

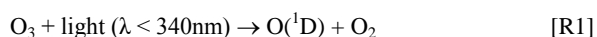
## Atmospheric chemistry at night

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  $\approx 12$  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:



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



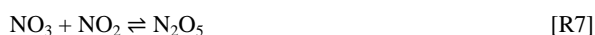
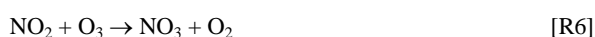
Reaction with oxidants such as OH is typically the rate determining step for removing trace gases from the atmosphere. Almost all gases emitted into the atmosphere derive from processes occurring at the Earth's surface (e.g. natural emissions from biota on land or in the oceans; anthropogenic emissions 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 ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). Reactions of OH with atmospheric trace gases usually produce hydroperoxy radicals,  $\text{HO}_2$ , which are recycled back to OH by reaction with NO. In the process, NO is oxidised to  $\text{NO}_2$ . The latter photolyses to produce ground-state oxygen atoms,  $\text{O}({}^3\text{P})$ , that recombine with molecular oxygen to produce ozone. Tropospheric ozone is a harmful air pollutant and a greenhouse gas.



### 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,  $\text{NO}_3$ , is generated at night by the reaction of  $\text{NO}_2$  with ozone.  $\text{NO}_3$  radicals further react with  $\text{NO}_2$  to establish a chemical equilibrium with  $\text{N}_2\text{O}_5$ .



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



**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  $\text{NO}_2$  to  $\text{NO}_3$ , and ozone is a product of day-time photochemistry. The chemistries of the two most important night-time species,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , are discussed below. For readers wishing to know more detail, I recommend a recent review of night-time chemistry by Brown and Stutz (2).

### $\text{NO}_3$ chemistry

The night-time oxidant,  $\text{NO}_3$ , is less reactive than its day-time counterpart, OH. For example, OH reacts with volatile organic compounds (VOC) by abstracting a hydrogen atom.  $\text{NO}_3$  generally does not perform hydrogen abstraction reactions, although there are some notable exceptions: the  $\text{NO}_3 + \text{CH}_3\text{SCH}_3$  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,  $\text{NO}_3$  more usually reacts with carbon-carbon double bonds; this reaction is also available to OH. Indeed OH reacts faster with double bonds than  $\text{NO}_3$  but, crucially,

because atmospheric concentrations of  $\text{NO}_3$  at night are typically two orders of magnitude greater than day-time OH concentrations, the amounts of unsaturated VOCs oxidised by  $\text{NO}_3$  are comparable to, and sometimes exceed, the amounts oxidised by OH.  $\text{NO}_3$  reacts particularly rapidly with isoprene and terpenoid compounds emitted by plants, for which  $\text{NO}_3$  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  $\text{NO}_3$  + VOC reactions are usually stoichiometric in  $\text{NO}_3$ . The addition of  $\text{NO}_3$  to double bonds generates nitrate-substituted peroxy radicals, some of which react/decompose to generate  $\text{HO}_2$  radicals; it is thought that reaction of this  $\text{HO}_2$  with NO (R3) could generate low levels of OH at night, potentially propagating the oxidation of compounds that do not themselves react with  $\text{NO}_3$ . The non-radical oxidation products of  $\text{NO}_3$  + 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  $\text{NO}_3$  + VOC reactions than the corresponding OH reactions. Laboratory studies also suggest that  $\text{NO}_3$  radicals react directly with organic components in aerosol particles.

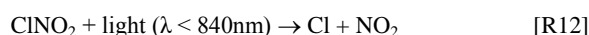
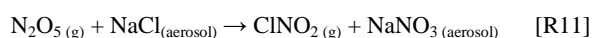
### $\text{N}_2\text{O}_5$ chemistry

Much of the atmospheric chemistry of  $\text{N}_2\text{O}_5$  occurs on the surfaces of, or inside, aerosol particles.  $\text{N}_2\text{O}_5$  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.

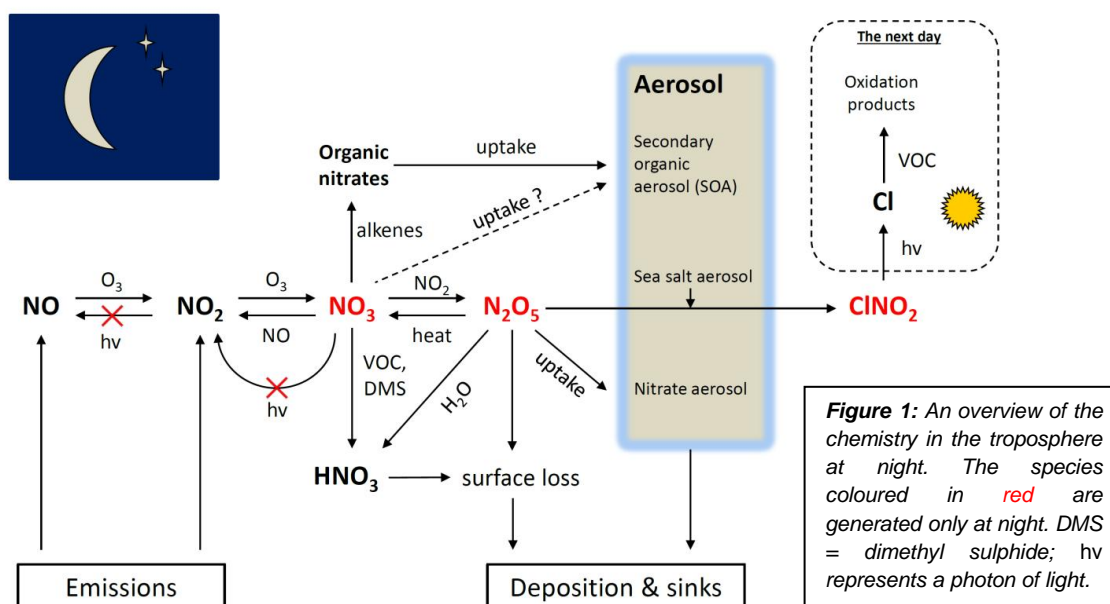


Reactions R9 and R10 and the subsequent deposition of nitrate aerosol to the surface is one of the few mechanisms by which  $\text{NO}_x$  is removed from the atmosphere. This night-time sink can remove as much  $\text{NO}_x$  as the day-time gas-phase reaction of OH with  $\text{NO}_2$  to produce nitric acid. Night-time loss of  $\text{N}_2\text{O}_5$  limits the availability of  $\text{NO}_2$  for the photochemical production of ozone the following day *via* reactions R4 and R5 (3).

Another intriguing aspect of the heterogeneous chemistry of  $\text{N}_2\text{O}_5$  is its reaction with chloride ions in sea salt aerosol to produce nitryl chloride.  $\text{ClNO}_2$  is stable at night, but is photolysed within approximately 1 hour of sunrise the next morning. Photolysis liberates chlorine atoms which react with VOCs.



*Via* the above chemistry, night-time processes enhance the VOC oxidation chemistry occurring the next morning (4). Interestingly, the  $\text{NO}_2$  co-product of photolysis R12 remains available to contribute to photochemical ozone production, circumventing the usual process by which  $\text{N}_2\text{O}_5$  uptake onto aerosol removes  $\text{NO}_x$  from the atmosphere. Chlorine atoms are more reactive than  $\text{NO}_3$  radicals (and more reactive than OH), and so chlorine activation leads to the oxidation of VOCs that do not react with  $\text{NO}_3$  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.



**Figure 1:** An overview of the chemistry in the troposphere at night. The species coloured in red are generated only at night. DMS = dimethyl sulphide; hv represents a photon of light.

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## Measurement of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>

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 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> *in situ*. Before these techniques, the first measurements of ambient NO<sub>3</sub> reported in the late 1970s and early 1980s used differential optical absorption spectroscopy (DOAS) at red visible wavelengths. The very low concentrations of ambient NO<sub>3</sub> required that the absorption measurements be conducted over long light paths through the atmosphere (several kilometres), resulting in an inherent spatial averaging of the NO<sub>3</sub> concentrations measured along the light path, and consequent difficulties in interpreting the observations. The absorption spectrum of N<sub>2</sub>O<sub>5</sub> does not have absorption features at any convenient wavelengths, so such instruments could not detect N<sub>2</sub>O<sub>5</sub>. Instead N<sub>2</sub>O<sub>5</sub> concentrations had to be inferred from NO<sub>3</sub> and NO<sub>2</sub> measurements by applying the (then untested) assumption that these species were in equilibrium, R7.

The first *in situ* “point measurements” of NO<sub>3</sub> 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, NO<sub>3</sub> concentrations are suppressed by the fast reaction of NO<sub>3</sub> 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 NO<sub>3</sub> concentrations well above the ground. These measurements showed substantial NO<sub>3</sub> 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 NO<sub>3</sub> in the free troposphere that suggested large concentrations of NO<sub>3</sub> could exist aloft (7).

CRDS and CEAS instruments also enabled N<sub>2</sub>O<sub>5</sub> to be measured for the first time by drawing ambient air through a heated inlet to thermally dissociate N<sub>2</sub>O<sub>5</sub> and measuring the extra NO<sub>3</sub> signal (5). These measurements demonstrated that NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are in equilibrium, or at least close to equilibrium, in most regions of the atmosphere. There is also generally sufficient NO<sub>2</sub> to drive the equilibrium in favour of N<sub>2</sub>O<sub>5</sub>.

## References

1. M. King, ‘Calculating photolysis rates and estimating photolysis lifetimes’ (*ECG Environmental Brief* No 1), *ECG Bulletin*, July 2013, p 21.
2. S. S. Brown and J. Stutz, ‘Night-time radical observations and chemistry’. *Chem. Soc. Rev.*, **41**, 6405-6447, 2012; doi: 10.1039/c2cs35181a.
3. S. S. Brown *et al.*, ‘Variability in nocturnal nitrogen oxide processing and its role in regional air quality’. *Science*, **311**, 67-70, 2006; doi: 10.1126/science.1120120.
4. J. A. Thornton *et al.*, ‘A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry’. *Nature*, **464**, 271-274, 2010; doi:10.1038/nature08905.
5. S. S. Brown, H. Stark, S. J. Ciciora, and A. R. Ravishankara, ‘*In situ* measurement of atmospheric NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> via cavity ring-down spectroscopy’. *Geophys. Res. Lett.*, **28**, 3227-3230, 2001; doi: 10.1029/2001GL013303.
6. A. K. Benton *et al.*, ‘Night-time chemistry above London: measurements of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> from the BT Tower’. *Atmos. Chem. Phys.*, **10**, 9781-9795, 2010; doi: 10.5194/acp-10-9781-2010.
7. S. R. Aliwell and R. L. Jones, ‘Measurements of tropospheric NO<sub>3</sub> at mid-latitude’. *J. Geophys. Res. (Atmospheres)*, **103**, 5719-5727, 1998.

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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.*