

## STUDYING ETHER BOND CLEAVAGE IN KEROGEN BY PYROLYSIS OF MODEL COMPOUNDS – INSIGHTS INTO MAIN PRODUCTS AND REACTION PATHWAYS

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### Introduction

The thermal maturation of natural macromolecular matter (kerogen) results mainly in fragmentation and the gradual release of liquid and gaseous organic compounds, as well as CO<sub>2</sub> and H<sub>2</sub>O. An exact prediction of the composition of the released products and the kinetics of their formation is difficult due to the multitude of parallel individual thermochemical processes during maturation. By using structural models of kerogen, molecular modelling provides one opportunity to simulate a large number of thermochemical processes that are characteristic for maturation (Freund et al., 2007; Liu et al., 2015). A different avenue to improve the understanding of individual bond cleavage processes during kerogen maturation is the pyrolysis of organic model compounds representing functional groups in kerogen. The C-O ether bond is a labile bond type which occurs frequently in all kerogen types – often as linkage between different subunits. Thus, the cleavage of ether bonds in kerogen preferentially results in the fragmentation of subunits or, alternatively, in the formation of gas. Though, ether model compounds have been rarely investigated by means of pyrolysis (reviewed by Laidler and McKenney, 1967; Moldoveanu, 2010). Also, most ether pyrolysis studies were conducted at near-ambient pressure although elevated pressure in geologic settings may exert considerable influence on predominating reaction pathways and hence product distribution (Fabuss et al., 1964; Michels et al., 1995; Behar and Vandenbroucke, 1996).

### Results

Here we present the results of closed-system pyrolysis experiments with different ether compounds like butyl ethyl ether (BEE) (additional results to Alpermann and Ostertag-Henning, 2017) and 1-phenoxy-2-phenylethane (PPE) as models for different types of ether linkages in kerogen. The experiments were conducted at different, but elevated pressures ( $\leq 20$  MPa) and temperatures (200-345°C) to simulate thermochemical reactions under geological conditions. The decomposition of BEE yields C<sub>1</sub>-C<sub>4</sub> alkanes and CO as main products and alkenes as by-products. Phenol, ethylbenzene and CO<sub>2</sub> are the main products in the pyrolysis of PPE along with other aromatic compounds as by-products. The product distribution can be explained by a radical chain mechanism initiated by the C-O bond cleavage and secondary reactions of reactive intermediates. A systematic variation of partial pressure in BEE pyrolysis experiments results in significant changes of product distribution and conversion rate.

### Conclusions

The results document main reaction pathways in the pyrolysis of different ethers at elevated pressure, which should operate during kerogen breakdown in geologic settings and allow for a refined assessment of kinetics of kerogen breakdown and hydrocarbon or CO<sub>2</sub> formation. The impact of partial pressure on product distribution as observed in BEE pyrolysis demonstrates an influence of pressure on prevailing reaction pathways in the pyrolysis of

organic model compounds. Thus, results of pyrolysis studies at elevated pressures are an important complement to mechanistic and kinetic data derived from pyrolysis experiments at near ambient pressure conditions.

## References

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