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Detecting intermediates and products of fast heterogeneous reactions on liquid surfaces via online mass spectrometry

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ABSTRACT

One of the research priorities in atmospheric chemistry is to advance our understanding of heterogeneous reactions and their effect on the composition of the troposphere. Chemistry on aqueous surfaces is particularly important in this regard because of their ubiquity and expanse. They range from the surfaces of oceans (360 million km^2), cloud and aerosol drops (~ 10 trillion km^2) to the fluids lining the human lung (~ 200 m^2). Typically, ambient air contains reactive gases that may affect human health, influence climate and participate in biogeochemical cycles. Despite their importance, reactions between gases and solutes at air-aqueous interfaces are not well understood. New, surface-specific techniques are required that detect and identify the intermediates and products of such reactions as they happen on liquids. This is a tall order because genuine interfacial reactions are faster than mass diffusion into bulk liquids, and may produce novel species at low concentrations. Herein, we review evidence that validates online pneumatic ionization mass spectrometry of liquid microjets dosed by reactive gases as a technique meeting such requirements. Next, we call attention to results obtained by this approach on reactions of ozone, nitrogen dioxide and hydroxyl radicals with various solutes on aqueous surfaces. The overarching conclusion is that the outermost layers of aqueous solutions are unique media, where equilibria shift and reactions proceed faster than, in some cases along different pathways from the bulk liquids. The fact that the rates and mechanisms of reactions at air-aqueous interfaces may not be deduced from experiments in bulk liquids opens new conceptual frameworks and lines of research, and adds an overlooked dimension to atmospheric chemistry.

KEYWORDS - fast gas-liquid reactions; online electrospray ionization mass spectrometry; heterogeneous atmospheric chemistry.

1. INTRODUCTION

A recent expert report delineated the research priorities in atmospheric chemistry. It called for “developing a stronger understanding of the influences that heterogeneous chemistry exerts on tropospheric composition”, “developing the next generation of accurate, sensitive and specific measurement capabilities for atmospheric constituents… on surfaces”, and “identifying and quantifying the individual oxidants in the condensed phase that contribute to toxicity”.[1] Together, these issues point to surfaces as significant media in atmospheric chemistry.

“God made the bulk. Surfaces were invented by the devil”, Wolfgang Pauli famously said. If only because even defining what a surface is raises thorny questions: how thick is the layer of atoms or molecules that can be considered the surface of an object, i.e., where do surfaces end and the bulk begin. Or, what is more relevant to the topic at hand, how do air-liquid interfaces behave when probed from the liquid or the airside? These are fundamental questions, to which experimental and theoretical studies have provided perspectives as varied and conflicting as those of the six blind men about the elephant.[2]

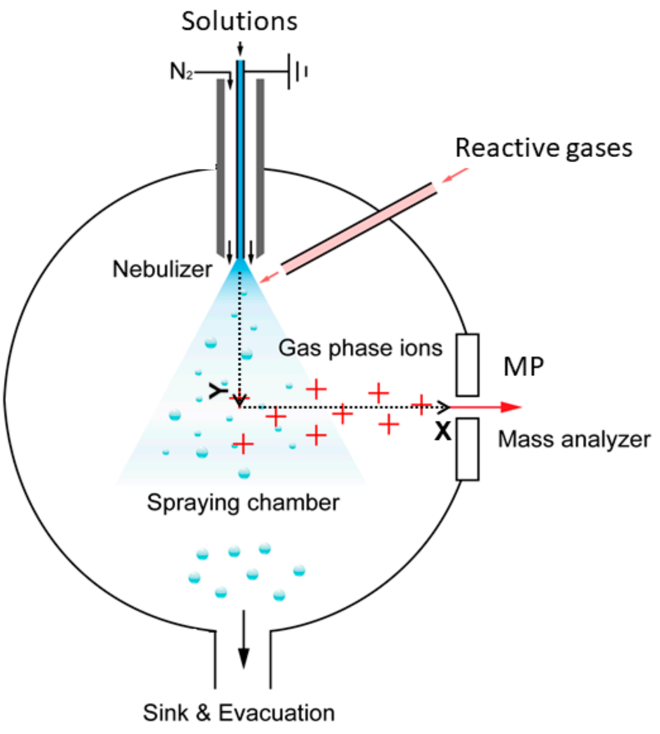
The surface of water is prominent in this regard because it is everywhere. The interfacial layers of water represent a distinct phase where the density of water drops five orders of magnitude (from 1 g cm^{-3} to 1.7×10^{-5} g cm^{-3} at 300 K over pure water) in less than 1 nm. This precipitous density gradient at the molecular scale represents a steep slide where species nevertheless find standing points according to their properties. Hydrophobic gases, such as hydrocarbons, will tend to accumulate at the relatively dry interface rather than immerse in bulk water,[3-4] while ions will do the opposite. Reactive gases could be depleted so fast by aqueous solutes in interfacial layers that they would not reach bulk water. These are issues for which one would like to make educated guesses. One might ask whether the vast information available on the structure of interfacial water, obtained by surface-specific spectroscopies and molecular dynamics calculations, could provide useful hints about interfacial chemistry. An obvious caveat is that the temporal and spatial scales of the interfacial structures revealed by the various spectroscopies might not match those of interfacial reactions. In this context, it is fair to say that the relative sparsity of dynamic vs structural studies[5-6] is not on par with the importance of interfacial processes. For this reason, we wanted to call attention to our experiments on interfacial chemistry, and some of the results we obtained. Because these experiments have not been performed before, and many results were unprecedented, we considered that we had to explain what we did, how we did it, and what we found.

The plan of the paper is to validate online pneumatic ionization mass spectrometry (o-PI-MS, a variant of electrospray ionization mass spectrometry, see below) of liquid microjets dosed by reactive gases as a versatile technique to investigate interfacial processes, and to review atmospherically relevant results obtained by this approach. Validation was considered necessary because it might not be readily apparent that o-PI-MS could be applied to study interfacial reactions.[5, 7] The main reason is that transferring ions from liquids to the gas-phase is a complex phenomenon. In contrast with the monochromatic signals and selection rules of surface-specific spectroscopies, one faces a sequence of events that begins with the nebulization of liquids into microscopic droplets carrying net charges, followed by rapid solvent evaporation, a sequence of Coulomb explosions, and the ultimate release of solvated ions to the gas-phase.

Questions arise about whether o-PI mass spectra can be assigned to the products of gas-liquid reactions occurring in the outermost interfacial layers of liquid microjets. Are the detected species drawn from the interfacial layers or the bulk of liquid microjets? Do the electric fields required for detection affect the chemistry? Below we analyze experiments specifically designed to address these questions. We want to point out that our approach to studying interfacial processes via o-PI-MS is neither a new idea nor as farfetched as it might seem. Yamashita and Fenn had already suggested that electrospray ionization mass spectrometry could be used to investigate liquid interfaces in their seminal 1984 paper,[8].

2. OUR EXPERIMENTS

Because our experimental platform has been described in several publications from our laboratories, here we focus on its essential features. It should be emphasized that electrospray ionization mass spectrometers are not all alike. Key differences are whether the nebulizer is grounded or not, and whether the liquid microjets are directly ejected (along the x-axis) (see Scheme 1) towards the entrance orifice of the metal plate (MP) separating the spraying chamber from the low pressure section of the mass spectrometer, along a perpendicular (y-axis) direction, or in a Z-configuration.[9] Comparisons among results obtained in different instruments should bear in mind these issues.



SCHEME 1

The essentials of our experimental setup. MP is a metal plate polarized at high voltage (relative to the grounded nebulizer) that has a pinhole inlet to the mass analyzer section of the mass spectrometer (not shown).

In our experiments, solutions of diverse solutes in water or its mixtures with fully miscible organic solvents such as acetonitrile, tetrahydrofuran or 1-4 dioxane, are pumped through a grounded stainless steel syringe injector (100 µm bore). They emerge as ~ 10 cm s^{-1} microjets into the spraying chamber of the mass spectrometer (kept at 1 atmosphere and room temperature). The microjets are swept forward by much faster N_2(g) flows (> 100 m s^{-1} through an outer sheath coaxial with the syringe injector, which results in their nebulization into charged microdroplets (~ 10 micrometer diameter)[10-11] within ~ 10 microseconds.[12-15] In this process, the kinetic energy of the nebulizing gas provides energy for creating the surfaces of microdroplets, and for charging microdroplets by separating the anions and cations present in the microjets. Nebulization is the single event that generates the net charges ultimately detected by the mass spectrometer. Note that Coulomb explosions of charged microdroplets pull apart charges of the same sign, rather than generating additional net charge.

That the droplets of mists produced by nebulizing liquids are charged was known for more than a century,[12-13] and has important applications.[16] This charging process does not require,[17-18] although it may be enhanced, by the presence of an electric field. Below we show that in our setup the creation of net charge is mainly due to pneumatic nebulization rather than to the applied electric field. This is the reason why we refer to our technique as online pneumatic ionization mass spectrometry o-PI-MS.

Because the surface of microjets consisting of aqueous electrolyte solutions is equipotential with the grounded injector, the electric field inside the microjets is null. Electric fields, however, induce surface charges of densities determined by MP voltage and the local curvature of the liquid surface. The sign of surface charges is determined by the voltage polarization, i.e., a MP at positive voltage relative to ground induces negative charges on the surface of microjets, and vice versa. Below, we show that the surface charges induced by the applied electric play a minimal role, if any, in our experiments.

In a typical experiment, streams of reactive gases, such as O_3(g) or NO_2(g), are directed to the liquid microjets as they emerge from the nebulizer. Some reactions between gases and solutes at the air-liquid interface are so fast that they proceed within the ~ 10 μs lifetimes of intact microjets.[14] It is apparent that only very fast heterogeneous reactions meet such constraint. A host of results from our laboratories revealed that the mass spectra reflected the composition of the outermost interfacial layers of the liquid microjets. The observed products and intermediates were produced on the surface of the intact liquid microjets, rather than on the daughter microdroplets or in the gas-phase. The applied electric fields needed to deflect the charged microdroplets toward the MP did not appreciably affect the chemistry. We drew these conclusions from mapping the response of mass spectra to experimental parameters rather than from a priori arguments, which we consider could not capture the complexity of the process.

3. MASS SPECTRA REFLECT THE COMPOSITION OF THE OUTERMOST INTERFACIAL LAYERS OF THE LIQUID MICROJETS

The first indication that we sampled interfacial layers was provided by the mass spectra of equimolar solutions of the sodium salts of various anions.[19-20] We found that anion signal intensities were not identical, as expected from the equimolar concentrations of the pre-existing anions in bulk solutions, but scaled exponentially with anion radii. This outcome suggested that anions fractionate to interfacial layers according to a Hofmeister series.[21] We obtained more compelling evidence from various experiments. We illustrate with two examples.

In one set of experiments, liquid microjets of hexanoic acid (PCOOH, $pK_a = 4.8$) solutions in 1:1 (vol:vol) H_2O/D_2O at pH 7 (reported pH is always of the bulk solutions to be injected, as measured with a calibrated pH-meter. pD = pH + 0.4) were dosed with $HNO_3(g)$ or $DNO_3(g)$ streams.[22] Mass spectra in the negative mode revealed that hexanoate signals (m/z = 115) decreased and nitrate signals (m/z = 62) increased upon increasing $HNO_3(g)$ and $DNO_3(g)$ flow rates, as expected from the acidification of the media from where these signals originated. In the same experiments, mass spectra in the positive mode revealed the presence of hydronated (by H^+ or D^+) hexanoic acid $PCOOH_2^+$ (m/z = 117), $PCOOHD^+$ (m/z = 118) and $PCOOD_2^+$ (m/z = 119).[23] The key observation was that the relative intensities of the hydronated PCOOH signals significantly changed upon switching from $HNO_3(g)$ to $DNO_3(g)$. From the flow rates of the liquid microjets and the gas streams, we estimated that the number of H/D atoms injected per second in the spraying chamber by the liquid microjets was > 1000 times larger than those carried by $HNO_3(g)$ or $DNO_3(g)$. The finding that the isotopic composition of the hydronated PCOOH signals changed upon switching from $HNO_3(g)$ to $DNO_3(g)$ therefore implied that the hydronation of PCOOH took place in thin interfacial layers (< 1 nm estimated thickness) rather than in the bulk liquid. We realized that the dependence of mass spectral signals on pH along sharp titration curves also reveals that the interfacial layers have well-defined H^+/D^+ concentrations (which may not be necessarily identical with H^+/D^+ bulk concentrations) rather than the random concentrations expected to develop in evaporating microdroplets.

A second piece of evidence was obtained in the competitive protonation vs lithiation of gas-phase trimethylamine TMA(g) on the surface of aqueous microjets containing 100 mM LiCl at various pH values.[24] Plots of the intensities of $TMAH^+$ (m/z = 60) and $TMALi^+$ (m/z = 66) signals as functions of TMA(g) concentration showed that $TMAH^+$ signals plateaued above a few parts per million by volume (ppmv) TMA(g) both at pH 2.0 and 3.5, while $TMALi^+$ kept increasing up to 150 ppmv TMA(g). These titration experiments reveal that the pool of protons available to TMA(g) was finite. That could happen only if such protons were those initially present in interfacial layers (rather than in the much larger pool provided by the bulk liquid), and the self-ionization of water were too slow to replenish with protons the interfacial layers within ~10 μs. In another set of experiments, acidified D_2O microjets were simultaneously exposed to TMA(g) and $H_2O(g)$. The detection of $TMAD^+$ and $TMAH^+$ signals of comparable intensities, despite the fact that the inflow of H_2O was < D_2O/1000, confirmed that TMA(g) was hydronated in nanoscopic interfacial layers.

4. PRODUCTS OF GAS-LIQUID REACTIONS ARE FORMED ON LIQUID MICROJETS RATHER THAN ON DAUGHTER MICRODROPLETS

One can envision a reaction chamber filled with a reactive gas and a mist of microdroplets. One can also think that reactions could take place indiscriminately on all gas-liquid interfaces, both of the liquid microjets and of the microdroplets mists that, after all, have much larger surface areas. Two considerations should caution us about rushing to such conclusion. The first one is that the concentrations of reactant gases carried by the gas streams are highest at the point where they intersect the liquid microjets at the tip of the nebulizer (Scheme 1). The second one is that charged microdroplets are accelerated in the electric field with accelerations that scale with their charge-to-mass ratio (see below). Since the masses of the microdroplets continuously decrease by solvent evaporation while their charges do not, microdroplets are doubly accelerated, i.e., they have very short lifetimes in the spraying chamber. Therefore, microdroplets are in contact with very dilute reactant gases for very short times.

The experiments that provided direct evidence supporting the title statement involved the ozonolysis of β-caryophyllene (a very reactive sesquiterpene that adds O_3(g) within ~ 10 μs) in two different configurations. In the first, one microjets of 1 mM β-caryophyllene solutions in acetonitrile/water mixtures containing 1 mM NaCl (to bind the neutral α-hydroxyhydroperoxide products into detectable chloride adducts)[25] were injected at 100 μL min^{-1} (which corresponds to the injection of 1×10^9 β-caryophyllene molecules s^{-1} into the spraying chamber) and dosed on and off by O_3(g) streams. Intense mass spectral signals of functional carboxylates (FC, m/z = 251) and chloride adducts of the α-hydroxyhydroperoxides (HH, m/z = 305 and 307), the products of reactions of the Criegee intermediates generated in the ozonolysis of β-caryophyllene, appeared upon exposure to O_3(g). In the second set of experiments, microjets of 1 mM NaCl in acetonitrile/water solutions (i.e., without β-caryophyllene) were injected into the spraying chamber simultaneously with O_3(g) and β-caryophyllene vapor (at 4×10^{15} β-caryophyllene molecules s^{-1}). Although the flow of β-caryophyllene molecules injected into the spraying chamber in this case was much larger than in the first set of experiments, product signals remained within background noise (Figure S2, Reference 26).[26] We inferred that most if not all of the FC and HH products we observed were produced on the surface of intact liquid microjets rather than on microdroplets or in the gas-phase. Similar experiments on the protonation of isoprene on acidic water, in which we tested the effect on product signals of the relative distance between the isoprene gas streams and the tip of the nebulizer, led to the same conclusion.[27]

5. APPLIED ELECTRIC FIELDS DEFLECT CHARGED MICRODROPLETS BUT DO NOT AFFECT INTERFACIAL CHEMISTRY

Initial evidence of the role of electric fields came from experiments involving the protonation of gas-phase trimethylamine TMA(g)[24] and the deprotonation of gas-phase carboxylic acids CA(g) (such as acetic and hexanoic acids)[28] on the surface of water as a function of bulk pH. In the CA experiments,[28] we detected carboxylate anions by polarizing the metal plate MP at positive voltages. In this case, electrostatics dictates that the electric field induces negative surface charge density on the microjets, i.e., an overpopulation of interfacial hydroxide ions.[29-30] Therefore, CA(g) should be deprotonated on the surface of water at pH values lower than in bulk water. This prediction was apparently correct: 50% of CA(g) were deprotonated on the surface of pH = 2.8 water, i.e., two pH units lower than their pK_a = 4.8 in bulk water.[28] The same logic would predict that gas-phase TMA should be protonated on the surface of water of pH values higher than its pK_a = 9.8 in bulk water. However, at variance with the prediction, we found that TMA(g) was protonated only on the surface of pH < 4 water![24] It is apparent that the shifts of the titration curves of *both* gas-phase acids and bases on the surface of water towards pH values lower than in bulk water are not due to the surface charges induced by the applied electric fields, but to an unrelated phenomenon. The fact that both gas-phase bases and acids are protonated and deprotonated on the surface of water of pH ~ 3 ± 1 suggests that the underlying mechanism is associated with the properties of interfacial water itself, as we and others have proposed elsewhere.[31-32]

More direct evidence was obtained from the dependence of the FC and HH (see entry 4, above) products signal intensities in the ozonolysis of β-caryophyllene as functions of the applied polarizing voltage.[26] It was found that both signal intensities strictly increased (with a correlation coefficient $\rho^2 = 0.99$) with the square root of the polarizing voltage $V^{½}$ (see Figure S3 of Reference 26).[26] We inferred the signature of a purely kinematic effect on the trajectories of charged microdroplets in the spraying chamber, rather than electric field effects on chemistry.

This is borne out by the following considerations. In our setup, microdroplets are carried forward (along the y-axis, Scheme 1) by the nebulizer gas at > 100 m/s. At these speeds, microdroplets cover the 2 cm separating the tip of the nebulizer from the x-axis pinhole in τ <

0.250 milliseconds. In order to capture charged microdroplets, and ultimately detect the ions they carry, an electric field must be applied to deflect microdroplets along to the x-axis towards the MP. The instantaneous acceleration *a* imposed on the microdroplets by the electric field along the x-axis is given by equation SE1:

$$a = \left(\frac{ne^-}{m}\right) \frac{V}{d} \tag{SE1}$$

where ne^- is the charge and *m* the mass of microdroplets, V is the potential difference between the tip of the grounded nebulizer and MP, and *d* the distance between the tip of the nebulizer and MP. As noted above, the mass of microdroplets is not constant due to continuous solvent evaporation. The net charge of microdroplets, in contrast, only changes in the Coulomb explosions undergone by microdroplets upon reaching Rayleigh's thresholds.[33] It is apparent that the applied voltages V must be such that the Δx = 1 cm distance between the y-axis and the MP is covered by the accelerated microdroplets in $t \leq \tau$ times, equation SE2:

$$\Delta x = ½ \left(\frac{ne^-}{m}\right) \frac{V}{d}\, t^2 \tag{SE2}$$

i.e., $t \propto V^{-1/2}$. Thus, the shorter the flight times *t* the larger number of microdroplets deflected towards the polarized MP, i.e., mass spectral signal intensities should increase as $(1/t) \propto V^{1/2}$, as observed. We ascribe the stronger $V^{1/2}$ dependence of the HH signals relative to FC signals (see Figure S3 in Reference 26) to the fact that the neutral α-hydroxyhydroperoxides will only bind to Cl^- after microdroplets are desolvated in the mass analyzer section and, therefore, will evaporate in the spraying chamber. Hence, evaporation losses of neutral α-hydroxyhydroperoxides will be minimized at shorter the flight times *t*. The net result is that larger amounts of α-hydroxyhydroperoxides will be detected (as Cl^- adducts) at shorter *t* times, an effect that follows the same $V^{1/2}$ dependence and combines with that of the kinematics of microdroplets deflection. This analysis also shows that mass spectra preferentially reflect the composition of the lighter, more easily deflected microdroplets sheared from the outermost interfacial layers of the microdroplets. The larger inertia of the heavier microdroplets generated from the core of the microjets carries them forward to the bottom of the spraying chamber, and escape detection. Summing up: in the configuration of our setup, an electric field must be applied to deflect the charged microdroplets towards the MP. The surface charges induced by these electric fields have a negligible effect on chemistry under our experimental conditions.

6. INSIGHTS GAINED FROM OUR EXPERIMENTS

Among the various issues we touched during the last decade, we chose three cases to illustrate how our studies led to unexpected perspectives on important atmospheric processes. We demonstrated that I^- catalyzes the oxidation of Br^- by $O_3(g)$ on the surface of marine aerosols, and pointed out that this process should be a significant source of the pool of photoactive bromine underlying the so called "bromine explosion" in the Arctic boundary layer in early spring.[34-35] We found that the hydrolytic disproportionation of $NO_2(g)$ on aqueous surfaces is catalyzed by anions, and suggested that this process represents the daytime "unknown source of nitrous acid" in urban air. We showed that it also explains the nearly constant values ($\tau_D = 4 \pm 1$ h) of the decay lifetimes of $NO_2(g)$ in the urban plumes sighted by satellites over several megacities.[36-37] Other experiments showed that the oxidation of glutathione, the main antioxidant in the lining fluids of human lungs, by ozone and OH-radicals produces sulfenic and sulfinic acids via an unprecedented, highly selective process.

7. IODIDE CATALYZES OZONE OXIDATIONS IN MARINE AEROSOLS[38]

A few bromine atoms per trillion trigger the fast destruction of ozone in the polar boundary layer in early spring. This phenomenon implies the pre-existence of a significant pool (≥ 10 pptv) of Br-containing gas-phase species that can be rapidly photolyzed into Br-atoms by sunlight (photo-Br). It is apparent that photo-Br must be produced from seawater Br^-, the sole source of bromine in remote regions, by a dark process during polar winters. The goal of our study was to elucidate the mechanism of the thermal oxidation of marine Br^- into photo-Br. The standing hypothesis at the time of our study was that photo-Br was the end product of the short wavelength photolysis of long-lived Br-containing gases, such as biogenic methyl bromide of marine origin and anthropogenic halons. Models based on such assumption, however, significantly underpredicted field measurements of proxy BrO radicals.[39]

Fine marine aerosol drops, which are known to be highly enriched in Br^- and I^- relative to seawater,[40] and remain suspended long enough to undergo significant chemical processing, are ideal vehicles for Br^- activation. We reasoned that the thermal, dark oxidizer had to be pervasive, persistent $O_3(g)$. The direct oxidation of $Br^-(aq)$ by $O_3(g)$, however, is a relatively slow reaction: $k(Br^- + O_3) = 248\ M^{-1}\ s^{-1}$, in bulk water. A significant clue was that more $Br_2(g)$ is emitted from sea salt than from pure NaBr upon exposure to $O_3(g)$. It seemed that the oxidation of Br^- by $O_3(g)$ was catalyzed by unidentified components of sea salt.[41]

We addressed this puzzle by performing experiments in which we exposed microjets of micromolar NaI, NaBr or NaI+NaBr solutions in water to $O_3(g)$. In the first case, we readily detected the formation of iodate IO_3^- (m/z = 175) and triiodide I_3^- (m/z = 381), as expected, in proportions that depended on solute and gas reactants concentrations. NaBr solutions under the same conditions did not produce new mass spectral signals, in accordance with the inertness of $Br^-(aq)$ towards $O_3(g)$. The ozonation of mixed (NaI + NaBr) solutions, however, led to mass spectra displaying strong signals at m/z = 285 ($I^{79}Br^{79}Br^-$), 287 ($I^{79}Br^{81}Br^-$) and 289 ($I^{81}Br^{81}Br^-$). The presence of two bromines in these trihalide anions meant that at least one of them had to be a Br^0 atom, i.e., that $O_3(g)$ rapidly oxidizes Br^- in the presence of I^- at the air-water interface. We inferred that the (I^- + O_3) reaction generates an intermediate that oxidizes Br^- faster than O_3 itself. We hypothesized that the intermediate could be hypoiodous acid HOI from an O-atom transfer to I^-, or the trioxide I-OOO$^-$. Unpublished results from experiments in our laboratory subsequently revealed that the latter was the case. A related surface-specific Br-OOO$^-$ intermediate was recently identified by X-ray photoelectron spectroscopy.[42]

A key observation was that the reactions that took place on the surface of liquid microjets were much faster than expected from the rate constant $k(I^-+O_3) = 1.2 \times 10^9\ M^{-1}\ s^{-1}$ in bulk water, and the $O_3(aq)$ concentration in equilibrium with the $O_3(g)$ number densities used in our experiments. The acceleration of interfacial relative to reactions in the bulk liquids has proved to be a general phenomenon.[43] it should be emphasized that I^- will always outcompete Br^- for $O_3(g)$ in marine aerosols because although I^- is present at concentrations $\sim 10^{-3}$ times smaller than Br^-, it reacts 10^7 times faster. In short, our experiments revealed that I^- is the “unidentified component of sea salt” that catalyzes the oxidation of Br^- by $O_3(g)$ on sea salt and marine aerosol drops. On this basis, we suggested that the iodide-catalyzed oxidation of Br^- by $O_3(g)$ on the surface of marine aerosols naturally enriched in Br^- and I^- is a major source of photo-Br in the Arctic boundary layer during the polar night.

8. THE DISPROPORTIONATION OF NITROGEN DIOXIDE ON AQUEOUS AEROSOLS CATALYZED BY ANIONS IS THE "UNKNOWN SOURCE OF NITROUS ACID"[36, 44-46]

Modeling the production of the secondary organic aerosol (SOA) has become a major endeavor in tropospheric chemistry. This goal is approached via 3D transport models that include gas/vapor emission strengths, gas-phase chemistry and aerosol microphysics. An implicit assumption common to most studies is that aerosols are a chemical dead end, i.e., that once formed they cease to participate in tropospheric chemical cycles. Since "the key to understanding tropospheric chemistry begins with the OH radical",[47] a critical test for any model is how well it reproduces OH-radical concentrations under diverse conditions. Suggestively, the most important deficiencies of current models is their failure to simulating how OH-radical concentrations respond to actinic flux and NOx level variations, and to systematically under-predicting nitrous acid (HONO) concentrations. Since the rapid $\lambda \leq 395$ nm photolysis of HONO produces OH-radicals with unitary quantum efficiency, R1:

$$HONO + h\nu = NO + \cdot OH \qquad (R1)$$

the noted deficiencies point to a mechanistic feature that couples OH-radical and HONO chemistries. What is apparently missing is a strong, yet unidentified, heterogeneous reaction that produces HONO from primary $NO_2(g)$ at significant rates. This is the problem generally described as the "unknown source of HONO".[48-49] The consensus is that the mechanism of the "unknown source of HONO" will be revealed by additional field measurements performed with improved instrumentation.[49]

The standard view is that the "unknown source of HONO" cannot be the reaction that would produce HONO from $NO_2(g)$ on aqueous surfaces, such as SOA surfaces in humid air, R2:

$$2\ NO_2 + H_2O = HONO + NO_3^- + H^+ \qquad (R2)$$

because the uptake coefficient $NO_2(g)$ on pure water is very small: $\gamma(NO_2)_w < 1 \times 10^{-7}$.[50] Not only $NO_2(g)$ is relatively insoluble in pure water (Henry's law constant = 0.01 M atm^{-1}), but it dissolution is very slow. This argument overlooks that aqueous aerosols are not pure water but a mixture of organic and inorganic electrolytes. Defying expectations and prevailing assumptions, we found that the uptake coefficient of $NO_2(g)$ on the surface of aqueous electrolyte microjets, $\gamma(NO_2)_e = 10^{-3} - 10^{-4}$, is orders of magnitude larger than $\gamma(NO_2)_w$. The underlying process is genuinely interfacial, because $\gamma(NO_2)_e$ is significantly enhanced by cationic surfactants, weakly depressed by anionic surfactants, and unaffected by hydrophobic 1-octanol.[44-46, 51-52] Significantly, our results are consistent with the $\gamma(NO_2)_e \sim 10^{-4}$ values measured on ~3 mM NaCl droplets in a cloud chamber,[53-54] a finding that remained unexplained vis-à-vis the $\gamma(NO_2)_w < 1 \times 10^{-7}$ value previously measured on pure water, and consequently ignored by the atmospheric chemistry community. In short, in the presence of dense aerosols, such as those that develop in urban smog at noon, reaction R2 can become competitive with the photolysis of $NO_2(g)$, R3:

$$NO_2 + h\nu = NO + O(^3P) \qquad \text{(R3)}$$

thereby switching the source of OH-radicals from the photolysis of O_3 (produced from the $O(^3P)$ atoms generated in R3) to the more direct and faster photolysis of HONO via R1.

We have shown that our proposal rationalizes the trends of $NO_2(g)$, HONO(g) and OH-radical concentrations as functions of the $J(NO_2)$ and J(HONO) actinic fluxes determined in a comprehensive field study.[55] An important corollary is that the existence of alternative photochemical sources of OH-radicals, i.e., the photolyses of HONO and O_3 at relative rates determined by the competition between R2 and R3 as a function of aerosol surface density, will buffer OH-radical concentrations.[36] Our proposal also provides an explanation for the constant value ($\tau_D = 4 \pm 1$ h) of the decay lifetimes of $NO_2(g)$ in urban plumes retrieved from satellite sightings of megacities ranging from Singapore to Moscow at all seasons.[36-37] This finding is extraordinary because it challenges the textbook assumption that the decay of $NO_2(g)$ into photochemically inert $HNO_3(g)$ is controlled by OH-radical concentrations via R4,

$$NO_2 + \cdot OH\ (+ M) = HNO_3\ (+ M) \qquad \text{(R4)}$$

Since OH-radical concentrations “follow the sun”,[56] i.e., they roughly scale with solar irradiance, the expectation was that $\tau_D = (k_4\ [OH])^{-1}$ should significantly increase in winter and at high latitudes. From the perspective afforded by our experiments, a relatively constant τ_D value is consistent with a combination of alternative $NO_2(g)$ decay processes. $NO_2(g)$ will decay in part into NO_3^- via R2, whose rate depends on aerosol surface area density, or into $HNO_3(g)$ via R4, whose rate depends on OH-radical concentrations buffered by R2 (+ R1).

Summing up: our experiments showed that the surfaces of aqueous aerosols might be the substrates of unanticipated processes in tropospheric chemistry. Also, that in all probability, R2 is the “unknown source of HONO”. It is interesting to consider whether the “unknown source of HONO” could have been ascertained by field campaigns, model parametrizations or theoretical calculations.

9. CHEMISTRY ON THE SURFACE OF THE HUMAN LUNG IS UNUSUALLY SELECTIVE

The causality of the adverse effects of air pollution on human health is yet to be established. Numerous epidemiological studies have consistently noticed positive correlations of cardiovascular (CV) and all-cause (AC) premature mortalities with O_3 and $PM_{2.5}$ (particulates of < 2.5 micrometer diameter) levels in ambient air.[57] A recent statistical analysis of the most extensive air pollution data and age-specific CV and AC premature mortality rates for 483 counties in 15 US states from 2000 to 2010 indeed confirmed the positive associations reported by previous studies.[58] However, the same study revealed that the ~30% decreases of $PM_{2.5}$ and O_3 levels achieved in that period, thanks to the implementation of more stringent emission controls, did not translate into statistically significant changes in premature mortality rates. This is an important finding that begets the question of how stringent future regulations on air quality should be in order to achieve tangible improvements. It is apparent that socially optimal levels of control, i.e., which balance marginal benefits versus the marginal costs of abatement, cannot be designed solely based on epidemiological data alone, but require information on the detailed chemical and biological mechanisms of the adverse health effects induced by specific air pollutants.

Inhaled oxidants, such as $O_3(g)$ and $NO_2(g)$, do not reach the lung tissue, as it is generally assumed, because they are scavenged by antioxidants contained in the epithelial fluids (ELFs) lining the respiratory tract. Evidence that adverse health effects do not involve local injury to the lung tissue is that inhalation of oxidant pollutants impairs the functions of both heart and lungs within hours. Mortality from acute cardiovascular syndromes markedly increase *during* high O_3 and $PM_{2.5}$ episodes. This phenomenon strongly suggests a rapid, systemic response of the innate immune system to oxidative insult.

The major antioxidant in ELFs is reduced glutathione (GSH, 100−500 μM), an endogenous tripeptide (γ-L-glutamyl-L-cysteinyl-glycine) with a –SH thiol group. The main function of GSH was deemed to scavenge exogenous oxidants into innocuous "ox-GSH" species. The current notion, however, is that GSH not only deactivates oxidants, but the [GSH]/["ox-GSH"] ratios generated in ELFs relay the intensity of oxidative stress to the immune system, thereby unleashing systemic responses. In this connection, a tantalizing possibility is that a nonspecific systemic immune response would be expected if all inhaled oxidants converted GSH to common "ox-GSH" species. Given the exquisite selectivity of the immune system the issue is, of course, the identity of "ox-GSH" species. It was long assumed that "ox-GSH" was the disulfide GSSG that would be produced from the recombination of the thiyl GS·− radicals ensuing H-abstraction from S−H by OH-radicals.

Reduced glutathione GSH is a diacid that can exist as a mono- or di-anion, depending on the pH. We found that at physiological pH ~ 7.5, O_3(g) rapidly oxidizes the dianion GS^{2-}(aq) (but not the monoanion GS^-) to a sulfonate GSO_3^- rather than to GSSG.[59] Under the same conditions, the oxidation of cysteine (Cys), the S-containing residue in GSH, by O_3(g) at the air−water interface yields Cys-sulfenic, Cys-sulfinic, and Cys-sulfonic acids rather than CySSCy.[60] In more recent experiments, we found that the monoanion GS^-(aq) is oxidized by OH-radicals even in pH ≤ 5 media to a sulfenic acid GSOH (a weak acid), a sulfinate GSO_2^- and a sulfonate GSO_3^-, via ·OH additions to S-atoms (rather than to $GS^{\cdot-}$ radicals and GSSG).[61] We have shown that in the presence of pervasive transition metal ions such as Fe^{2+}, O_3(g) is able to oxidize the monoanion GS^- to the same products, conceivably via the reactive intermediates generated in fast Fenton-type chemistry at the air−water interface.[62]

The relevance of our findings is highlighted by the increasing recognition of the biochemical role of sulfenic and sulfinic acids in regulating the activity of the immune system, such as the promotion of B- and T-cells.[63-65] In hindsight, the reason for the belated awareness of the importance of sulfenic acids was the lack of suitable analytical techniques for their identification and quantitation at the low concentrations they reach in vivo. This fact underscores the power of our technique for identifying novel species down to submicromolar concentrations in complex mixtures.

From a purely chemical point of view, our experiments reveal the extraordinary specificity of ·OH for attacking the S-atom of GSH on the surface of water vs its lack of selectivity in bulk water. Such specificity implies an unprecedented steering mechanism during [·OH---GSH] interfacial encounters at the air-water interface. In fact, ·OH bypasses fast, unselective H-abstractions (in bulk water) from S−H and the multiple C−H and N−H bonds of GSH. Gratifyingly, our observations are in line with a previous theoretical study on radical recognition and steering mechanism, in which ·OH is captured by GSH carboxylic groups and directed toward the reactive −SH group by a concerted process involving multiple H-bonded interactions within a flexible GSH framework.[66]

10. SUMMARY

The novelty and relevance of the results obtained underscore the unique advantages of online mass spectrometric detection over alternative surface-specific techniques. It probes the surfaces of fresh, uncontaminated, fast flowing liquids. It is very sensitive, being able to routinely detecting < 1 μM ionic species, i.e., at much lower concentrations than in most spectroscopic studies. It unambiguously characterizes species via their mass-to-charge ratios, prescinding from spectroscopic fingerprints and spectral deconvolution analyses. It may offer limitless possibilities to studies of interfacial reactions on liquids.

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