

Identification of methylnitrocatechols in atmospheric particulate matter: quantum chemical calculations and experimental evidence

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Brown carbon (BrC), as highly variable fraction of organic aerosols, represents an important atmospheric light absorbing particulate matter (PM), which has recently attracted much interest because of its potentially large effect on the Earth's climate. It has been suggested that nitroaromatic compounds (NACs) and, in particular, abundant methylnitrocatechols (MNCs), are the major contributors to atmospheric BrC (Claeys *et al* 2012). Moreover, semi-volatile MNCs are regarded as tracers of processed biomass-burning emissions as well as aged anthropogenic aerosols, whose (trans)formations in the atmospheric waters are completely unknown. Aqueous-phase (non)radical reactions have been the subject of significant interest in the scientific community as they represent potential pathways contributing to the formation and processing of SOA, yet their magnitude in current tropospheric models often remains underestimated. Recent experimental-modeling kinetic study of wood burning pollutant guaiacol nitration under atmospherically relevant conditions highlighted electrophiles as important reactive species in the atmospheric waters, contributing substantially to the transformation of aromatic compounds especially during the night time (Kroflič *et al* 2015).

Assuming that electrophilic nitration is also relevant for atmospheric methylcatechols, structural isomers of guaiacols, we performed quantum chemical calculations of favourable pathways of aqueous-phase electrophilic substitution of 3-methylcatechol with nitronium ion (NO_2^+). The theory predicted the formation of 3-methyl-5-nitrocatechol (3M5NC) and 3-methyl-4-nitrocatechol (3M4NC), while only negligible amounts of 3-methyl-6-nitrocatechol (3M6NC) were expected to form as it is graphically presented in Figure 1. Previous studies report on the overall domination of 4-methyl-5-nitrocatechols (4M5NC), 3M5NC, as well as 3M6NC in nitroaromatic fraction of atmospheric aerosols, together with 4-nitrocatechol (4NC). However, there has been no evidence of the presence of 3M4NC in field aerosols. These facts motivated our evaluation of theoretical predictions through a detailed LC/(-)ESI-MS/MS chemical analysis of MNCs in ambient PM_2 samples by using commercial as well as *de novo* synthesized authentic standards. For the first time we report on the presence of 3M4NC besides 3M5NC in ambient aerosols, while contrary to previous reports no

3M6NC was detected. Although an agreement between calculated and observed 3M5NC/3M4NC ratios cannot unambiguously confirm that the aqueous-phase electrophilic reaction is the exclusive formation pathway of MNCs in the atmosphere, the examined mechanism is supported because (1) no 3M6NC was detected in ambient aerosols and (2) fixed 3M5NC/3M4NC ratio in aerosols indicates their common formation pathways. We will highlight the importance of maximum molecular level identification of atmospheric organics to understand their sources and properties as well as to properly represent formation pathways of specific SOA tracers in atmospheric models. Thus, the magnitude of error one could make by incorrect identification of 3M4NC as 3M6NC in ambient aerosols will be presented.

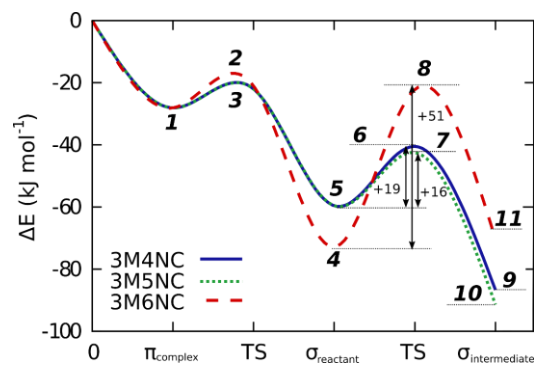


Figure 1. Graphical representation of potential energy surface for nitration of 3-methylcatechol (3MC) with NO_2^+ . Three different pathways corresponding to the formation of 3-methyl-4-nitrocatechol (3M4NC, **9**), 3-methyl-5-nitrocatechol (3M5NC, **10**), and 3-methyl-6-nitrocatechol (3M6NC, **11**) are shown.

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