Atmospheric chemistry at night

Atmospheric chemistry is driven, in large part, by sunlight. Air pollution, for example, and especially the formation of ground-level ozone, is a day-time phenomenon. So what happens between the hours of sunset and sunrise?

This Brief examines the night-time chemistry of the troposphere (the lower-most atmospheric layer from the surface up to ≈12 km). Atmospheric chemistry is predominantly oxidation chemistry, and the vast majority of gases from emission sources are oxidised within the troposphere. The unique aspects of atmospheric oxidation chemistry at night are best appreciated by first reviewing the day-time chemistry.

**Day-time tropospheric chemistry**

The first Environmental Brief (1) considered in detail the photolysis of ozone at near-ultraviolet wavelengths to generate electronically excited oxygen atoms:

\[ \text{O}_3 + \text{light} (\lambda < 340\text{nm}) \rightarrow \text{O}(^{1}\text{D}) + \text{O}_2 \]  

**[R1]**

Reaction R1 is a key process in tropospheric chemistry because the O(\(^{1}\text{D}\)) atom has sufficient excitation energy to react with water vapour to produce hydroxyl radicals:

\[ \text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \]  

**[R2]**

Reaction with oxidants such as OH is typically the rate determining step for removing trace gases from the atmosphere. Almost all gases emitted into the atmosphere derive from processes occurring at the Earth’s surface (e.g. natural emissions from biota on land or in the oceans; anthropogenic emissions from agriculture or from fossil fuel combustion for energy generation, industry and transport). Thus gases enter the atmosphere “from the bottom”, where they also encounter the OH radical. Only the few gases that are unreactive towards OH radicals (e.g. chlorofluorocarbons) persist long enough in the troposphere to be transported up to the stratosphere.

The chemistry of OH is inextricably linked to the chemistry of nitrogen oxides (NO\(_x\) = NO + NO\(_2\)). Reactions of OH with atmospheric trace gases usually produce hydroperoxy radicals, HO\(_2\), which are recycled back to OH by reaction with NO. In the process, NO is oxidised to NO\(_2\). The latter photolyses to produce ground-state oxygen atoms, O(\(^{3}\text{P}\)), that recombine with molecular oxygen to produce ozone. Tropospheric ozone is a harmful air pollutant and a greenhouse gas.

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  

**[R3]**

\[ \text{NO}_2 + \text{light} (\lambda < 420\text{nm}) \rightarrow \text{NO} + \text{O}(^{3}\text{P}) \]  

**[R4]**

\[ \text{O}(^{3}\text{P}) + \text{O}_2 \rightarrow \text{O}_3 \]  

**[R5]**

**Night-time tropospheric chemistry**

It is an obvious statement: there is no sunlight at night. Therefore the night-time concentration of OH is (almost) zero. Instead, another oxidant, the nitrate radical, NO\(_3\), is generated at night by the reaction of NO\(_2\) with ozone. NO\(_3\) radicals further react with NO\(_2\) to establish a chemical equilibrium with N\(_2\)O\(_5\).

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  

**[R6]**

\[ \text{NO}_3 + \text{NO}_2 \equiv \text{N}_2\text{O}_5 \]  

**[R7]**

Reaction R6 happens during the day too. However, NO\(_3\) is quickly photolysed by daylight, and therefore NO\(_3\) and its equilibrium partner N\(_2\)O\(_5\) are both heavily suppressed during the day.

\[ \text{NO}_3 + \text{light} (\lambda < 590\text{nm}) \rightarrow \text{NO}_2 + \text{O}(^{3}\text{P}) \]  

**[R8]**

**Figure 1** provides an overview of night-time chemistry. It is worth noting that night-time chemistry could not exist in isolation from day-time chemistry: reaction R6 needs ozone to oxidise NO\(_2\) to NO\(_3\), and ozone is a product of day-time photochemistry. The chemistries of the two most important night-time species, NO\(_3\) and N\(_2\)O\(_5\), are discussed below. For readers wishing to know more detail, I recommend a recent review of night-time chemistry by Brown and Stutz (2).

**NO\(_3\) chemistry**

The night-time oxidant, NO\(_3\), is less reactive than its day-time counterpart, OH. For example, OH reacts with volatile organic compounds (VOC) by abstracting a hydrogen atom. NO\(_3\) generally does not perform hydrogen abstraction reactions, although there are some notable exceptions: the NO\(_3\) + CH\(_3\)SCH\(_3\) reaction is an efficient sink for the dimethyl sulphide emitted by plankton in the surface ocean, and is a route to produce sulphate aerosol around which marine cloud droplets can nucleate.

Instead, NO\(_3\) more usually reacts with carbon-carbon double bonds; this reaction is also available to OH. Indeed OH reacts faster with double bonds than NO\(_3\) but, crucially,
because atmospheric concentrations of NO₃ at night are typically two orders of magnitude greater than day-time OH concentrations, the amounts of unsaturated VOCs oxidised by NO₃ are comparable to, and sometimes exceed, the amounts oxidised by OH. NO₃ reacts particularly rapidly with isoprene and terpenoid compounds emitted by plants, for which NO₃ is often their dominant sink. An important difference is that the radical chain reactions subsequent to the initial OH + VOC reaction recycle OH to react again (R3), whereas NO₃ + VOC reactions are usually stoichiometric in NO₃. The addition of NO₃ to double bonds generates nitrate-substituted peroxy radicals, some of which react/decompose to generate HO₂ radicals; it is thought that reaction of this HO₂ with NO₃ (R3) could generate low levels of OH at night, potentially propagating the oxidation of compounds that do not themselves react with NO₃. The non-radical oxidation products of NO₃ + VOC reactions are multi-functional organic nitrates containing alcohol, peroxide or carbonyl groups. These compounds have low vapour pressures and consequently partition onto atmospheric particles to generate secondary organic aerosol (SOA) which is an air pollutant. Laboratory experiments have found higher SOA yields from NO₃ + VOC reactions than the corresponding OH reactions. Laboratory studies also suggest that NO₃ radicals react directly with organic components in aerosol particles.

**N₂O₅ chemistry**

Much of the atmospheric chemistry of N₂O₅ occurs on the surfaces of, or inside, aerosol particles. N₂O₅ is readily taken up by aqueous inorganic particles and water droplets, where it undergoes hydrolysis with liquid water to produce nitric acid. The latter is then often neutralised by the uptake of ammonia.

$$N₂O₅(g) + H₂O(aerosol) \rightarrow 2 HNO₃(aerosol) \quad [R9]$$

$$NH₃(g) + HNO₃(aerosol) \rightarrow NH₄NO₃(aerosol) \quad [R10]$$

Reactions R9 and R10 and the subsequent deposition of nitrate aerosol to the surface is one of the few mechanisms by which NO₃ is removed from the atmosphere. This night-time sink can remove as much NOₓ as the day-time gas-phase reaction of OH with NO₂ to produce nitric acid. Night-time loss of N₂O₅ limits the availability of NO₂ for the photochemical production of ozone the following day via reactions R4 and R5 (3).

Another intriguing aspect of the heterogeneous chemistry of N₂O₅ is its reaction with chloride ions in sea salt aerosol to produce nitryl chloride. ClNO₂ is stable at night, but is photolysed within approximately 1 hour of sunrise the next morning. Photoysis liberates chlorine atoms which react with VOCs.

$$N₂O₅(g) + NaCl(aerosol) \rightarrow ClNO₂(g) + NaNO₃(aerosol) \quad [R11]$$

$$ClNO₂ + \text{light} (\lambda < 840nm) \rightarrow Cl + NO₂ \quad [R12]$$

$$Cl + CH₄ \rightarrow CH₃ + HCl \quad [R13]$$

Via the above chemistry, night-time processes enhance the VOC oxidation chemistry occurring the next morning (4). Interestingly, the NO₂ co-product of photolysis R12 remains available to contribute to photochemical ozone production, circumventing the usual process by which N₂O₅ uptake onto aerosol removes NOₓ from the atmosphere. Chlorine atoms are more reactive than NO₃ radicals (and more reactive than OH), and so chlorine activation leads to the oxidation of VOCs that do not react with NO₃ directly. Chlorine atom-initiated oxidation of methane R13 has been proposed as an additional minor sink constraining the atmospheric lifetime of this important greenhouse gas.
Measurement of NO₃ and N₂O₅

In large part, the substantial improvements made over the last decade to our understanding of night-time chemical processes are due to the advent of new measurement techniques able to quantify concentrations of NO₃ and N₂O₅ in situ. Before these techniques, the first measurements of ambient NO₃ reported in the late 1970s and early 1980s used differential optical absorption spectroscopy (DOAS) at red visible wavelengths. The very low concentrations of ambient NO₃ required that the absorption measurements be conducted over long light paths through the atmosphere (several kilometres), resulting in an inherent spatial averaging of the NO₃ concentrations measured along the light path, and consequent difficulties in interpreting the observations. The absorption spectrum of N₂O₅ does not have absorption features at any convenient wavelengths, so such instruments could not detect N₂O₅. Instead N₂O₅ concentrations had to be inferred from NO₃ and NO₂ measurements by applying the (then untested) assumption that these species were in equilibrium, R7.

The first in situ “point measurements” of NO₃ were made by electron spin resonance (ESR). However, nowadays most instrumentation uses variants of cavity ring-down spectroscopy (CRDS) and cavity enhanced absorption spectroscopy (CEAS) (5, 6). These methods use many reflections of the probe light beam to achieve multi-kilometre absorption paths through gas samples held inside a high finesse optical cavity. At ground level, and especially if pollution sources are nearby, NO₃ concentrations are suppressed by the fast reaction of NO₃ with NO, the latter being a component of fresh emissions from fossil fuel combustion. Because CRDS and CEAS instruments can be made relatively compact, they have been flown on aircraft (3) and deployed from tall buildings (6) to measure NO₃ concentrations well above the ground. These measurements showed substantial NO₃ concentrations are present away from the surface, indicating that night-time chemistry is more active than previously thought based on ground-based DOAS measurements, and confirming some intriguing earlier DOAS measurements of NO₃ in the free troposphere that suggested large concentrations of NO₃ could exist aloft (7).

CRDS and CEAS instruments also enabled N₂O₅ to be measured for the first time by drawing ambient air through a heated inlet to thermally dissociate N₂O₅ and measuring the extra NO₃ signal (5). These measurements demonstrated that NO₃ and N₂O₅ are in equilibrium, or at least close to equilibrium, in most regions of the atmosphere. There is also generally sufficient NO₃ to drive the equilibrium in favour of N₂O₅.

References


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Pre-flight preparations of the FAAM (Facility for Airborne Atmospheric Measurements) BAE-146 research aircraft before a flight to measure atmospheric composition at night. RONOCO campaign, East Midlands Airport, January 2011.