

## Thermodynamic constraints on methanogenic PAH degradation

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Methanogenic degradation of hydrocarbons has long been considered impossible, but recent evidence from contaminated near surface environments and biodegrading petroleum reservoirs suggests that this is not necessarily the case. We have developed the concept of a 'window of opportunity', and used it to evaluate the range of conditions under which methanogenic degradation of alkanes and selected polycyclic aromatic hydrocarbons (PAHs) is thermodynamically feasible [1, 2]. Here we take this approach one step further and apply it to the group additivity equations underlying the structure of PAHs. This allows us to (i) systematically evaluate the energetics of a wide variety of PAHs, including the complete EPA-16 series typically studied in environmental chemistry and toxicology, and (ii) to predict which PAHs should resist methanogenic degradation on thermodynamic grounds.

Under standard conditions (25°C, PAHs at their aqueous solubilities, gases at 1 atm) methanogenic degradation of the EPA-16 PAHs yields between 188 and 357 kJ/mol. Per mole of methane produced this is 19 to 39 kJ/mol, indicating that PAH based methanogenesis is exergonic for all PAHs in the EPA-16 series. There is a clear correlation between C/H and  $\Delta G^\circ$  in kJ/mol CH<sub>4</sub>, except in PAHs that contain a 5-carbon ring. This trend suggested to us that above a certain size methanogenic degradation of PAHs will be endergonic.

The  $\Delta G^\circ$  values for the methanogenic conversion of the various constituent groups of benzenoid rings range between 13 and -34 kJ/mol CH<sub>4</sub>. The highest value is found for carbon atoms that are bound to aromatic carbons only. Based on these values we calculate that for selected condensed structures consisting of more than 40 6-carbon rings (C<sub>106</sub>H<sub>28</sub>) methanogenic degradation of PAHs is endergonic.

[1] Dolfing *et al.* (2008) *The ISME J.* **2**, 442-452. [2] Dolfing *et al.* (2009) *Microb. Biotechnol.* **2**, (in press), doi:10.1111/j.1751-7915.2009.00096.x

## On the formation of organic acids during the photooxidation of $\alpha$ -pinene and trimethylbenzene

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### Introduction

Organic acids in the atmosphere are formed via the ozonolysis of alkenes and reactions of OH radicals with volatile organic compounds (VOC). Due to their low vapour pressure they are often found in secondary organic aerosol. It has also been hypothesized that organic acids are involved in the particle nucleation process [1].

### Experimental

We used a wet effluent diffusion denuder and aerosol collector sampling system in combination with ion chromatography (IC) coupled to mass spectrometry (MS) to sample and analyze organic acids in the gas and the aerosol phase. Measurements were performed quasi-online during  $\alpha$ -pinene/NO<sub>x</sub> and 1,3,5-trimethylbenzene/NO<sub>x</sub> photo-oxidation experiments in a smog chamber. The elemental composition of most acids were determined from additional high resolution Orbitrap-MS measurements.

### Discussion of Results

The current knowledge of the oxidation of VOCs is to a large degree implemented into models such as the Master Chemical Mechanism (MCM) [2]. A comparison of our measurements with the MCM revealed that organic acid formation in the model is not well represented. We observed many more acids than contained in the mechanism and in many cases organic acids do appear in a much earlier phase of the reaction than predicted. This may play an important role in the formation and growth of secondary organic aerosols.

[1] Zhang *et al.* (2004) *Science* **304**, 1487-1490. [2] Saunders *et al.* (2003) *Atmos. Chem. Phys.* **3**, 161-180.