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The in-situ formation of methyl-nitrate during NO_x re-cycling involving $CH3O_2$: global impacts and implications in the troposphere

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Organic nitrates are formed via chain termination steps involving peroxy-radicals and NO thus impacting the efficiency of ozone production and global oxidative capacity, especially in low NO_x environments (Browne and Cohen, 2012). Recently the direct formation of methyl nitrate ($CH3ONO_2$) has been observed during the re-cycling of NO_x by $CH3O_2$ (Butkovskaya et al., 2012) with a branching ratio of 1.0(+/-)0.7% for tropospheric conditions. Considering that the $CH3O_2$ route acts as the second most important radical mechanism of NO_x re-cycling at global scale implies that this sequestration of reactive nitrogen into a more long lived reservoir could potentially decrease the efficiency of tropospheric ozone production, especially in the tropical regions where the highest mixing ratios of $CH3O_2$ exist as a result of methane oxidation. Past measurements of alkyl-nitrates have shown that although resident mixing ratios of organic nitrates are high under urban conditions, they are also present in the more pristine regions of the tropical Pacific (e.g. Blake et al, 2003) and above Antarctica (i.e. in low NO_x environments). Using the global 3D TM5 model we investigate the impact that the direct in-situ formation of $CH3ONO_2$ has on global tropospheric composition. By comparing against measurements we also show that such a process could go part way towards explaining the distribution of $CH3ONO_2$ in the tropical troposphere, where direct emissions from the ocean have previously been used to explain observations (Neu et al, 2008).

Browne and Cohen, Atms. Chem. Phys., 12, 11917-11932, 2012.
Butkovskaya et al., J. Phys. Chem. A., 116(24), 5972-5980, 2012.
Blake et al., J. Geophys. Res., 108(D2), 8242, 2003.
Neu et al., Geophys. Res. Letts., 35, L13814, 2008.