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.

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FORMALDEHYDE AS A PROBE OF RURAL VOLATILE ORGANIC COMPOUND OXIDATION

by

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Chapter 1

Introduction[1]

1.1 Trace Species and Air Quality

Our atmosphere consists of roughly 78% nitrogen gas, 20% oxygen gas, 1% argon gas, as much as 1% water vapor, and less than 0.05% other gases and airborne particles. While oxygen gas (O_2) is incredibly important to human life on Earth, that small fraction of other material often profoundly affects our everyday lives. In particular, two of these, ozone and small particulate matter, can have a negative impact on the quality of air we breathe. Air quality is a general concept which is related to how hazardous the air in a given area is to animal and plant life. It is strongly dependent on the amount of these trace materials. If the air quality is “poor”, this denotes that there is an increased health risk to people, animals, and plants due to these materials. In order to attempt to control and analyze these effects, we first must understand the effects that these species may have on animal and plant life and second accurately predict the concentration of these species in the atmosphere.

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[1] This 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.”

1.1.1 Harmful effects of ozone and aerosol

Ozone is a trace gas naturally present in our atmosphere. Most people have heard of ozone in the context of the "ozone layer" high in the atmosphere which protects us from solar ultraviolet radiation. Ozone also exists in the troposphere, the layer of the atmosphere closest to the surface, in which we live, though in much smaller concentrations. While beneficial higher in the atmosphere, ozone near the surface can be quite harmful to plant and animal life. Increased ozone concentrations have been associated with increased incidences (about 20%) of cardiac-related emergency room visits (Stieb et al., 2000). Additionally, as much as 4% of respiratory-related ER visits have been attributed to tropospheric ozone, comparable to that of many common allergens (Stieb et al., 2000). A more recent study reported that increased ozone concentrations can lead to a more than 300% increase respiratory-related death in urban areas compared to rural/remote areas (Jerrett et al., 2009). Ozone has also been shown to be detrimental to plant life, by damaging sensitive tissue and stimulating stress reactions by the plants (Mauzerall and Wang, 2001). This can affect humans indirectly by decreasing crop yields in areas with increased concentrations of ozone.

Airborne particulate matter, also known as aerosol, also can contribute to poor air quality. Aerosols are small particles, either liquid or solid, that are suspended in air. They are emitted and/or formed by various processes, such as volcanic eruption, wind sweeping up dust, vehicle emissions, and chemical reactions which occur in the atmosphere. Many studies have shown a high agreement between increased concentrations of aerosol and increased mortality rates due to respiratory-related illnesses (Ostro, 1993; Laden et al., 2000). Additionally, increased aerosol concentrations were found to correlate with increased ER cases of cardiac dysrhythmia (irregular heart beat) (Stieb et al., 2000). Figure 1.1 shows the results of a highly-cited case study of six small U.S. cities (Dockery et al., 1993). This study reported a linear trend where increased aerosol concentrations corresponded to increased mortality.

1.1.2 Quantifying poor air quality and mitigation

To raise awareness of current air quality conditions, the U.S. Environmental Protection Agency reports a quantity called the Air Quality Index (AQI). The AQI acts similar to a weather report, with a scale of 0 - 500, which denotes the level of risk that the air in your area poses to your immediate health (`http://www.airnow.gov/index.cfm?action=aqibasics.aqi`). Higher AQI indices indicate higher risks to your health. Also similar to weather reports, the EPA forecasts future AQI for the following day. By predicting future air quality, state and local government officials can dictate policy to try to avoid or minimize the negative effects of the poor air quality. For example, when a high AQI is predicted for a particular day, many cities will declare an "Ozone Awareness Day", or something similar. As a result, public transportation may operate at reduced or no cost to encourage its use, people may be asked not to mow the grass, or relief shelters may be set up for groups at risk without adequate shelter or protection.

While relief shelters help to reduce the consequences of the poor air quality, reducing vehicle and lawnmower emissions focuses on lowering the intensity of the event by reducing the sources. Computer models containing the meteorology and chemistry of the atmosphere can help predict which approaches are both useful and cost-effective. The processes that determine air quality are incredibly complex and interconnected. For example, ozone production in the atmosphere is highly dependent on the particular trace species present in the air. Under some conditions, decreasing emissions results in less ozone production while under other conditions, decreasing emissions results in more ozone production (Finlayson-Pitts and Pitts Jr., 2000). The effectiveness of these models depends on a thorough understanding of the chemical and physical processes controlling the production of ozone and aerosols, such as the oxidation of volatile organic compounds.

1.2 Volatile Organic Compounds

The chemical production in the atmosphere of both ozone and certain aerosols is tied to a group of trace gases called volatile organic compounds, or VOCs. A VOC is any organic (carbon-based) chemical that exists as a vapor in the atmosphere. The most common VOC in the atmosphere is methane. Methane is emitted from various sources, ranging from livestock emission to oil mining/refining to swamps and wetlands. Annually, roughly 600 Tg, or 650 million tons, of methane are emitted into the atmosphere globally (Seinfeld and Pandis, 1998). Isoprene is another common VOC and has larger emissions than any other non-methane VOC, roughly 500 Tg, or 550 million tons, annually (Finlayson-Pitts and Pitts Jr., 2000). Isoprene is a biogenic VOC, or BVOC, which specifies it is from natural sources. In this case, isoprene is primarily emitted by leafy (deciduous) trees and plants. Other common VOCs include aromatic species (benzene, toluene), small terpenes (plant resin), and other hydrocarbons (propane, hexane) (Seinfeld and Pandis, 1998).

1.2.1 Emission and Processing

Emission of VOCs typically falls into one of two categories: anthropogenic, or the result of human activity, and biogenic, or the result of natural activity. Anthropogenic VOCs, or AVOCs, are emitted by factories, refineries, vehicles, agriculture, livestock, or any other forms directly attributable to humans. Biogenic VOCs, or BVOCs, are predominantly emitted from wetlands and non-agricultural plant life (forests, jungles, natural plains, oceans).

Once in the atmosphere, all VOCs are oxidized in a light-driven process which couples two families of very reactive, or radical, atmospheric compounds called NO_x and HO_x (Fig. 1.2). NO_x consists of two chemical species: nitrogen oxide (NO) radical and nitrogen dioxide (NO_2) radical. Tropospheric ozone is produced by the conversion of NO_2 to NO by ultraviolet (UV) light from the sun. NO can then react with ozone to once again form NO_2. The presence of HO_x, which consists of the chemical species hydroxyl (OH) radical and hydroperoxyl (HO_2) radical, results in another pathway to convert NO to NO_2. HO_2 can react with NO to form OH and NO_2. OH is then converted back to HO_2 by reaction with VOCs. Since there is no net loss of HO_x or NO_x in this process, it can be described simply as in Eqn. 1.1:

$$VOC \overset{light}{\rightarrow} Products + Ozone \tag{1.1}$$

Additionally, as NO_x and HO_x are not destroyed in this process, a small amount of these radical species can create a large amount of ozone.

However, HO_x and NO_x can be destroyed through reactions between themselves. Higher concentrations of HO_x and NO_x increases the rate by which they are destroyed. For example, at very high concentrations of NO_x, such as in heavily polluted environments, the speed by which NO reacts with other radical species may be faster than the rate of reaction of NO with HO_2. If these very high NO_x concentrations are decreased, ozone production can actually increase as there is less destruction of these reactive species (Finlayson-Pitts and Pitts Jr., 2000). Complexities, such as these, in the chemical pathways of the atmosphere make regulation difficult, so it is important to characterize them properly in order to accurately predict the effects of any mitigation strategy.

1.2.2 Oxidized Volatile Organic Compounds

The products created in Eqn. 1.1 are more specifically oxidized VOCs, or OVOCs. These are essentially VOCs which have more oxygen attached to them. As each type of VOC reacts differently, oxidation of each type of VOC can make different OVOCs. OVOCs are usually relatively stable, meaning they can exist in the atmosphere for longer than a few minutes and have higher boiling temperatures than VOCs. Once created in the atmosphere, OVOCs can be lost in two ways. The first is to react just like a VOC to make different OVOCs and additional ozone. This process can continue until carbon monoxide is formed. Secondly, as OVOCs have higher boiling points, they may no longer be volatile enough to stay in the atmosphere and can condense onto a surface. For example, if the OVOC encounters a small particle in the atmosphere, like an aerosol, it can stick to it (Pankow, 1994a,b; Odum et al., 1996). This is how a particular form of aerosol, secondary organic aerosol (SOA), is formed: by many gas molecules sticking together. SOA is usually a major portion of the total amount of aerosol and can contribute 18-70% of the mass of all aerosols, depending on the region (Zhang et al., 2007; Jimenez et al., 2009).

1.2.3 Models and VOC oxidation

Models of air quality contain mechanisms of VOC oxidation in order to account for this production of ozone and SOA. VOC emissions for the model are estimated from satellite, aircraft, and/or ground measurements. These models then calculate what they expect for OVOC concentrations based on those VOC concentrations, the amount of solar radiation, concentrations of $\mathrm{HO_x}$ and $\mathrm{NO_x}$, as well as other factors. We can compare the OVOC concentrations predicted by the models with measurements of these OVOCs. This allows us to gauge how accurate the model is for those given conditions. By identifying which OVOCs do not match with models, we can determine what parts of a model still need improvement.

A great deal of effort has been put into validating, or checking, the accuracy of these models. This has been performed using both controlled conditions (Lee et al., 2006a,b; Carrasco et al., 2007; Galloway et al., 2011b) and real world conditions present in ambient air (Choi et al., 2010; Huisman et al., 2011). Overall, models and measurements of OVOC concentrations can be fairly consistent when there are high concentrations of $\mathrm{NO_x}$, such as in urban areas (since anthropogenic activity can emit large quantities of $\mathrm{NO_x}$). However, in rural or remote areas where $\mathrm{NO_x}$ is low, the consistency between models and measurements breaks down, even with respect to concentrations of HO_x (Hofzumahaus et al., 2009; Paulot et al., 2009; Peeters et al., 2009). In order to improve these models, we must further develop accurate ways to detect OVOCs in the atmosphere. This will grant additional points of reference for model outputs.

1.3 Formaldehyde in the Atmosphere

The simplest aldehyde, formaldehyde (HCHO) is formed in the oxidation of nearly all VOCs. Because of this, it is one of the most common OVOCs. As with most trace gases, HCHO concentrations are quite small: 0.02-0.2 parts per billion by volume, or ppb_v, high in the troposphere (Fried et al., 2008a,b), 1-20 ppb_v in rural areas near the surface (Apel et al., 1998; Lee et al., 1998; Müller et al., 2006; Choi et al., 2010; Galloway et al., 2011a), and as much as 45 ppb_v in urban areas (Dasgupta et al., 2005). Due to its prevalence in the atmosphere as a central OVOC, measurements of HCHO are of vital importance to validate any model of atmospheric chemistry.

1.3.1 Production and destruction

Figure 1.3 shows a schematic of HCHO production and destruction in the atmosphere from one of the simplest cases: the oxidation of methane. Tropospheric methane oxidation starts with reaction with OH, which removes a hydrogen atom to make methyl radical (CH_3) and water (H_2O). CH_3 quickly reacts with (O_2) in the air to form CH_3O_2, which is one of a family of compounds called alkylperoxy radicals (generally represented as RO_2). While RO_2 molecules can react in various ways (see Chap. 4) for a brief discussion), one of the primary ways involves converting NO to NO_2. This results in the formation of CH_3O, which reacts quickly with O_2 to form HO_2 and HCHO. There are two additional points of interest about this production method for HCHO. The first is that there is no net change in the amount of HO_x, only a conversion from the OH to HO_2 form. Again, this results in increased ozone production from the conversion of NO_2, which was produced during this process, to NO.

The lower part of Fig. 1.3 shows three pathways through which HCHO can be destroyed in the atmosphere, two initiated by sunlight and one by OH. The right pathway is the most likely during the daytime (about 50%), and directly results in the production of carbon monoxide (CO) and hydrogen gas (Seinfeld and Pandis, 1998). This pathway is largely uninteresting in terms of atmospheric chemistry, as no HO_x, NO_x, or OVOCs are involved. The left pathway is the second most likely in the daytime (about 39%). Light energizes the HCHO molecule, after which it reacts with O_2 to form HO_2 and HCO, which also quickly reacts with O_2 to form CO and a second HO_2 (Seinfeld and Pandis, 1998). As a result, this pathway creates two HO_x molecules, increasing the oxidizing capacity of the air. The third pathway is the least likely during the daytime (about 11%). OH reacts with HCHO to make water and HCO, which again quickly reacts with O_2 to form CO and HO_2 (Seinfeld and Pandis, 1998).

There is an additional pathway of atmospheric HCHO loss that is not pictured in Fig. 1.3, in which HCHO condenses onto a surface, called dry deposition (see Chap. 3.4 for more details). Contributions from dry deposition are highly dependent on the surface conditions and aerosol concentrations, as it depends on the amount of surface area. At night, this last pathway usually is the most significant near to the surface as no sunlight is present to enable the other three.

Overall, atmospheric HCHO destruction results in a net increase in HO_x, making HCHO one of the largest sources of HO_x. As HO_x is needed to oxidize VOCs in the first place in order to make HCHO, this creates positive feedback for the production of HO_x in the atmosphere. By monitoring concentrations of HCHO, we can measure the amount of HO_x added to the atmosphere by this pathway. As HO_x is a major component in the production of ozone due to VOC oxidation, HCHO concentrations are important to be able to constrain HO_x production in a model.

1.3.2 Importance and Challenges

As HCHO is formed in the oxidation of nearly all VOCs and OVOCs, concentrations of HCHO can give us information about the total amount of VOCs present in a particular parcel of air. If ambient measurements of HCHO concentrations do not match concentrations predicted by computer models, then it shows that the models are still missing some aspect of VOC oxidation. This makes measurements of HCHO critical to validate models of atmospheric chemistry.

Measurements of HCHO do face significant challenges, however. Concentrations of HCHO are quite small and are difficult to detect accurately and selectively (in other words, detecting only HCHO). In order to detect concentrations of HCHO at typical atmospheric levels, it is necessary to use sophisticated, usually expensive, equipment. In addition, the use of HCHO to investigate VOC oxidation can be complicated by direct emissions of HCHO from many sources. These include rural sources, such as trees (Kesselmeier et al., 1997; Villanueva-Fierro et al., 2004) and soil or forest ground litter (see Chap. 3), as well as urban sources, such as industrial processes and vehicles (Anderson et al., 1996; Kean et al., 2001; Garcia et al., 2006; Reyes et al., 2006; Lei et al., 2009). While unimportant far above the emission sources, these direct emissions can be significant near the surface. For HCHO to be useful as a VOC oxidation tracer, it is necessary to know when these emissions are significant and, if so, how to account for them.

1.4 Summary

The consequences of poor air quality to life on Earth are broad and include effects such as increased respiratory/cardiac illness, premature death, and crop failure which can result in famine. In order to understand and reduce poor air quality, it is vital to understand the processes involved in its production. The major contributors to poor air quality include the production of tropospheric ozone and aerosols. These are strongly tied to the oxidation of volatile organic compounds, or VOCs. Oxidized VOCs, or OVOCs, are produced as intermediates in this oxidation. They can either continue reacting in the atmosphere, resulting in further production of ozone, or can stick to particles to form a particular form of aerosol, secondary organic aerosol. HCHO is a key OVOC for two reasons. HCHO is created in the oxidation of nearly all VOCs, making it an ideal marker of VOC oxidation. HCHO is also a significant source of HO_x, a family of compounds involved in VOC oxidation.

In the work presented in this thesis, HCHO is used as a way of quantifying the amount of VOC oxidation occurring in a given volume of air. Chapter 2 discusses some of the specific challenges with regard to HCHO measurement and the FILIF technique that was developed to address these challenges. Chapter 3 discusses using the FILIF technique for HCHO detection in combination with a technique called eddy covariance. The combination of these techniques enabled the measurement of the amount of HCHO moving out of a forest canopy which provided insight into the chemistry inside the forest canopy. Chapter 4 discusses the combination of HCHO measurements with measurements of a different OVOC, glyoxal, to be able to estimate changes in the types of VOCs reacting in a volume of air.

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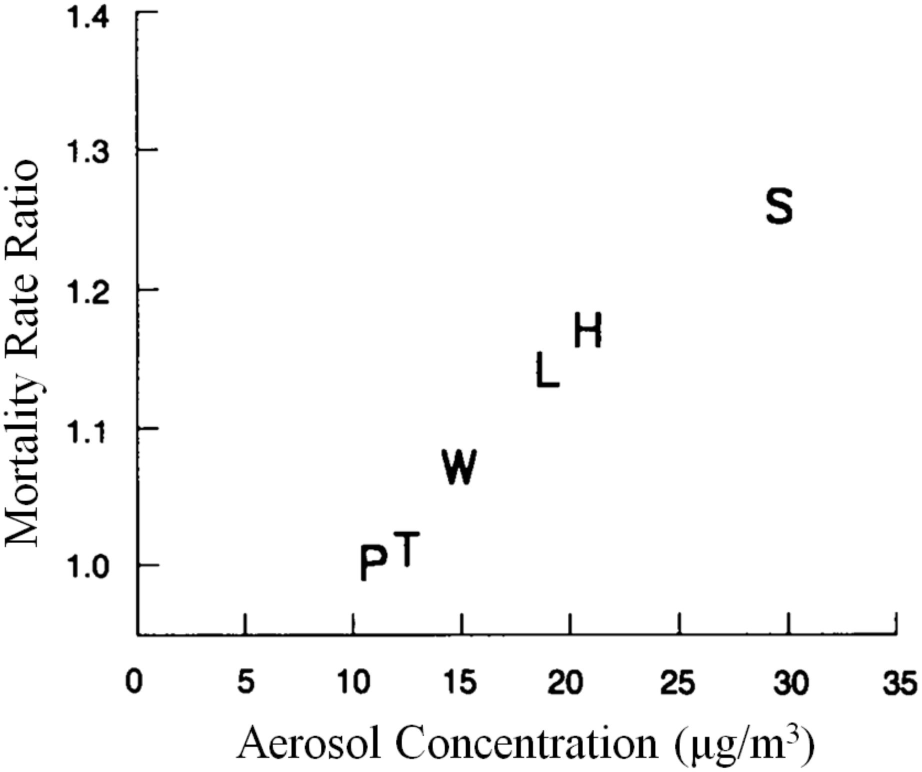

Fig. 1.1.— Reproduced from Dockery et al. (1993). Correlations of aerosol concentrations with increased mortality rate in six U.S. cities: Watertown, Massachusetts (W); Harriman, Tennessee (H); St. Louis, Missouri (L); Steubenville, Ohio (S); Portage, Wisconsin (P); and Topeka, Kansas (T). The y-axis represents the ratio of deaths in a given city normalized by the deaths in Portage, WI.

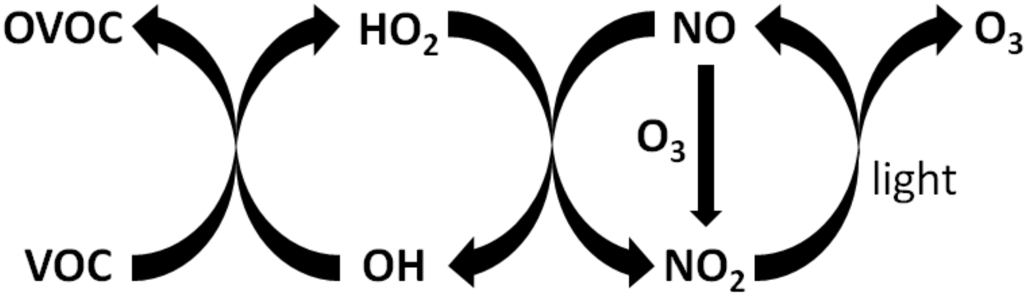

Fig. 1.2.— Formation of tropospheric ozone (O_3) through the cycling of HO_x and NO_x. VOC oxidation results in an additional way to convert NO to NO_2, which leads to more O_3.

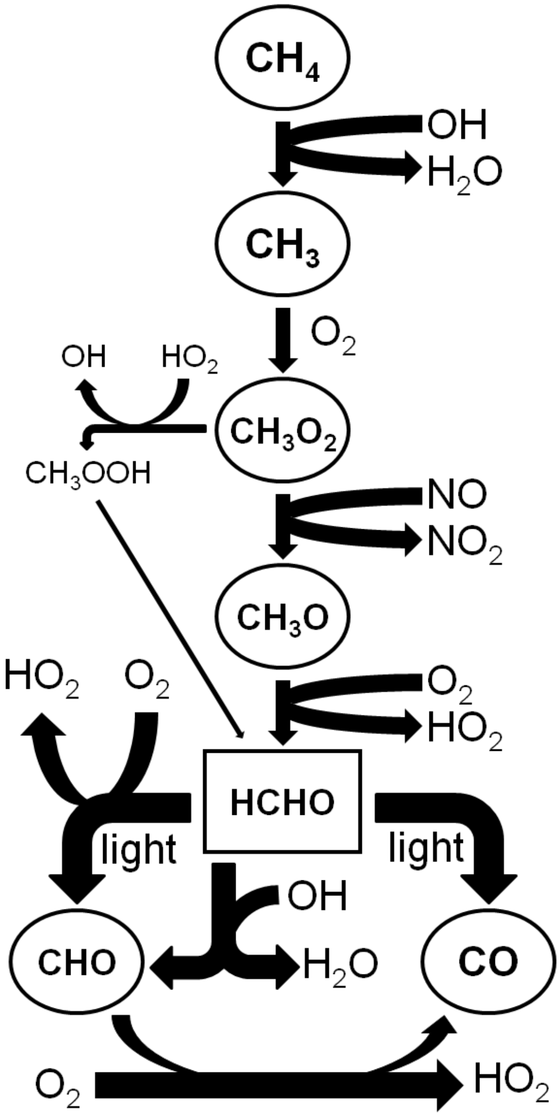

Fig. 1.3.— Schematic of methane (CH_4) oxidation showing the production and destruction of HCHO. The vertical pathway (reaction with NO) production pathway is dominant under urban conditions. The reaction of the RO_2 radical (CH_3O_2) with HO_2 becomes more significant under remote conditions and leads to different oxidation products, such as peroxides (ROOH). These peroxides can still form HCHO, but a different amount than formed by the NO pathway.