The atmospheric fate of methacrolein and a formation path for atmospheric aerosols

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The oxidation of isoprene by the hydroxyl radical is known to produce aerosol in small yields (1). Aerosol production in laboratory chamber studies occurs in both high and low NOx environments. With low NOx, oxidation of isoprene is known to produce epoxides (IEPOX) in high yield (2). In chamber studies performed with high NOx, it has been shown that aerosol production follows the oxidation of a second generation oxidation product, MPAN, which is formed from methacrolein (MACR) (3).

Here we investigate the oxidation chemistry of MACR using quantum molecular calculations. We investigate both the reaction mechanism of hydrogen abstraction by OH (4) and the OH addition (5). The hydrogen abstraction reaction leads to either methyl-peroxyacetylnitrate (MPAN) or methyl peracrylicacid (MPAA) depending on whether the peroxyacetyl radical reacts with NO2 or HO2. High level quantum chemical calculations show, that the oxidation of MPAN leads to formation of hydroxymethyl-methyl-α-lactone (HMML) in high yield (4). HMML production follows a low potential energy path from both MPAN and MPAA following addition of OH (via elimination of the NO3 and OH from MPAN and MPAA, respectively). HMML is a plausible precursor for the formation of methyl glyceric acid (2-MG) and similar products, as lactones are known to undergo facile polymerization reactions (6). The addition of OH to MACR is expected to be followed by reaction with O2 leading to the formation of hydroxyl peroxy radical. This radical undergoes a fast (0.5±0.3 s-1 at T=296K) isomerization involving the 1,4-H-shift of the aldehydic hydrogen to the peroxide group (6) leading to hydroxyl hydroperoxy carbonyl radical, which decompose rapidly into hydroxyacetone and with a regeneration of OH.

References

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