

Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded \$500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

Wisconsin Initiative for Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

UW-Madison Department of Chemistry
1101 University Avenue
Madison, WI 53706-1396
Contact: Prof. Bassam Z. Shakhshiri
bassam@chem.wisc.edu
www.scifun.org

January 2011

MECHANISMS OF VOC OXIDATION AND AEROSOL FORMATION:
ATMOSPHERIC ORGANIC CHEMISTRY OF GLYOXAL

by
Melissa M. Galloway

A dissertation submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
(Chemistry)

at the
University of Wisconsin–Madison

2011

Chapter 1

Introduction¹

1.1 The Earth's Atmosphere

The Earth's atmosphere consists of several layers of which the troposphere is the closest to the surface. The troposphere extends from the Earth's surface to the tropopause, which is approximately 10-15 km in altitude, depending on the location and time of year (Seinfeld and Pandis, 1998). At the tropopause, the pressure in the atmosphere is 1/100 of the pressure at the Earth's surface. It is a very small part of the total volume of the atmosphere, but it contains approximately 80% of the total atmospheric mass (Seinfeld and Pandis, 1998). The troposphere is a complex mixture of suspended gases and particles that can react and interact with each other, with the light entering the atmosphere from the sun, and with the heat emitted from the Earth's surface. Biogenic particles and gases are those released into the atmosphere from natural sources such as plants, microorganisms, oceans, and lightning. Those that are emitted as a result of human activities, such as from vehicles or industry, are called anthropogenic species. These designations are important for atmospheric policy makers because it is difficult for humans to control biogenic emissions, but it is possible to

¹This introduction will be part of a series compiled by the Wisconsin Initiative for Science Literacy (WISL) to "promote literacy in science, mathematics and technology among the general public." It is intended to "explain [this] scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress."

control pollution from anthropogenic sources through emissions regulations and laws.

Nitrogen (78%) and oxygen (21%) make up the majority of atmospheric gases (excluding water). Their concentrations are very stable and they are present in such large quantities in the atmosphere that they are considered background gases. Water vapor concentrations vary widely, depending on location and altitude, and can contribute up to 3% of the gases in certain regions. Argon (0.9%) is the next most abundant, but it does not undergo any chemical reactions and does not affect human health or global climate change. The trace gases, the remaining 0.01%, are the most chemically interesting. Even though their concentrations are small, these gases affect pollution, human health, and climate. Government agencies regulate some of these gases and aerosols, while others are important for their role in the production of pollutants and greenhouse gases. Therefore, it is important to understand their production and fate in the atmosphere.

1.1.1 Ozone and VOC oxidation

Ozone (O_3) has come to public awareness as a species of high importance to both climate change and its effect on incoming solar radiation. However, O_3 is a pollutant in the troposphere, and also has adverse effects on human and plant health and can often be a component of smog. The photolysis, or reaction with light, of NO_2 produces NO and O_3 , which can then react to form NO_2 .



Since these reactions essentially cancel each other out, this leads to no net production or loss of any species. However, an increase of the concentration of one of the species will change the concentrations of each of the others. One such perturbation to the O_3/NO_x (NO

and NO_2) system occurs through the oxidation of volatile organic compounds (VOCs) via the hydroxyl radical (OH, a highly reactive radical species). VOCs are emitted from sources such as vegetation, industry, and automobiles (Figure 1). This VOC oxidation is coupled to O_3 formation in the troposphere. When OH reacts with a hydrocarbon (RH), where R is any size hydrocarbon, it forms an alkyl peroxy radical (RO_2):



This alkyl peroxy radical is very reactive, and can react with NO to lose an oxygen atom, forming an alkoxy radical (RO).



The formation of NO_2 in Eq. 1.2 perturbs the O_3/NO_x cycle, resulting in the formation of O_3 . As the alkoxy radical is still very reactive, it will react with the oxygen molecule (O_2) to form a stable carbonyl compound ($\text{R}'\text{CHO}$) and HO_2 .



The HO_2 goes on to react with another NO to produce more OH and NO_2 , therefore perturbing the O_3/NO_x steady state even more and producing another O_3 .



Combining and balancing these equations gives the net reaction between the hydrocarbon and OH.



Since OH is regenerated in the final step, the net overall reaction does not consume the OH and produces a carbonyl, a water, and two O_3 molecules for each hydrocarbon reaction. O_3

formed in this way is a substantial component of tropospheric O_3 . Since OH is a radical species and is regenerated in each hydrocarbon reaction, reactions will continue until a chain termination reaction occurs. This reaction between two radical species forms a neutral species, thereby stopping the radical reaction chain. These chain propagation steps are important to accurately model hydrocarbon reactions, as small changes can drastically alter predicted radical concentrations. One such chain termination step is the reaction of OH with NO_2 to form nitric acid (HNO_3):



This step seems relatively straightforward, but adds complexity to the reaction system. NO is important in the production of OH (e.g., Eq. 1.5) and is coupled to NO_2 , but NO_2 is important for OH destruction. Therefore, these interconnecting pathways make predictions of the concentrations of these radical species difficult, which leads to inaccurate models of O_3 .

As O_3 is formed from the combination of oxidation of VOC oxidation and direct sunlight, O_3 concentrations are often higher in the summertime. Therefore, some cities implement ‘ O_3 Action Days’ during the summer. During very hot and sunny days with very little wind, the conditions are right for O_3 formation. Therefore, local authorities ask people to refrain from driving, mowing their lawns, and filling their gas tank in order to reduce gasoline emissions. Gasoline is a hydrocarbon, therefore gasoline from engines that has not been fully combusted and that lost while filling a gas tank can contribute to heightened O_3 and carbon monoxide levels, especially when there is a lot of sunlight to photolyze NO_2 to NO and O_3 . Combustion engines are also the main NO_x source in cities, so running a car or lawn mower will increase NO_x levels, in turn increasing O_3 concentrations.

To make effective decisions regarding emissions regulations, policymakers must understand the effect of regulations on atmospheric chemistry and pollution. For example, since

O₃ formation requires both VOCs and NO_x, decreasing NO_x concentrations may actually increase O₃ concentrations, depending on VOC concentrations. Interactions like these make this a very complex system, and one which must be studied to determine whether NO_x regulations (for example) will increase or decrease local O₃ pollution. Computer models of atmospheric chemistry using chemical information gained from laboratory and field measurements provide a tool for estimating these effects before enacting legislation. For these models to be accurate, it is necessary to have an accurate understanding of the chemical processes and rates occurring in the atmosphere, as well as the meteorology of the area of interest. Missing or incorrect processes in the model can be determined by comparing ambient measurements with these models. Laboratory experiments can then address the process in question and help determine the source of the error. The resulting changes in chemical processes can then be implemented in the model, which can then once again be compared to measurements. In this way, atmospheric models are altered until they match measurements and are constantly evolving and improving.

1.1.2 Atmospheric aerosol

While the chemistry and impacts of carbon dioxide are well understood, atmospheric aerosols are one class of atmospheric constituents that has very large uncertainties (Forster et al., 2007). Aerosols are suspended particles that can be liquid, solid, or a combination of both. Atmospheric aerosol typically ranges in size from a few nanometers (nm) to tens of micrometers (μm) in diameter. Dust, soot, and sea salt are considered primary aerosol, as they are emitted directly into the atmosphere. Secondary organic aerosol (SOA) is formed when gas-phase species react with atmospheric oxidants such as OH or O₃, forming less volatile species. When these species encounter aerosol in the atmosphere they are accumulated by the aerosol if they have low enough volatility (e.g., are sticky enough). Once a compound is in the aerosol, it can react with other molecules to form new organic products. Addition-

ally, SOA provides a surface onto which water can condense to form clouds and provides a surface on which chemical reactions may occur. Aerosols have both direct and indirect effects on climate. SOA directly affects climate by scattering (in essence reflecting) sunlight back into space, preventing it from reaching the surface of the Earth, thus contributing to a cooling of the atmosphere (Forster et al., 2007). Clouds also reflect sunlight back into space, and can be formed through the condensation of water onto aerosol surface. In this way, aerosol indirectly affects climate. This is the other half of the global climate change equation; greenhouse gases contribute to the warming of the atmosphere, but aerosols and clouds help to counteract that effect by cooling the atmosphere. Despite this importance, SOA composition, formation, and surface reactions are not well understood by the scientific community. These uncertainties lead to very large errors in our predictions of how aerosol affects global climate change and the magnitude of its cooling effect. Due to this lack of knowledge, the uncertainties in aerosol contribution dominate the uncertainties of our models of the magnitude of global climate change (Forster et al., 2007).

1.2 Glyoxal in our atmosphere

Glyoxal is a gas-phase oxidation product of atmospheric VOCs, as well as a component of atmospheric aerosol (Liggio and McLaren, 2003; Matsunaga et al., 2004), and can be used as a tracer for SOA growth. Volkamer et al. (2007) found that measured glyoxal concentrations are much lower than modeled, suggesting that atmospheric models are either over-predicting gas-phase glyoxal production or under-predicting the contribution of glyoxal to aerosol. A model based on the MCM database also over-predicts glyoxal concentrations in a forested area without much contribution to aerosol (Huisman et al., 2011). To estimate the contribution of glyoxal to SOA, both gas-phase glyoxal production and glyoxal uptake onto aerosol need to be studied. There are no significant direct sources of glyoxal, so if gas-phase glyoxal is present, it must be the result of the oxidation of larger VOCs. Glyoxal also has a

very short atmospheric daytime lifetime in the atmosphere, as it reacts away within a couple of hours in direct sunlight (Volkamer et al., 2005; Huisman et al., 2011). Therefore, glyoxal is indicative of relatively local gas-phase oxidation chemistry and is useful for comparison of measurements to models. As a tracer of local VOC oxidation, glyoxal can also be used to gain insight into O_3 production. The presence of glyoxal and its reaction products in ambient aerosol also makes it a useful model for understanding organic chemistry within the aerosol.

The dominant source of glyoxal in forested areas is the reaction of biogenic VOCs (e.g., isoprene and 2-methyl-3-buten-2-ol) with OH (Fu et al., 2008; Myriokefalitakis et al., 2008; Stavrou et al., 2009). Isoprene is one of the most abundant hydrocarbons in the atmosphere, and it has been estimated that over 500 Tg of isoprene are emitted into the atmosphere each year (Guenther et al., 1995). The reaction of isoprene with OH has been studied in detail (Tuazon and Atkinson, 1990; Paulot et al., 2009; Archibald et al., 2010) and many products have been identified. However, gas-phase glyoxal has traditionally been hard to measure, and new measurements have shown discrepancies between measurements and models (Volkamer et al., 2007; Huisman et al., 2011). Understanding atmospheric concentrations requires an understanding of both production and loss mechanisms of the species of interest. Glyoxal production from isoprene and 2-methyl-3-buten-2-ol has been studied in the laboratory, but not all production pathways have been studied in detail. One first-generation pathway from isoprene to glyoxal has been suggested that is not included in current models (Volkamer et al., 2006; Paulot et al., 2009). Therefore, more work is necessary to understand glyoxal production from isoprene. Hydrocarbon loss processes include reaction with OH, photolysis, and deposition to SOA and other surfaces. Laboratory studies have confirmed that the oxidation of glyoxal by OH and glyoxal photolysis are well constrained, but the loss of glyoxal to SOA is still an area of uncertainty. This makes the contribution of

glyoxal to SOA an important area of study for atmospheric scientists in order to understand the complete atmospheric cycle of glyoxal production and loss. Recent improvements in detection techniques have allowed for the in situ, high time resolution detection of low glyoxal concentrations (Huisman et al., 2008). The use of the Madison Laser-Induced Phosphorescence (Mad-LIP) instrument has made it possible to perform laboratory studies of VOC oxidation to determine the kinetics of glyoxal formation.

1.2.1 Understanding gas-phase glyoxal

Many VOC gas-phase oxidation studies are performed in atmospheric chambers. These are made of metal or Teflon bags, and allow simulation of the atmosphere while controlling conditions such as temperature, light intensity, and concentrations of VOCs and oxidants. The composition of the air within the chambers is much simpler than the atmosphere, but it allows for examination of individual processes that would otherwise be difficult to disentangle from other interactions. Therefore, a chamber experiment may be used to determine the rate, or speed, at which a reaction progresses, and the yield of the products, or the fraction of reacted initial species that form a particular product. We can combine these reaction rates and yields from each individual process and apply these to our understanding of the more complex atmosphere, often in atmospheric models. In order to gain a complete understanding of the chemistry occurring in the chambers, it is necessary to measure conditions and the concentrations of as many compounds as possible. Therefore, atmospheric chambers have instruments measuring temperature, relative humidity, O_3 , NO_x , and many gas-phase species. In a typical OH-initiated isoprene oxidation experiment, gas-phase isoprene is added to the chamber and allowed to mix completely. An OH precursor, typically a molecule that will form OH upon irradiation with sunlight, is added at the same time. Once the blacklights, used to simulate sunlight in the chamber, are turned on, the OH precursor is photolyzed to form OH, and isoprene and OH begin to react. The first stable products

of isoprene oxidation (first-generation oxidation products), such as methyl vinyl ketone and methacrolein, begin to form. These will then react with OH to form second-generation products. This process will continue until there is no more OH or until the VOCs in the chamber are fully oxidized.

Through these atmospheric chamber studies, we can compare measured concentrations of many compounds that are important in the atmosphere to calculated model concentrations. Gas-phase formation kinetics and yields can also be determined from the experimental concentrations and compared to those in the model. This will allow us to evaluate how well atmospheric models reproduce important atmospheric processes. Once this is accomplished, changes can be incorporated into the widely available kinetics databases for distribution to other models.

1.2.2 Glyoxal in aerosol

Glyoxal can undergo many reactions within the aerosol, both with itself and with other molecules. Therefore, it is useful as a model system for organic aerosol formation. Many condensed-phase studies are performed with many milliliters of solution. Since an aerosol is less than 10 μm in diameter, the surface area to volume ratio is much greater than it is in a bulk solution. This can change the chemistry occurring in the aerosol and may change the rate at which gas-phase species will partition to the condensed-phase. Therefore, atmospheric chambers are also used to study uptake kinetics and reactions in the aerosol. The same chambers are used as with gas-phase studies, and many of the same instruments are used to monitor the reactions.

The uptake of gas-phase compounds onto atmospheric aerosols is important in understanding aerosol formation. Since many ambient aerosols contain salt, particles made up of aqueous salt solutions (e.g. ammonium sulfate) are often used as seed aerosols to provide a surface for uptake of organic molecules. The size and composition of the aerosols are moni-

tored along with the gas-phase concentrations of all species of interest. These experiments are carried out in different light and oxidant conditions to simulate different ambient conditions. The chemistry of the atmosphere is drastically different during night and day due to the presence of sunlight and higher concentrations of oxidizing species during the day, and it is important to study chemistry in various conditions to get a complete picture of atmospheric processes. By performing a variety of experiments, comparing how fast glyoxal is incorporated into the aerosol, and examining the products formed under each condition, we can determine which conditions are responsible for any changes in these properties. Finally, from chamber experiments, we can calculate the probability that a glyoxal molecule encountering an aerosol will result in glyoxal adsorption onto the aerosol. This quantity is useful in atmospheric models to determine aerosol growth and to increase the accuracy of the modeled contribution of glyoxal to aerosol. Instrumentation that measures aerosol composition allows us to compare the products formed in bulk and chamber studies and to determine which products will actually be formed under atmospheric aerosol conditions.

Once glyoxal becomes part of the aqueous aerosol-phase, the aldehyde groups in glyoxal quickly hydrate, or react with water, and form alcohol groups. When hydration changes glyoxal from the α -dialdehyde into another form of glyoxal, the equilibrium shifts to bring more glyoxal into the aerosol-phase. Once glyoxal is in the condensed-phase, a glyoxal molecule can undergo one of several reactions. At high concentrations, glyoxal will oligomerize (specifically form acetal oligomers), or react with itself to form chains of hydrated glyoxal molecules (Whipple, 1970). Glyoxal hydration and oligomerization are reversible reactions; the concentration of each reactant depends on the concentrations of all others. Glyoxal uptake in the chambers has also been found to be reversible (Kroll et al., 2005). Decreasing gas-phase glyoxal concentrations result in glyoxal partitioning back to the gas-phase from the aerosol-phase in order to re-establish equilibrium between the gas- and condensed-phase.

Glyoxal can also undergo irreversible chemical reactions once in the aqueous phase. For example, ambient aerosol often contains both ammonium and sulfate ions. Several chamber and ambient studies have detected a molecule with a mass that corresponds to glyoxal sulfate (Surratt et al., 2007, 2008), which could be formed through reaction of glyoxal with the sulfate ion. The ammonium ion has traditionally been considered chemically inert in the aerosol. Several studies of glyoxal and methylglyoxal in solution with ammonium salts have shown that ammonium will in fact react with these compounds to form dark brown solutions (Debus, 1858; Nozière et al., 2009; Shapiro et al., 2009). If these compounds are formed in the aerosol, even a small amount could change the optical properties of the aerosol. This means that instead of reflecting sunlight back to space, brown aerosols absorb light and retain some of that energy in the atmosphere, changing some of the cooling effect of aerosol into a warming effect. In order to understand the effects of these colored compounds on global climate change, we must first determine the likelihood of their formation and their prevalence in the atmosphere.

1.3 Summary

The Earth's atmosphere is a complicated system of gases and aerosols. Greenhouse gases such as carbon dioxide have been studied in detail, and are understood by atmospheric scientists. However, there are great uncertainties in our understanding of atmospheric aerosols, leading to uncertainties in our predictions of these species. Emissions reduction strategies are often based on atmospheric models that reflect our understanding of atmospheric processes. Therefore, these models must be as accurate as possible. Through comparison to field and laboratory studies, we can identify necessary model improvements. Glyoxal is a VOC oxidation product and component of SOA that is not well represented by current atmospheric models. To resolve the discrepancy between atmospheric measurements and models, laboratory chamber studies are often performed. Reaction rates and product

formation observed during these studies can be applied to models in order to bring the models and measurements into agreement. Since glyoxal is also a component of ambient aerosol, gas-phase reactions are not the only processes that must be considered when studying glyoxal concentrations in the atmosphere. Studies of gas-phase uptake onto aerosol can provide insight into both how quickly glyoxal partitions into the aerosol and its chemical reactions within the condensed-phase. Each process we can begin to understand through these laboratory studies can be applied to models to predict atmospheric conditions, and the information we learn about glyoxal may be able to be applied to similar molecules in the atmosphere.

1.4 Bibliography

- Archibald, A. T., Jenkin, M. E., and Shallcross, D. E.: An isoprene mechanism intercomparison, *Atmospheric Environment*, 44, 5356–5364, doi:10.1016/j.atmosenv.2009.09.016, 2010.
- Debus, H.: Ueber die Einwirkung des Ammoniaks auf Glyoxal, *Annalen der Chemie und Pharmacie*, 107, 199–208, doi:10.1002/jlac.18581070209, 1858.
- Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: *Changes in Atmospheric Constituents and in Radiative Forcing*, Report, Cambridge University Press, 2007.
- Fu, T. M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *Journal of Geophysical Research-Atmospheres*, 113, D15 303, doi:10.1029/2007JD009505, 2008.

Guenther, A., Hewitt, C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W., Pierce, T., Scholes, B., Steinbrecher, R., Tallamaraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic-compound emissions, *Journal of Geophysical Research-Atmospheres*, 100, 8873–8392, doi:10.1029/94JD02950, 1995.

Huisman, A. J., Hottle, J. R., Coens, K. L., DiGangi, J. P., Galloway, M. M., Kammrath, A., and Keutsch, F. N.: Laser-induced phosphorescence for the in situ detection of glyoxal at part per trillion mixing ratios, *Analytical Chemistry*, 80, 5884–5891, doi:10.1021/ac800407b, 2008.

Huisman, A. J., Hottle, J. R., Galloway, M. M., DiGangi, J. P., Coens, K. L., Choi, W. S., Faloon, I. C., Gilman, J. B., Kuster, W. C., de Gouw, J., Bouvier-Brown, N. C., LaFranchi, B. W., Cohen, R. C., Wolfe, G. M., Thornton, J. A., Docherty, K. S., Farmer, Delphine, K., Cubison, M. J., Mao, J., Brune, W. H., and Keutsch, F. N.: Photochemical modeling of glyoxal at a rural site: observations and analysis from BEARPEX 2007, *Atmospheric Chemistry and Physics Discussions*, 11, 13 655–13 691, doi:10.5194/acpd-11-13655-2011, 2011.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *Journal of Geophysical Research-Atmospheres*, 110, D23 207, doi:10.1029/2005JD006004, 2005.

Liggio, J. and McLaren, R.: An optimized method for the determination of volatile and semi-volatile aldehydes and ketones in ambient particulate matter, *International Journal of Environmental Analytical Chemistry*, 83, 819–835, doi:10.1080/03067310310001597653, 2003.

- Matsunaga, S., Mochida, M., and Kawamura, K.: Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan, *Journal of Geophysical Research-Atmospheres*, 109, D04 302, doi:10.1029/2003JD004100, 2004.
- Myriokefalitakis, S., Vrekoussis, M., Tsigaridis, K., Wittrock, F., Richter, A., Brühl, C., Volkamer, R., Burrows, J. P., and Kanakidou, M.: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution, *Atmospheric Chemistry and Physics*, 8, 4965–4981, 2008.
- Nozière, B., Dziedzic, P., and Cordova, A.: Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by ammonium ions (NH_4^+), *Journal of Physical Chemistry A*, 113, 231–237, doi:10.1021/jp8078293, 2009.
- Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmospheric Chemistry and Physics*, 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley-Interscience, New York, 1998.
- Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R., and McNeill, V. F.: Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics, *Atmospheric Chemistry and Physics*, 9, 2289–2300, 2009.
- Stavrakou, T., Muller, J., DeSmedt, I., Van Roozendaal, M., Kanakidou, M., Vrekoussis, M., Wittrock, F., Richter, A., and Burrows, J.: The continental source of glyoxal estimated

- by the synergistic use of spaceborne measurements and inverse modelling, *Atmospheric Chemistry and Physics*, 9, 8431–8446, 2009.
- Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for Organosulfates in Secondary Organic Aerosol, *Environmental Science and Technology*, 41, 517–527, doi:10.1021/es062081q, 2007.
- Surratt, J. D., Gomez-Gonzalez, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *Journal of Physical Chemistry A*, 112, 8345–8378, doi:10.1021/jp802310p, 2008.
- Tuazon, E. C. and Atkinson, R.: A product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO_x, *International Journal of Chemical Kinetics*, 22, 1221–1236, doi:10.1002/kin.550221202, 1990.
- Volkamer, R., Molina, L. T., Molina, M. J., Shirley, T., and Brune, W. H.: DOAS measurement of glyoxal as an indicator for fast VOC chemistry in urban air, *Geophysical Research Letters*, 32, L08 806, doi:10.1029/2005gl022616, 2005.
- Volkamer, R., Barnes, I., Platt, U., Molina, L. T., and Molina, M. J.: Remote sensing of glyoxal by differential optical absorption spectroscopy (DOAS): Advancements in simulation chamber and field experiments, in: *Environmental Simulation Chambers: Application to Atmospheric Chemical Processes*, edited by Barnes, I. and Rudinski, J., vol. 62, Springer, Dordrecht, Netherlands, 2006.
- Volkamer, R., San Martini, F., Molina, L. T., Salcedo, D., Jimenez, J. L., and Molina,

- M. J.: A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol, *Geophysical Research Letters*, 34, L19 807, doi:10.1029/2007GL030752, 2007.
- Whipple, E. B.: The Structure of glyoxal in water, *Journal of the American Chemical Society*, 92, 7183–7186, doi:10.1021/ja00727a027, 1970.

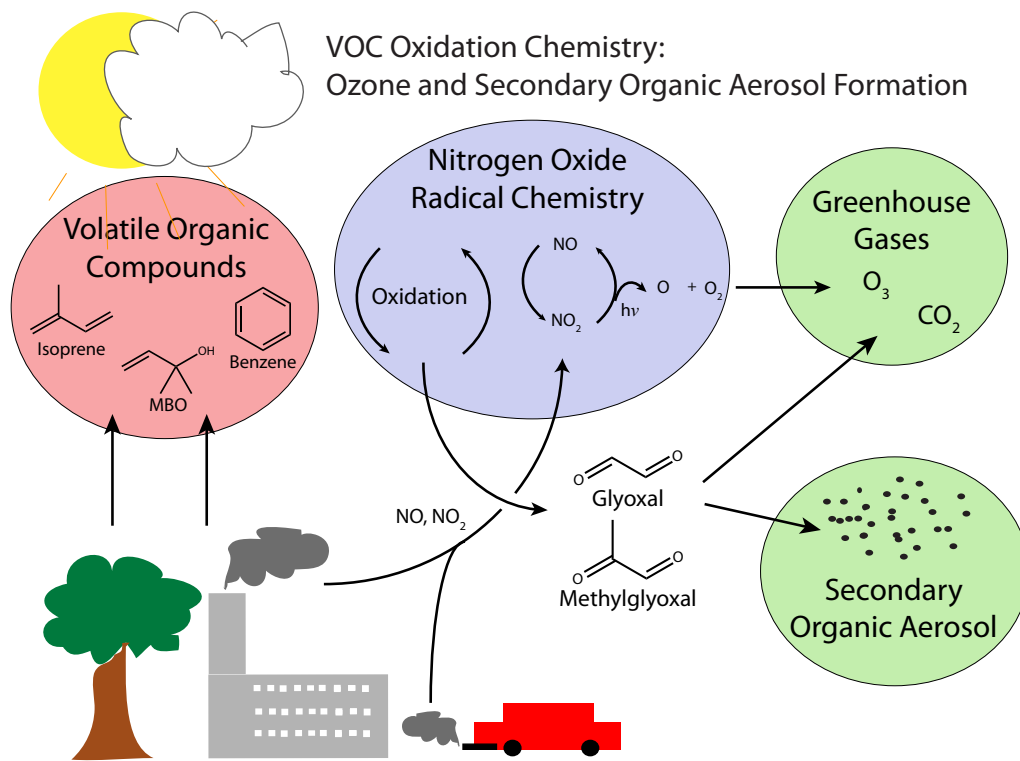


Fig. 1.1.— VOCs are emitted from sources such as vegetation, industry, and automobiles. These are oxidized by OH and NO_x and form ozone and oxygenated compounds (e.g., glyoxal and methylglyoxal). These compounds can either partition to SOA or other surfaces or be oxidized further, eventually becoming CO₂.