

The Role of Intramolecular H-Migration in Peroxy Radicals Formed in the Atmospheric Oxidation of Volatile Organic Compounds

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Peroxy radicals (RO_2) are formed in the atmospheric oxidation of VOCs. In the atmosphere, the RO_2 radicals are often assumed to react with NO and other peroxy radicals, and to lesser extent with NO_3 . RO_2 radicals are also formed in the low-temperature combustion of VOCs, where they undergo intramolecular H-migration as $\text{ROO} \rightleftharpoons \text{QOOH} \rightarrow \text{Products}$. Because of the high endothermicity and high barriers, the H-migration are often excluded in the atmospheric oxidation mechanism of VOCs. Recent studies, however, showed that the H-migration in the peroxy radicals can be important in the atmospheric oxidation of certain types of VOCs at least when the NO concentrations are low. Under these conditions, the unimolecular isomerization, followed by O_2 addition as $\text{ROO} \rightleftharpoons \text{QOOH} \rightarrow \text{O}_2\text{QOOH} \rightarrow \text{Products}$, might be able to compete with their bimolecular reactions with the trace radicals in the atmosphere. These unimolecular processes might lead to the formation of multifunctional hydroperoxides and carbonyls, which usually possess extremely low vapor pressures and therefore might contribute to SOA formation. H-migration in certain peroxy radicals would recycle OH radical, resulting in auto-oxidation of these VOCs without the involvement of NO_x and the formation of ozone. Here we report our preliminary studies on the role of intramolecular H-migrations in the atmospheric oxidation of ethers, carbonyl compounds, and substituted benzenes by using theoretical quantum chemistry and RRKM-ME calculations.

References

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