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# Atmospheric and Environmental Physical Chemistry: Pollutants without Borders

Research progress in the fields of atmospheric and environmental chemistry has occurred via the interplay of three key subdisciplines: field observations, modeling, and laboratory/theoretical studies. While many outstanding scientists who were trained as physical chemists are making important contributions in all three of these subdisciplines, research published in *J. Phys. Chem.* is primarily in the laboratory/theoretical studies area; this research has provided much of the scientific underpinning needed for models that are used both for interpreting field observations and for predicting the future state of the environment.

Much of the most significant laboratory research in atmospheric chemistry has traditionally been published in *J. Phys. Chem.* During the 1970s and early 1980s, this research focused on experimental work aimed at obtaining a quantitative understanding of the reaction kinetics and photochemistry of gas-phase atmospheric constituents. The need to consider multiphase processes was unequivocally brought to light during the late 1980s following the discovery of the Antarctic ozone hole. Over the last two decades, the increasing focus on health effects of pollutants and climate change has stimulated interest in understanding the formation, growth, and chemical evolution of atmospheric particulate matter. For modeling climate change, not only must the light-scattering and light-absorbing characteristics of atmospheric particles be understood (the so-called “direct effect”) but so must the role of particles in controlling cloud optical properties (the so-called “indirect effect”). Over the past decade, advances in methodology and computing power for electronic structure calculations, reaction rate calculations, and molecular dynamics simulations have facilitated a much greater contribution from theoretical studies toward answering important questions in atmospheric and environmental chemistry. As is the case for laboratory studies (see above), much of the most significant theoretical research is being published in *J. Phys. Chem.* This issue contains two Perspectives that highlight current important topics in atmospheric and environmental physical chemistry.<sup>1,2</sup>

Mineral dust aerosols affect climate by scattering incoming solar radiation and absorbing outgoing terrestrial radiation. In addition, the surfaces of mineral dust aerosols serve as a medium for chemical change that can affect levels of gas-phase trace species as well as change the physicochemical properties of particle surfaces, thereby affecting the ability of the particles to serve as cloud condensation nuclei. The Perspective by Rubasinghege et al.<sup>1</sup> discusses laboratory experiments that elucidate aspects of the surface photochemistry and redox chemistry of both natural and anthropogenic types of mineral dust particles. It is generally believed that  $\text{HNO}_3$  is a sink for  $\text{NO}_x$  (as well as  $\text{HO}_x$ ) radicals in the troposphere since it is rapidly incorporated into particles as  $\text{NO}_3^-$  and irreversibly removed from the atmosphere by particle deposition processes. Rubasinghege et al. demonstrate that  $\text{NO}_x$  radicals

can be reintroduced into the gas phase following photoexcitation of  $\text{NO}_3^-$  adsorbed on mineral dust surfaces. They also show that  $\text{SO}_2$  adsorbed on  $\text{TiO}_2$  surfaces can be oxidized to  $\text{SO}_4^{2-}$  as a result of photon absorption by the  $\text{TiO}_2$  substrate. Finally, they demonstrate enhanced redox chemistry in goethite ( $\alpha\text{-FeOOH}$ ) and silver-containing anthropogenic particles for nm-sized particles as compared to  $\mu\text{m}$ -sized particles. The surface photochemistry studies of Rubasinghege et al. represent one example of the importance of interfacial processes in atmospheric and environmental chemistry. Studies of interfacial processes represent a rapidly expanding area of environmental chemistry research, some further examples of which are mentioned below. Direct observation of trace species (particularly radicals) at interfaces remains an extremely difficult experimental challenge for future research.

Persistent organic pollutants (POPs) are halogenated organic compounds that have been identified because of their long-term persistence in the environment, their potential for bioaccumulation, their potential for long-range transport, and their adverse effects on biota.<sup>2</sup> The Perspective by Valsaraj and Thibodeaux employs reactive transport modeling to evaluate the global fate and long-range transport of POPs.<sup>2</sup> The article outlines in some detail the framework of the models, which are common research tools in the environmental engineering and geosciences communities but are less familiar to most chemists. While long-range transport is thought to occur via the atmosphere, the models are very complex and must consider other environmental compartments including waters, sediments, soils, and the biosphere. Of particular interest for potential contributors to *J. Phys. Chem.* is Table 3, where the authors assess the degree of confidence in the multitude of model input parameters that describe phase equilibria, mass transfer between environmental compartments, and chemical reaction rates. Focusing on phase equilibria and chemical reaction rates, which tend to be of primary interest to physical chemists, rates of multiphase reactions on particles in air and also air–water interface partition coefficients are assigned a poor degree of confidence (on a poor, fair, good, excellent scale). Interestingly, homogeneous gas-phase and aqueous-phase reaction rates as well as a number of important partition coefficients are known with a degree of confidence that is only rated as fair.

During the early part of 2010, three articles of interest to the atmospheric chemistry community have appeared in *J. Phys. Chem. Lett.* Rincon et al.<sup>3</sup> describe studies of the optical properties of model secondary organic aerosol (“brown carbon” in the lingo currently in vogue in the atmospheric aerosol community). Cheng et al.<sup>4</sup> employ confocal fluorescence microscopy to investigate the morphology and composition of interstitial fluids in freezing electrolyte solutions. Among

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other potential applications, their results have implications for the interpretation of polar ice core records. Finally, Li et al.<sup>5</sup> employ molecular dynamics simulations to investigate the distribution of *cis*-pinonic acid, an oxidation product of biogenic organic compounds in the atmosphere, in small aqueous droplets. They find that *cis*-pinonic acid accumulates near the surface, thus affecting the droplet surface tension and, therefore, the ability of the droplet to become a cloud condensation nucleus.

In addition to the papers that have appeared in *J. Phys. Chem. Lett.*, numerous papers on topics relevant to atmospheric and environmental chemists have appeared in *J. Phys. Chem. A* during early 2010; some of the more important new results (in the view of this author) are highlighted below. Focusing first on gas-phase chemistry, North and co-workers report isomer-selective kinetic and mechanistic studies of OH reactions with isoprene,<sup>6,7</sup> the single most important atmospheric biogenic hydrocarbon, and with 1,3-butadiene,<sup>8</sup> while Lin and co-workers report a molecular beam measurement of the photodissociation cross section for the key polar stratospheric intermediate ClOOCl.<sup>9</sup> Lester, McCoy, and co-workers report a combined experimental/theoretical study that constrains the bond dissociation energy of the potentially important hydrogen-bonded complex H<sub>2</sub>O–OH.<sup>10</sup> In purely theoretical studies, McCoy, Sprague, and Okumura report on the role of torsion/torsion coupling in the vibrational spectrum of *cis*–*cis*-HOONO,<sup>11</sup> Fang and co-workers report that the conical intersection dominates the generation of OH from the (currently controversial) reaction of photoexcited NO<sub>2</sub> with H<sub>2</sub>O,<sup>12</sup> Gerber and co-workers report high-level ab initio calculations on clusters containing water, HCl, and ON–ONO<sub>2</sub> that help to elucidate the mechanism for heterogeneous formation of ClNO,<sup>13</sup> Dixon and co-workers report high-level electronic structure calculations of the thermodynamic properties of a variety of halogen oxides,<sup>14</sup> and Green and co-workers investigate intramolecular hydrogen migration in alkylperoxy and hydroalkylperoxy radicals.<sup>15</sup> Studies of interfacial chemistry include the study of Malin and Geiger, who employ nonlinear optical techniques to investigate uranyl adsorption and speciation at the fused silica/water interface,<sup>16</sup> as well as the study of Zhu and co-workers, who couple laser flash photolysis with cavity ringdown spectroscopy to investigate photolysis of HNO<sub>3</sub> on aluminum surfaces and ice films.<sup>17</sup> Studies of heterogeneous chemistry by Kanji and Abbatt,<sup>18</sup> Reid and co-workers,<sup>19</sup> Bogdan and Molina,<sup>20</sup> and Pope and co-workers<sup>21</sup> all focus on the thermodynamics of aqueous particle formation and growth. Finally, important research in the area of mechanism development has been reported by Seinfeld and co-workers,<sup>22</sup> who use observation of gas-phase and particle-phase products in a smog chamber to elucidate the mechanism for secondary organic aerosol formation from the photooxidation of naphthalene, and by Bock and Jacobi,<sup>23</sup> who have developed a mechanism for nitrate photochemistry in snow that is constrained by laboratory experiments carried out with artificial snow.

As described above, *J. Phys. Chem.* continues to be a preferred publication venue for top-level experimental and theoretical research targeted at improving our understanding of atmospheric and environmental chemistry. The editorial

staff is looking forward to receiving future first-rate submissions in these important areas of research.

**J. Phys. Chem. continues to be a preferred publication venue for top-level experimental and theoretical research targeted at improving our understanding of atmospheric and environmental chemistry.**

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