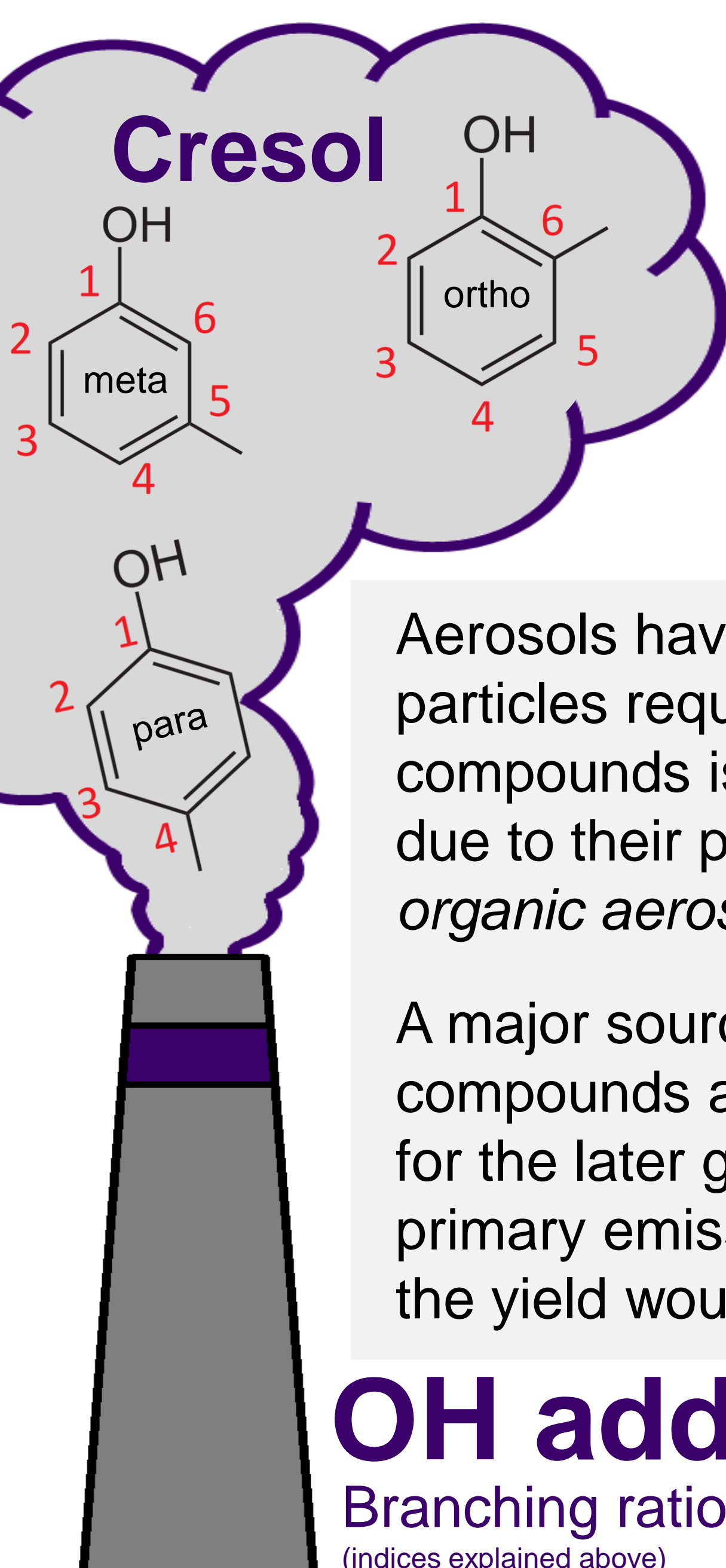


Computational study of cresol autoxidation: Cresol to aerosol precursor via fast ring opening

Aliisa Ojala, Siddharth Iyer

Tampere University, Faculty of Engineering and Natural Sciences, Aerosol Physics



Overview

Aerosols have an impact on the climate and human health. They originate from various sources and grow by condensation. Small particles require extremely low volatility compounds to explain the observed growth. A mechanism for the formation of these compounds is the oxidation of *volatile organic compounds* (VOCs). This can lead to *highly oxygenated molecules* (HOMs), which due to their polar functional groups have low volatility. They therefore enhance particle growth and acts as a source of *secondary organic aerosol* (SOA).

A major source of VOCs are anthropogenic aromatic compounds, especially BTEX (benzene, toluene, ethylbenzene, xylenes) compounds and their later generation products. While the first generation has received a great deal of attention, this is less the case for the later generation products. In this work, all three cresol isomers are studied computationally. They can originate from both primary emissions and as second-generation oxidation products of toluene with a high yield ~20%. Their impact is even higher than the yield would imply, with the cresol pathway expected to account for up to 40% of toluene-related SOA formation^[1].

OH addition

Branching ratios (%)
(indices explained above)

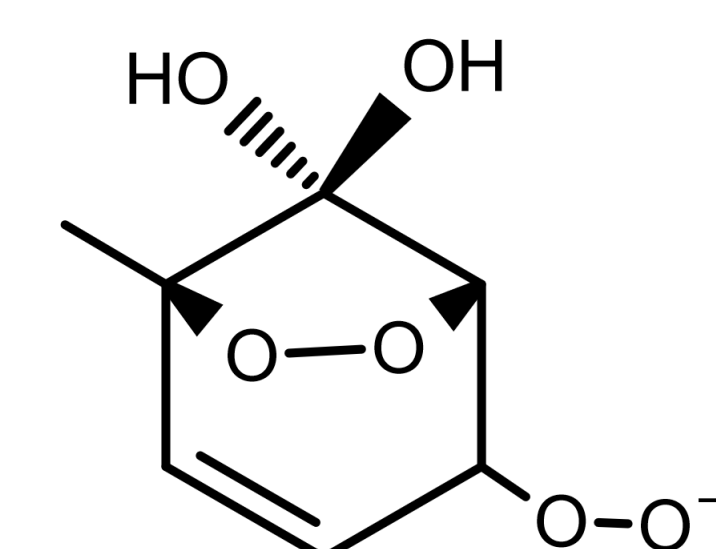
cresol	1	2	3	4	5	6
ortho	6.2	69.9	0.4	1.5	0.8	21.2
meta	0.1	76.7	0.2	5.1	0.1	17.9
para	2.2	92.2	1.6	4.1	-	-

... followed by
multiple steps of

Autoxidation

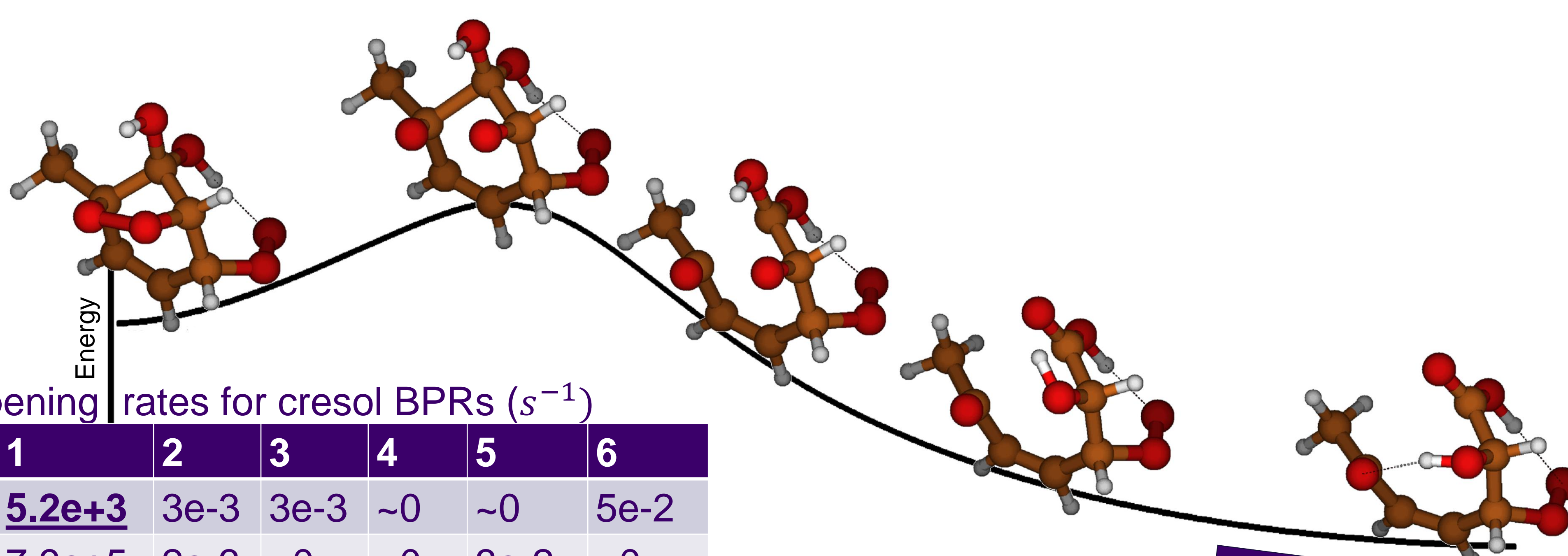
...leads to

Bicyclic peroxy radicals (BPRs)



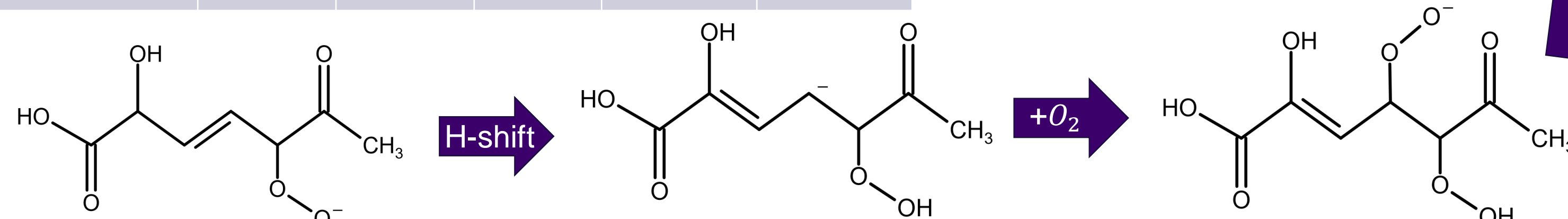
o-cresol BPR (pos. 1)

HOMs can form via *autoxidation*, which is a sequential process of intramolecular reactions of peroxy radicals followed quickly by O_2 additions. This can be initiated by an OH-radical. OH addition for cresols can happen to different positions. After multiple autoxidation steps, this can lead to bicyclic peroxy radicals (BPRs), which are the focus of this work. The BPR structures differ depending on the OH addition position. BPRs can undergo *ring opening* studied in this work, which lifts the steric hindrance of the ring structure^[2]. This leads to rapid HOM formation via further autoxidation, which then acts as aerosol precursor. DFT calculations are done at ω B97X-D/aug-cc-pVTZ-level for geometry optimization and frequency calculations with single point energies calculated at ROHF-ROCCSD(T)-F12a/cc-pVDZ-F12-level. Single conformer TST values are presented.



Ring opening rates for cresol BPRs (s^{-1})

cresol	1	2	3	4	5	6
ortho	5.2e+3	3e-3	3e-3	~0	~0	5e-2
meta	7.9e+5	2e-3	~0	~0	3e-2	~0
para	1.1e+5	5e-2	~0	9e-2	-	-



... that can undergo
Ring opening

Rapid autoxidation!

...eventually forming
Highly oxygenated molecules (HOMs)

...that acts as aerosol precursor.

Conclusions

Position 1 addition shows fast ring opening rates similar to primary aromatics, but with notably higher rates ($k_{cresol} \gg 1s^{-1}$). For ortho-cresol this position has a reasonable yield and notable HOM formation is expected on sub-second timescales. The hydrogen shifts after opening are similar, allowing for further autoxidation. Secondary aromatics seem to autoxidize similarly to primary ones. The results of this study shed light on the SOA formation processes in the atmosphere, especially in urban areas. This will improve current models of SOA formation, which are known to have inconsistencies^[3].

References

- [1] Schwantes et al. Atmos. Chem. Phys., 17, 3453–3474, 2017
[2] Iyer et al. Nat Commun 14, 4984, 2023
[3] Nault et al. Atmos. Chem. Phys., 21, 11201–11224, 2021

Acknowledgements

Research Council of Finland (project 355966) and CSC are gratefully acknowledged for funding and computing resources respectively.

Contacts

Aliisa Ojala
aliisa.ojala@tuni.fi