Heterogeneous ozonation kinetics of phenanthrene at the air–ice interface

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Abstract
Phenanthrene ozonation kinetics were measured on ice at −30 and −10°C, and on a water surface at 22°C using glancing angle laser-induced fluorescence. A Langmuir–Hinshelwood type kinetic mechanism was observed on ice. The maximum ozonation rates were a factor of ten higher on ice than on water. No temperature dependence to the kinetics was observed between −30 and −10°C, suggesting that the differences in the rates on ice and water are due to different physical properties at the two surfaces. Fluorescence spectra of phenanthrene show significant self-association on ice that is not observed on water, adding further evidence for the hypothesis that the quasi-liquid layer at the air–ice interface presents a very different environment to liquid water.

Keywords: heterogeneous chemistry, kinetics, PAHs, ozone

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are predominantly found in urban environments [1–3]. These products of incomplete combustion are considered important pollutants due to their carcinogenic and mutagenic effects [4]. Understanding the chemical fates of PAHs is quite important, since their oxidation and nitration products are often more toxic than the parent compounds [4]. Reaction with gas-phase hydroxyl radical is the most important transformation process for volatile PAHs; atmospheric lifetimes tabulated by Finlayson-Pitts and Pitts [4] show that reaction with other gas-phase species is generally unimportant. However, heterogeneous reactions of surface-bound PAHs with oxidizing gases such as ozone could be important loss mechanisms for larger, less volatile PAHs in urban centres [5]. Ozonation kinetics of a range of PAHs have been measured on substrates including soot, organic and inorganic aerosols, water, and organic films. A review of these studies is provided in Kwamena et al [6].

Frozen water, in the form of terrestrial snow and ice, has received a good deal of attention from the atmospheric community as a substrate for a range of reactions [7]. While the bulk of research has focused on reactions which can affect the oxidizing capacity of the overlying boundary layer, such as the photolysis of NO₃ or H₂O₂, the evolution of organics, and bromine explosion events, the role of this substrate in the fate of organic compounds such as PAHs has received increased attention in recent years. PAHs have been detected in urban [8] and arctic [9, 10] snows. Recent investigations have examined the scavenging ability of snow [11], the uptake kinetics of PAHs onto ice [12], and the reaction kinetics and products of PAH photolysis in snow and ice [13, 14]. Although to date studies have primarily focused on polar environments, we believe that frozen water could be a reaction substrate of equal, if not greater, importance in urban centres, where there are high concentrations of PAHs and of oxidizing gases such as ozone. Reactions of PAHs in urban snow and ice could have significant consequences for human health, especially given the labile nature of these substrates and the likely eventual inclusion of oxidized reaction products in groundwater.

Ice is a complex reaction substrate, due largely to the presence of a disordered region at the air–ice interface,
commonly referred to as the quasi-liquid layer (QLL) [7, 15]. Compounds in solution can be excluded to this region during freezing, and species deposited to ice and snow from the gas phase must initially come into contact with the QLL. This means that the QLL (or quasi-brine layer, which may be a more appropriate term in the presence of solutes) can potentially contain very high concentrations of pollutants, which will likely be available for interaction with gas-phase species such as ozone.

Although the QLL appears to present an environment that is distinct from liquid water or supercooled water (see for example [15]), it is possible that kinetics from bulk aqueous reactions can be extrapolated to those on ice. This does in fact appear to be the case for the photolysis of some small inorganic species [16, 17]. If this holds true for other species and other types of reactions, this would greatly enhance our understanding of the role of ice as a reaction substrate and significantly simplify modelling; it is currently very difficult to probe the QLL, either to determine its physical characteristics or to observe its role in chemistry. Recent work in our laboratory [14], however, has shown that the PAHs anthracene and naphthalene experience different intermolecular interactions at ice and liquid water surfaces, in that they self-associate very readily in the QLL compared to on a liquid water surface. Further, direct photolysis rates for both of these PAHs are significantly enhanced at the air–ice interface compared to the air–water interface. However, the degradation rate of anthracene on ice does not change in the presence of NO$_3^-$ or H$_2$O$_2$: we conclude that indirect photolysis due to the presence of photoformed hydroxyl radicals is suppressed in the QLL. These results indicate that liquid water might not always be a good proxy for the QLL. The observation of no enhancement in anthracene’s degradation rate due to indirect photolysis raises the question of the effect of the QLL on bimolecular reaction kinetics. Some bimolecular reactions demonstrate enhanced rates in ice compared to in liquid water, but this is often due to enhanced reagent concentrations in micropores within the ice matrix [18]. We are not aware of any studies directly examining rates of bimolecular reactions taking place exclusively in the QLL.

In this work, we examine the role of the QLL in the ozonation kinetics of phenanthrene. Through a comparison of ozonation rates on the water surface at room temperature and on ice at two different temperatures, we show that the difference in rates on ice and on liquid water are due to differences in the local environment rather than to changes in temperature. To our knowledge, this work represents the first investigation of a reaction between an organic compound in the QLL and a gas-phase reagent, as well as the first investigation of a temperature dependence for such processes.

2. Experimental details

The reaction chamber used for the ozonation experiments on ice has been described in detail elsewhere [14]. In short, it consists of a 500 ml Teflon box with side ports through which gases can be introduced and vented. The copper plate that forms the chamber floor is soldered to copper coils through which a temperature control fluid is circulated. The only modification to the chamber from previous experiments is the inclusion of a stainless steel plate which sits immediately above the copper floor to prevent oxidation of the copper by ozone. Experiments were done at $-11$ and $-30$ °C.

Ice samples were prepared as described previously [19], by placing $\sim$0.8 ml of 18 M2 deionized water on a stainless steel plate in the centre of the reaction chamber and allowing it to cool to the desired temperature. After freezing, ice samples were inverted to present a flat surface to the laser. Phenanthrene was deposited onto the ice and water surfaces by flowing a stream of nitrogen over a few grams of solid phenanthrene held in a separate vessel which was heated to $\sim$50 °C to enhance its partial pressure. The phenanthrene travelled through $\sim$50 cm of room temperature 1/4" Tygon tubing before entering the reaction chamber. Ozone was introduced to the chamber in a stream of oxygen using a variable ozone generator. Ozone concentrations were monitored by the attenuation of a 254 nm mercury lamp by ozone flowing through an in situ 10 cm pathlength absorption cell, situated upstream of the reaction cell.

The experimental setup for ozonation experiments on liquid water has been described previously [20]. Briefly, a three-necked round-bottom flask containing $\sim$100 ml of water served as the reaction vessel. All experiments on water were performed at room temperature (22 °C).

Fluorescence was induced by the unfocused 266 nm output of a frequency-quadrupled Nd:YAG laser (pulse energy $\sim$0.5 mJ) or by the 266 nm or 293 nm output of a Nd:YAG-pumped optical parametric oscillator (OPO) (pulse energy 0.1–1.8 mJ). The laser beam entered and exited the Teflon chamber and the round-bottom flask through quartz windows. The incident angle of the laser was $\sim$87° from the surface normal for experiments performed in the Teflon chamber, and $\sim$80° for experiments performed in the round-bottom flask.

Fluorescence was collected perpendicular to the surface using a liquid light guide suspended 1 cm above the sample, then imaged into a monochromator, and the transmitted intensity was detected by a photomultiplier tube and sent to a digital oscilloscope and computer for analysis. The digital oscilloscope averaged the intensity versus time signal over 64 laser shots; a 100–200 ns segment of each averaged decay profile was sampled by the computer and stored.

Fluorescence spectra were acquired by scanning the monochromator across the desired wavelength range in 3 nm increments. Ozonation kinetics were obtained by monitoring the time dependence of phenanthrene fluorescence intensity at 348 nm while ozone was introduced to the reaction chamber.

3. Results and discussion

3.1. Spectra of phenanthrene on water and ice

Figure 1 shows fluorescence spectra of phenanthrene excited at 266 nm on water and ice surfaces. Although peaks occur at the same wavelengths for both substrates, clear differences in the relative intensities of the peaks are observed. Specifically, phenanthrene’s most intense fluorescence is observed at 348 and 368 nm on water, but on ice these peaks have only a quarter of the intensity of the peaks at 384 and 406 nm.
The differences in the fluorescence spectra on water and on ice can be explained by enhanced self-association of phenanthrene on ice. A relative shift of fluorescence intensity to higher wavelength peaks is a hallmark of phenanthrene excimer formation [21–23]. We have observed enhanced self-association of the PAHs naphthalene and anthracene on ice compared to on liquid water as well [14]. These observations provide some information on the microenvironments of the PAHs. Enhanced self-association on ice compared to on liquid water suggests that PAHs are not distributed evenly over the ice surface, but rather are present in clumps: this has been observed with anthracene both when it was introduced to the ice surface from the gas phase and when it was frozen from solution [14].

Molecular dynamics simulations [24] show that PAHs at the air–water interface do not penetrate the aqueous bulk to any significant extent. They tend to adopt a flat orientation relative to the water surface, consistent with π-bonding of the PAH to the dangling OH at the air–water interface. Several experimental studies [25–27] indicate that annealed ice surfaces are less polar than water surfaces, i.e. there are fewer dangling OH at the ice surfaces. Sum frequency generation measurements show clear differences in the amount of surface disordering at air–ice and air–supercooled water interfaces at the same temperatures [28]. Raman spectra of the OH-stretch band of water acquired at air–ice and air–water interfaces in this lab [19] show higher intensity of the low energy shoulder of the OH-stretch band at 3200 cm$^{-1}$ relative to the peak at 3450 cm$^{-1}$ at the air–ice interface compared to at the air–water interface, indicating a greater extent of hydrogen bonding at the ice surface, and thus a decrease in ‘free’ OH bonds. Fewer dangling OH bonds on the ice surface could result in reduced solvation of PAHs, leading to self-association, such as we observe.

3.2. Ozonation kinetics of phenanthrene on water and ice

For the ozonation experiments, a stream of pure oxygen was introduced into the chamber containing the phenanthrene-dosed ice or water. Fluorescence at 348 nm was monitored for approximately ten minutes to ensure that the intensity was not decreasing due to fluorescence quenching or evaporation. At this time, a known concentration of ozone was introduced into the gas stream, and fluorescence intensity was monitored until the reaction was complete (i.e. when the intensity stopped decreasing).

The time-dependence data of phenanthrene’s fluorescence intensity during ozonation were fit to the function:

$$I = I_0 e^{-k_{obs}t} + c$$

where $c$ accounts for variations in the background signal level and $k_{obs}$ yields the decay rate due to the reaction. The fluorescence decay was well described by a single-exponential fit in all cases, indicating that the reaction is first order with respect to phenanthrene concentration. To check for the possible involvement of OH (from ozone photolysis, followed by O$^{(1D)}$ reaction with water vapour), phenanthrene was monitored via excitation at 266 and 293 nm in different experiments. The observed decay rates were independent of probe wavelength, indicating that insignificant quantities of OH were produced from the photolysis of O$_3$, a process which is $\sim 10\times$ more efficient at 266 nm than at 293 nm.

Plotting the observed rate constants against gas-phase ozone concentration gives the overall dependence of the reaction rate on gas-phase ozone concentration. This is shown for phenanthrene ozonation on ice and on water in figure 2. The dependence of the rate on gas-phase ozone is not linear, but shows an initial increase followed by a saturation in the observed rate at high ozone concentrations. The plots in figure 2 are consistent with a Langmuir–Hinshelwood (L–H) mechanism [29]. This mechanism describes a surface process in which one reagent, in this case ozone, is in rapid equilibrium between the gas and condensed phases, and partitions to the surface.

![Figure 1. Fluorescence spectra of phenanthrene on a liquid water surface (solid/blue trace), and on an ice surface (dashed/red trace).](image1)

![Figure 2. Pseudo-first-order phenanthrene decay rate coefficients as a function of gas-phase ozone concentration on ice surfaces at $-10\degree$C (solid blue triangles); and $-30\degree$C (open red circles). The curved traces are fits of the individual data points to equation (2). The error bars represent one standard deviation about the mean for at least three measurements. The dashed (green) horizontal trace represents the maximum ozonation rate of phenanthrene at an air–water interface at 22\degree C.](image2)
condensed phase before undergoing reaction. It takes the following form:

\[ k_{\text{obs}} = \frac{A \times [\text{O}_3(\text{g})]}{B + [\text{O}_3(\text{g})]} \]  

(2)

where \( A \) is a combination of the number of surface sites available to ozone and the second-order rate constant for the reaction, and \( B \) is a ratio of the rates of desorption and adsorption of ozone to the ice surface from the gas phase. On a solid surface, \( B \) is the inverse of the gas–surface partition coefficient. L–H type mechanisms have been observed for heterogeneous ozonation of PAHs on a number of substrates, including soot, inorganic and organic aerosols, water surfaces, and organic films [20, 30–33].

The fits to the data on ice are good, indicating that the ozonation of phenanthrene follows a L–H mechanism on this substrate. We were unable to obtain rate constants at low ozone concentrations on water due to the slow reaction rate, and so could not fit the data to a L–H mechanism. However, the maximum ozonation rate on a water surface is identical to that observed previously at an air–decanol interface. Interestingly, we have also observed similar ozonation rates for anthracene on water and organic films [20, 30].

The maximum ozonation rate measured on water and on decanol [30] was \((4 \pm 2) \times 10^{-4} \text{ s}^{-1}\), while the maximum rate on ice was an order of magnitude greater: \((7 \pm 1) \times 10^{-3} \text{ s}^{-1}\). This enhancement on ice is not strictly due to a temperature dependence, as evidenced by the identical kinetics at \(-10\) and \(-30^\circ\text{C}\), which suggest that it is the physical nature of the QLL that is altering the observed kinetics as opposed to the temperature difference between the experiments on water and on ice.

It is possible that phenanthrene surface coverage could affect the observed ozonation rates. Higher surface loading, which might be expected at lower temperatures, could alter or mask other temperature effects. Using a snow–air partitioning coefficient of \(10^{-1.03} \text{ m} \) [11], based on a linear free energy relationship [34], we can estimate an equilibrium surface coverage of \(5 \times 10^{13} \text{ molec cm}^{-2}\). This is an upper limit for the surface coverage in our experiments, as equilibrium conditions had not been reached after 15 min of deposition, at which time we still observed a linear increase in phenanthrene fluorescence at the air–ice interface. As discussed in Mnereki et al [35], this suggests that the experiments reported here were done in the unsaturated regime of phenanthrene surface coverage. On organic films [30], rates of anthracene ozonation are independent of surface coverage within a submonolayer regime. In other experiments, we have observed [36] that varying naphthalene deposition times between one and 20 min did not affect the observed ozonation kinetics at the air–ice interface. Given these observations, it seems unlikely that different surface loadings at the two temperatures on ice affected the observed kinetics to an appreciable extent.

A recent investigation of heterogeneous ozonation kinetics of fatty acid particles [37] provides the only other temperature dependence analysis for this type of reaction that we are aware of. Those authors observed a slight positive temperature dependence for the ozonation rates of three fatty acids. It is possible that a similar dependence exists on ice, but that enhanced partitioning of ozone to the ice surface at lower temperatures masks this effect. However, the values that we obtain for the \( B \) parameter of the L–H mechanism argue against this: we measure values of \((7 \pm 5) \times 10^{15} \text{ molec cm}^{-3}\) and \((8 \pm 6) \times 10^{15} \text{ molec cm}^{-3}\) at \(-10^\circ\text{C}\) and \(-30^\circ\text{C}\) respectively.

If enhanced ozone partitioning at lower temperatures is responsible for the large rate constants we observe on ice, we would expect to see a lower value for the \( B \) parameter at lower temperatures. It is also worth noting that the \( B \) parameter extracted from fits of the ozonation kinetics of all PAHs we have studied on water, octanol, and decanol surfaces is approximately \(2.1 \times 10^{15} \text{ molec cm}^{-3}\) [20, 30]; this indicates that ozone partitions more effectively to room temperature liquid surfaces than it does to ice, despite the temperature difference.

The results of the present investigation have implications on our understanding of the physical nature of the QLL. Although reports of QLL depth vary greatly [38–41], it is generally agreed that a gradient in its depth exists over our experimental temperature range (\(-30\) to \(-10^\circ\text{C}\)) [38, 39, 41]. While we can not comment directly on the depth of the QLL based on our results, we can make some inferences regarding the environment of the QLL based on our kinetics data.

The first conclusion we can draw is that the environment presented by the QLL affects phenanthrene’s reactivity toward ozone differently than does a liquid water surface. Kinetic data for heterogeneous ozonation of PAHs on ice, as well as for direct and indirect photolysis of PAHs on ice [14], likely should not be extrapolated from kinetic data in aqueous solutions or at air–aqueous interfaces.

The lack of temperature dependence for the reaction kinetics on ice also provides us with information regarding the QLL. Specifically, we can conclude that changes in the depth of the QLL between \(-30\) and \(-10^\circ\text{C}\) do not affect phenanthrene’s reactivity toward ozone. This could mean that at both temperatures the QLL is sufficiently deep to be the only medium in contact with phenanthrene (i.e. the phenanthrene is not in contact with bulk ice); or it could mean that it is the underlying ice substrate, rather than the QLL, that affects phenanthrene’s ozonation kinetics. It is also possible that changes in the depth of the QLL are negligibly small in this temperature range. Extending these experiments to lower temperatures might help to determine what is responsible for the identical ozonation kinetics within this temperature range, but with the present results we can conclude that at temperatures relevant to the Earth’s surface, changes in temperature will likely not affect the rate of phenanthrene ozonation on ice.

Our kinetic results also yield information about ozone’s interaction with the QLL. As discussed above, ozone partitions more effectively to room temperature water than to ice. This is further evidence that the environment of the QLL is different from that of liquid water: otherwise, enhanced partitioning of ozone to the surface should be observed at lower temperatures.

4. Atmospheric implications

In the gas phase, reaction with hydroxyl radicals is the dominant loss process for PAHs: homogeneous reactions with
other oxidizing gases, including ozone, are extremely slow [4]. A number of studies have shown that heterogeneous reactions of PAHs with oxidizing gases, and especially ozone, can occur much more quickly than the corresponding gas-phase reactions [6, 20, 30–33]. The substrate to which the PAH is partitioned has been shown to affect the observed kinetics; a review of some of these results is presented in Kwamena et al [6]. A large portion of the northern hemisphere experiences ice coverage for at least part of the year; ozonation of PAHs partitioned to this ice could be important to their fate.

Kwok et al [42] report a homogeneous ozonation rate for phenanthrene of \(4 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}\). This translates to an atmospheric lifetime of approximately 22 days, given an ozone mixing ratio of 50 ppb \((1.3 \times 10^{12} \text{ molec cm}^{-3})\). On the surface of water, we estimate an atmospheric lifetime of approximately 44 days. On ice, the atmospheric lifetime decreases to just under five days. This is not too different from the lifetime of gas-phase phenanthrene with hydroxyl radicals of just over one day as reported [42] for a daytime average OH concentration of \(1.6 \times 10^6 \text{ molec cm}^{-3}\). Based on an air–snow partitioning coefficient of \(10^{-1.03} \text{ m at } -6.8 \degree \text{C} [11]\), we calculate that roughly 10% of phenanthrene will be partitioned to snow and ice at that temperature. Depending on phenanthrene’s desorption rate from snow and ice, it is possible that heterogeneous ozonation on these media could account for a measurable fraction of phenanthrene’s loss during the winter, and that snow and ice could be chemical as well as physical sinks for phenanthrene.

Recently, Kwamena et al [5] investigated the fates of a suite of PAHs in urban environments using a multicompartamental box model. The loss processes investigated included advection, gas-phase oxidation by OH, and heterogeneous ozonation on aerosols and urban grime. Heterogeneous ozonation on urban grime proved to be an important chemical sink for larger PAHs such as pyrene and benzo[α]pyrene, which partition much more efficiently to the condensed phase than does phenanthrene. If these PAHs display similar ozonation rate enhancements on ice compared to on organic films as does phenanthrene, heterogeneous ozonation on ice would be an extremely important removal process for these compounds during urban winters.

Although the implications of rapid heterogeneous ozonation of PAHs on ice are significant in their own right, it should be remembered that ice can act as a substrate for other reactions as well. We have previously observed rapid photooxidation rates for PAHs on ice [14], and other oxidation processes including nitration could play important roles in the removal of PAHs from this medium. This research emphasizes the importance of ice as a reaction substrate, not only in remote polar environments, but also in snow-covered urban environments.

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