



## Application of Ion Chemistry to Tropospheric VOC measurements<sup>\*)</sup>

Armin Hansel, Armin Wisthaler, Martin Graus, Wolfgang Grabner

*Institut für Ionenphysik, Universität Innsbruck, Austria, armin.hansel@uibk.ac.at*

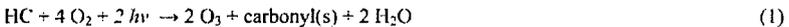
### Abstract

In Werner Lindingers laboratory we have developed a mass spectrometric technique, named Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS), which utilizes positive ion chemistry to measure trace neutral concentrations in air. During the last few years PTR-MS has been used in food research, in medical applications, and in environmental applications to gain gas phase information of volatile organic compounds (VOCs) at parts per trillion (pptv) levels. The real-time method relies on proton transfer reactions between  $\text{H}_3\text{O}^+$  primary ions and organic trace gases (VOCs) which have a higher proton affinity than water molecules. Organic trace gases such as hydrocarbons, carbonyls, alcohols, acetonitrile, and others can be monitored on-line. In this paper we will discuss the mass spectrometric method and present recent results on tropospheric VOC measurements.

### Introduction

The main interest in tropospheric VOCs originating from biogenic sources such as forests and from anthropogenic sources such as cities is that these reactive trace gases can have a significant impact on levels of oxidants such as ozone ( $\text{O}_3$ ) and the hydroxyl radical (OH), and on secondary organic aerosol formation [1]. In addition, oxygenated VOCs like acetone are an important source of  $\text{HO}_x$  ( $=\text{OH} + \text{HO}_2$ ) radicals in the upper troposphere [2]. Atmospheric degradation of acetone and acetaldehyde produce acetylperoxy radicals. These radicals associate with  $\text{NO}_2$  to form peroxyacetic nitric anhydride (PAN;  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ) which acts as a relatively unreactive temporary reservoir for nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). It is in this form that  $\text{NO}_x$  equivalents are transported over wide distances, e.g. from urban to rural areas, where they can contribute to photochemical ozone formation with biogenic VOCs.

Photochemical reactions of VOCs in the troposphere are complex, depending on the presence of OH,  $\text{NO}_x$  and ultraviolet light. The generally accepted net reaction of a simple hydrocarbon (HC) is the following [1]:



OH and  $\text{NO}_x$  do not appear in the net reaction as they are regenerated in other reactions. Notably, atmospheric oxidation of HC (at sufficient  $\text{NO}_x$ ) results in the production of ozone and carbonyl compounds that can undergo further photochemistry. A VOC generally contributes more to ozone formation the higher its density is and the faster its reaction with OH radicals proceeds. Thus, in order to understand quantitatively tropospheric ozone chemistry, it is a necessary prerequisite to know the VOC distribution within the troposphere as well as VOC fluxes from individual sources. The examples below illustrate how the use of the PTR-MS technology [3] has enhanced our understanding of anthropogenic VOC emissions, biosphere-atmosphere exchange processes, and photochemical processing of both anthropogenic and biogenic VOCs in the troposphere.

---

<sup>\*)</sup> This lecture is dedicated to the memory of our teacher, colleague and friend Prof. Werner Lindinger, who passed away in February 2001.

## Tropical Troposphere

Tropical regions with reactive hydrocarbon emissions from forests of greater than  $10^{15}$  g C per year are especially important in determining the oxidizing capacity of the atmosphere because of the high abundance of UV radiation and high relative humidity. An other important aspect of tropospheric chemistry is the influence of anthropogenic activities. The rapid growth of human population and industrial development in China and South East Asia will increase air pollution in these tropical regions. An increase in carbonyl compounds in the tropical boundary layer for example has the potential to influence the upper troposphere. Carbonyl compounds transported into the upper troposphere by convection may act as free radical precursor and directly influence the oxidizing capacity of the upper troposphere [2,4].

During the last few years PTR-MS [5] has been used in several field campaigns to gain gas phase information of VOCs at parts per trillion (pptv) levels. Organic trace gases such as hydrocarbons, carbonyls, alcohols, acetonitrile, and others have been recorded in two different tropical regions. In Amazonia (LBA-Claire 1999), a largely unpolluted region which is optimally located to study chemical processes induced by tropical forest emissions [6,7] and above the Indian Ocean. The Indian Ocean Experiment (INDOEX 1999) offered the opportunity to study the influence of anthropogenic pollution in the tropical troposphere. Asia is already a significant source of pollution. Carbon monoxide (CO) from Asia is estimated to be 50 % larger than the combined emissions from Europe and N-America. CO sources are different in Asia from those in Europe and N-America. In India and surrounding countries biofuel use and agricultural burning cause strong CO emissions. Acetonitrile ( $\text{CH}_3\text{CN}$ ) is a unique gaseous tracer for biomass burning and can, in combination with other species like acetone, methanol, and CO provide strong indications about air pollution sources. Ship- and airborne PTR-MS measurements of organic trace gases in real time over a broad spatial extent of the Indian Ocean turned out to be of great importance to detect pollution outflow from India and helped to quantify the relative amount of CO originating from biomass burning [8,9,10].

## Air Pollution in Cities

During the Southern Oxidants Study (SOS) 1999 campaign ambient air samples were analyzed at Cornelia Fort Airport, Nashville, TN. Even at a ground-based site a high time resolution in VOC measurements is useful to investigate the photochemistry of anthropogenic and biogenic emissions under the influence of varying meteorological conditions. Aromatic species such as benzene and toluene with long atmospheric lifetimes showed strong diurnal variations having enhanced concentrations during night time decreasing shortly after sunrise to rather low values during day time. This frequently found diurnal pattern was a result of strong boundary layer dynamics and local transportation related emission sources. As more reactive species are considered, such as isoprene, a biogenic hydrocarbon (BHC) and its oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR), the isoprene photochemistry [11] appeared to be occasionally enhanced in  $\text{NO}_x$  rich plumes that were advected to the site over deciduous forested land leading to enhanced peroxyacetic nitric anhydride (MPAN) values. MPAN is formed almost entirely from the oxidation of isoprene in the presence of  $\text{NO}_x$  and is an excellent indicator of recent ozone production from BHC. In contrast peroxypropionic nitric anhydride (PPN) is thought to be a marker for anthropogenic hydrocarbon (AHC) driven photochemistry [12]. Measurements [13] of peroxyacetic nitric anhydride (PAN), a general product of hydrocarbon- $\text{NO}_x$  photochemistry. MPAN and PPN were used to estimate the contribution of BHC and AHC to regional tropospheric ozone production, which is a serious air quality problem in the South East of the United States especially during summer time.

During the Texas Air Quality Study (TexAQ5 2000) ambient air was analyzed on-board the National Center for Atmospheric Research (NCAR) Electra aircraft using the Innsbruck PTR-MS. Molecular-level information of VOCs such as acetaldehyde, isoprene, toluene, ketones and PAN were obtained at parts per trillion (pptv) levels with a time resolution of typically 30 seconds. This high time resolution was useful in characterizing individual contributions of distinct sources for ozone production in the greater Houston area. On several flights, wind direction and speed were such that these airborne VOC measurements allowed to differentiate among anthropogenic petrochemical, urban, and power plant plumes. In-situ acetaldehyde measurements, taken in aircraft transects of the Houston metropolitan area, confirm the importance of propene emissions from localized point sources to the photochemical processing of NO<sub>x</sub> and the rapid formation of ozone and PAN within short distances from the co-located NO<sub>x</sub> and propene emission sources. Biogenic isoprene emissions contribute also to ozone formation. Fast response measurements of this compound and its photooxidation products MVK & MACR and hydroxyacetone revealed that biogenic emission sources are primarily located north east of Houston and contribute to ozone formation in the metropolitan Houston area only under certain meteorological conditions.

## References

- [1] Atkinson, R, 2000: Atmospheric chemistry of VOCs and NO<sub>x</sub>. *Atmos. Environ.* **34**, 2063-2101.
- [2] Singh, H. B., M. Kannakidou, P. J. Crutzen, & D. Jacob, 1995: High concentrations and photochemical fate of carbonyls and alcohols in the global troposphere. *Nature* **378**, 50-54.
- [3] Hansel, A., A. Jordan, R. Holzinger, P. Prazeller, W. Vogel, W. Lindinger, 1995: Proton transfer reaction mass spectrometry: on-line trace gas analysis at ppb level, *Int. J. of Mass Spectrom. and Ion Processes*, **149/150**, 609-619.
- [4] Wennberg, P. O. et al. 1998: Hydrogen radicals, nitrogen radicals, and the production of ozone in the upper troposphere. *Science* **279**, 49-53.
- [5] Lindinger, W., A. Hansel, and A. Jordan, 1998: Proton-transfer-reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels. *Chem. Soc. Rev.* **27**, 347-354.
- [6] Warneke, C., R. Holzinger, A. Hansel, A. Jordan, and W. Lindinger, U. Pöschl, J. Williams, P. Hoor, H. Fischer, and P.J. Crutzen, H. A. Scheeren, J. Lelieveld, 2001: Isoprene and its oxidation products methyl vinyl ketone, methacrolein, and isoprene related peroxides measured on-line over a tropical rain forest in Suriname in March 1998. *J. Atmos. Chem.* **38**, 167-185.
- [7] Pöschl, U., J. Williams, P. Hoor, H. Fischer, P. J. Crutzen, C. Warneke, R. Holzinger, A. Hansel, A. Jordan, W. Lindinger, H. A. Scheeren, W. Peters, J. Lelieveld, 2001: High Acetone Concentrations throughout the 0-12 km Altitude Range over the Tropical Rainforest in Surinam, *J. Atmos. Chem.* **38**, 115-132.
- [8] Lelieveld, J., et al., 2001: The Indian Ocean Experiment: Widespread Air Pollution from South and Southeast Asia. *Science*, **291**, 1031-1036.
- [9] Sprung, D., C. Jost, T. Reiner, A. Hansel, and A. Wisthaler, 2001: Airborne measurements of acetone and acetonitrile in the tropical Indian Ocean boundary layer and free troposphere: Aircraft-based intercomparison of AP-CIMS and PTR-MS measurements. *J. Geophys. Res.* **106**, 28511-28528.
- [10] Wisthaler, A., A. Hansel, R. R. Dickerson, and P. J. Crutzen, 2001: Organic trace gas measurements by PTR-MS during INDOEX 1999. *J. Geophys. Res.* in press.
- [11] Stroud, C.A., J.M. Roberts, E.J. Williams, D. Heried, D.D. Parish, W. Angevine, and F.C. Fehsenfeld, A. Wisthaler and A. Hansel, M. Martinez-Harder, H. Harder and W.H. Brune, B. Alicke and J. Stutz, A.B. White, 2002: Nighttime Isoprene trends at an urban forested site during the 1999 Southern Oxidant Study, *J. Geophys. Res.* in press.
- [12] Hansel, A., and A. Wisthaler, 2000: A Method for Real-Time Detection of PAN, PPN and MPAN in Ambient Air, *Geophys. Res. Lett.* **27**, 895-898.
- [13] Roberts, J.M., et al., 1998, *J. Geophys. Res.*, **103**, 22,473-22,490.