, which is estimated[36] to be about 3 kJ mol^{-1}, suggesting that ozone might enjoy stronger interactions with nonpolar organics than with water.

Following Poschl et al.,[17] we transform the pseudo-first-order rate coefficients to apparent reactive uptake coefficients for reaction at the aqueous surface. This quantity, γ_{rxn}, gives the fraction of collisions between gas-phase ozone and an adsorbed anthracene molecule that result in reaction. We estimate it using the relationship

$$\gamma_{\mathrm{rxn}} = \frac{4k_{\mathrm{obs}}}{\sigma_{\mathrm{An}}\omega_{\mathrm{O_3}}[\mathrm{O_3}]} \tag{4}$$

where ω_{O3} gives the mean thermal velocity of ozone, and σ_{An} represents the collision cross section of the anthracene molecule. We take the latter quantity to be the area of an anthracene molecule lying flat on the surface, although this could be smaller if ozone interacts with a single aromatic ring alone or if the anthracene is not flat on the surface. The resulting values are shown as the points in Figure 6. The solid lines give the result when the parameters given in Table 1 are used to predict k_{obs}.

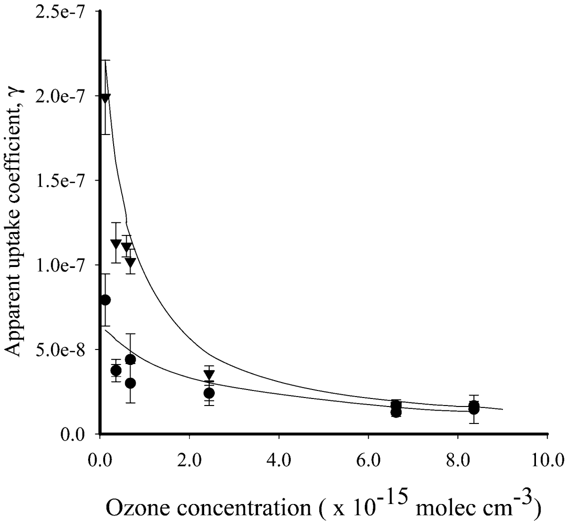

Figure 6. Apparent reactive uptake coefficients for anthracene−O_3 reaction as a function of gas-phase ozone concentration for the 2.5×10^{-3} M 1-octanol aqueous solution (inverted triangles) and uncoated water (circles). The solid lines give the predicted uptake coefficients, using data from Table 1. See the text for details.

TABLE 1. Fitting Parameters for Eq 3 to the Data in Figure 5 for the Dependence of the Pseudo-First-Order Rate Constant for the Reaction between Gas-Phase Ozone and Surface Adsorbed Anthracene on Gas-Phase Ozone

substrate	10^3A (s^{-1})	$10^{-14}B$ (molecule cm^{-3})	r^2
water	(2.55 ± 0.17)	(21.43 ± 4.41)	0.989
1-octanol aq solution (2.5×10^{-3} M)	(2.59 ± 0.14)	(5.08 ± 0.88)	0.981

The limiting values (at zero ozone concentration) of the apparent uptake coefficients are 6.5×10^{-8} on the clean water surface, and 2.8×10^{-7} on the 1-octanol-coated interface. Under tropospherically relevant conditions (50 ppb O_3) the uptake coefficients are essentially the same as the limiting values given above.

These uptake coefficients are smaller than those reported for ozone reaction with BaP adsorbed on soot[17] or on fused silica,[18] which are both on the order of 10^{-5}. Poschl et al. noted a decrease in γ at low ozone concentrations when the ambient relative humidity was increased to 25% from <1% and modeled this successfully assuming that water competed with ozone for adsorption sites on soot.[17] An alternative explanation might be that, at 25% relative humidity, soot has a monolayer (or greater) coverage of water,[37] and ozone must adsorb to this water layer in order to react with BaP. One might expect, on the basis of the results presented here, that a decrease in the apparent reactive uptake coefficient would result. Niki and co-workers[18] measured the rate of reaction of ozone with BaP and with perylene, when both were adsorbed on fused silica surfaces. Those authors reported rate coefficients corresponding to reactive uptake coefficients of 10^{-5} for BaP and 10^{-7} for perylene. The measured k_{obs} values were reported to vary linearly with the ozone concentration up to a mixing ratio of 10 ppm; however, a Langmuir−Hinshelwood type mechanism was not considered.

The present results indicate that ozone reactions occurring at the air−water interface do follow a Langmuir−Hinshelwood mechanism. A mechanism which involves an initial trapping of ozone at the interface is implied as well by the molecular dynamics simulations reported by Wadia et al.[3] for the reaction of O_3 with a monolayer film of unsaturated phospholipid at the water surface. In those simulations, the ozone molecules became "trapped" in the hydrophobic tails of the phospholipid, enhancing the reaction probability over that seen in the gas phase, as noted experimentally. For all of the reactions of ozone with adsorbed PAHs studied to date, the reactive uptake coefficients also imply reaction probabilities much larger than the corresponding gas-phase values,[1] which are generally on the order of 10^{-9}. This is very likely due to the surface reaction mechanism, in which ozone is physisorbed at the surface with the PAH, which allows more interaction between the two reactants.

The values of γ_{rxn} we measure here are small but could nevertheless be of some atmospheric consequence. Taking a value of 0.5 (mol m^{-2})/(mol m^{-3}) for the partition coefficient from air to the pure water surface,[38] and assuming a number density of 10^4 1-μm diameter droplets per cm^{-3} of air yields a fraction of anthracene adsorbed on droplet surfaces of about 1%. For an organic-coated surface, this could increase (through the partition coefficient)[26,27] to about 10%. Using a ratio of $[OH]/[O_3]$ of 10^{-6} and a gas-phase reaction probability[1] of anthracene with OH of 0.01−0.1, we estimate that the surface reaction could contribute significantly to atmospheric anthracene oxidation, perhaps as much as the gas-phase reaction with OH.

The findings that (i) ozone reacts with adsorbed species at the aqueous surface via a Langmuir−Hinshelwood mechanism and (ii) an organic film at the water surface enhances the reaction rate under typical ambient $[O_3(g)]$ by up to an order of magnitude are very significant. The uptake coefficient of ozone due to solution-phase reaction in a saturated anthracene solution (i.e. ignoring the surface reaction) may be estimated to be about 10^{-9}; we obtain values 10−100 times greater for reaction at the surface. If this is true for other oxidizable compounds at the air−water interface (as it is for phospholipids),[3] then surface reaction could play an important role in the atmospheric chemistry of these species. Because these experiments were carried out in ozone−oxygen mixtures, there is some possibility that molecular oxygen plays some role in the chemistry. We acknowledge this possibility but note that since the atmospheric O_2/N_2 ratio is 0.2, molecular oxygen could very well be involved under true atmospheric conditions as well. We have initiated product analysis studies which suggest this is not the case, however.[39]

Perhaps of even greater importance is the possibility of very efficient oxidation of chemical species in biofilms by ozone. The microlayer on marine and lake surfaces, and the phospholipids present in the lung and in plant leaves, all have the potential to increase the concentrations of species such as PAHs at the air−water interface. This has recently been demonstrated in our laboratory, where the surface uptake coefficient and the partitioning of hydrophobics to the surface is enhanced, when the water surface is coated by an organic film. Since the oxidation and nitration products of PAHs are typically highly toxic, this increase in concentration, in conjunction with the significant reaction probabilities for reaction on a coated surface, could have important health effects.

Conclusions

Anthracene adsorbed at the air−water interface reacts with gas-phase ozone following a Langmuir−Hinshelwood mechanism, with a reaction probability significantly greater than the corresponding gas-phase value. The reaction occurs with the same 2-dimensional rate coefficient both on "clean" water and on the 1-octanol-coated water surface. However, the net adsorption of ozone is greater in the latter case, yielding larger reactive uptake coefficients under atmospherically relevant conditions.

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