

FORMATION AND AGING OF NITROAROMATIC COMPOUNDS AS IMPORTANT CONSTITUENTS OF ATMOSPHERIC BROWN CARBON

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ABSTRACT

The understanding of atmospheric brown carbon (BrC) formation is of crucial importance for the accurate assessment of its influence on the radiative forcing. In the present thesis, different formation and degradation pathways of methyl-nitrocatechols (MNC), as important constituents of BrC, under atmospherically relevant aqueous-phase conditions were investigated.

The intriguing role of nitrous acid (HONO) in the dark aqueous-phase transformation of catechols was highlighted. HONO was found to have a dual role in the nitration of substituted aromatics; it acts as a catalyst and as an oxidant. In the dominant pathway, HONO is directly involved in the nitration of 3-methylcatechol (3MC) via consecutive oxidation and conjugated addition reactions (nonradical reaction pathway), forming two isomeric products, i.e. 3-methyl-5-nitrocatechol (3M5NC) as the main product and 3-methyl-4-nitrocatechol (3M4NC) as the minor one. The dominant pathway is expected to prevail at a pH typical for atmospheric aerosol (pH around the pK_a of HONO). Under very acidic conditions, two other nitration pathways, oxidative aromatic substitution (electrophilic) and radical recombination, gain in importance.

The subsequent electrochemical generation of 3-methyl-*o*-quinone (MoQ) at the electrode surface and its reaction with NO_2^- in the electrochemical cell allowed us to confirm unambiguously the proposed dominant reaction mechanism. In addition, a new pathway of nitrocatechol hydroxylation by oxidation and the addition of water was discovered. Because of the prolonged light absorption far in the visible light range, the new products (3M5NC-OH and ring cleavage products of 3M4NC) could significantly contribute to the atmospheric light absorption by BrC influencing the radiative balance of the Earth.

Furthermore, the aqueous-phase formation of BrC from 3MC in the presence of HONO/ NO_2^- under simulated sunlight conditions was investigated. Under illumination, the degradation of 3MC is faster in comparison to its degradation in the dark under the same solution conditions. On the other hand, the yield of the main two products of the dark reaction (3M5NC, and 3M4NC) is low, suggesting different degradation pathways of 3MC. Besides the known primary reaction products with distinct absorption at 350 nm, second-generation products responsible for the absorption above 400 nm (e.g., 3M5NC-OH, and the oxidative cleavage products of 3M4NC) were also confirmed in the reaction mixture. The characteristic mass absorption coefficient (MAC) values were found to increase with the increase of $\text{NO}_2^-/3\text{MC}$ concentration ratio and decrease with the increasing wavelength. Our findings reveal that the aqueous-phase processing of 3MC in the presence of $\text{HNO}_2/\text{NO}_2^-$, both under

the sunlight and in the dark, may significantly contribute to secondary organic aerosol (SOA) light absorption.

Keywords: brown carbon chromophores, biomass burning, photooxidation, nitration, hydroxylation, nitrophenols, methylnitrocatechols, mass absorption coefficient.