

BIOMASS-BURNING RELATED ATMOSPHERIC AQUEOUS-PHASE CHEMISTRY: KINETICS, PHOTOCHEMISTRY AND MODELLING

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Biomass burning (BB) is a phenomenon studied world-wide with increasing intensity. Recent results suggest that certain SOA products identified in particles originating from BB, have undergone aqueous-phase processing in aerosol-water containing particles, in haze or in clouds. Accordingly, we have studied numerous aqueous-phase reactions of relevance for these sub-systems in recent years in our laboratory and this contribution is giving an account of these studies.

Methoxyphenols are emitted from BB and may directly be oxidized through aqueous-phase reactions. Accordingly, temperature-dependent OH radical reactions have been investigated. Through the competition kinetics method using SCN⁻, rate constants for the reactions of OH have been determined for six substituted methoxyphenol. The reactions with OH are fast with, $k_{298\text{K}} = (1.0 \pm 0.1) \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ for 2-methoxyphenol. Kinetics of OH radical oxidation reactions of the BB related substituted benzoic acids have been studied and rate constants for 4 pairs of acids and their respective anions have been determined. For benzoic acid $k_{298\text{K}, \text{pH} = 1.5} = (3.7 \pm 0.1) \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_{298\text{K}, \text{pH} = 8} = (4.0 \pm 0.2) \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ were measured. These rate constants are moderately fast. For all OH kinetics, studied activation parameters are derived and rate constant compared to the diffusion limits calculated conventionally and by DFT.

To understand the impact of photosensitized reactions on BB SOA formation, different photosensitizers such as imidazole-2-carboxaldehyde (2-IC) and 3,4-dimethoxybenzaldehyde (DMB) were investigated regarding their photochemical properties. Therefore, trapping reactions were performed to determine the quantum yields of the excited triplet state of the photosensitizers ($\phi(2\text{-IC}) = 0.85$, $\phi(\text{DMB}) = 0.37$ at $\text{pH} = 5$ and $T = 298 \text{ K}$) as well as spectroscopic studies to observe the excited triplet state formation at a specific time after the laser pulse ($t_{\text{delay}} = 200 \text{ ns} - 500 \mu\text{s}$) resulting in time-resolved absorbance spectra ($\lambda = 200 - 800 \text{ nm}$).

All of the findings are expected to enhance the predictive capabilities of models such as the chemical aqueous-phase radical mechanism (CAPRAM). To understand the complex multiphase fate of oxygenated aromatic compounds, recently an aqueous-phase oxidation mechanism was developed. First multiphase chemistry model investigations of aromatic BB compounds revealed that the aqueous phase is an important media for oxidations as well as formation of higher nitrated aromatic compounds. Based on the existing aromatic module, it is planned to develop a dedicated BB aqueous-phase chemistry module.