

Rapid Hydrogen Shift Scrambling in Hydroperoxy-Substituted Organic Peroxy Radicals

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In the atmosphere, volatile organic compounds (VOCs) are oxidized to peroxy radicals (ROO), by the OH radical and O₂. It is well known that the ROO radical can undergo an isomerization reaction via intramolecular hydrogen shift (H-shift) reactions leading to the formation of hydroperoxyalkyl radicals (QOOH). The QOOH can either decompose or react with O₂ leading to the formation of a new peroxy radical, which again can undergo H-shift reactions. This ongoing series of uptake of O₂ and H-shift reaction is known as autoxidation, which is well known in the low temperature combustion chemistry. (1) Autoxidation has recently been showed to play an important role in the formation of secondary organic aerosols from VOCs in low-NO_x environments.(2,3)

Using quantum mechanical calculations, we have investigated hydrogen shift in three peroxy radicals CH₂OHCH(OO)CH(OOH)CH₂CH₃, CH₂OHCH(OO)CH₂CH(OOH)CH₃ and CH₂OHCH(OO)CH₂CH₂CH₂(OOH), where the peroxy group -OO is positioned on the second carbon and the hydroxyl group (OOH) moves position. The H-shift reaction of the hydrogen atom from the OOH group to the OO group is fast. We find that the rate constants of this type of H-shift reactions are greater than 10³ s⁻¹ for both the forward and the reverse reactions. (4) It leads to the formation of two different radical isomers that react through different reaction mechanisms and yield different products.

These very fast H-shift reactions from the OOH group are much faster than the reactions with NO and HO₂ under most atmospheric conditions and must be included in the atmospheric modeling of volatile organic compounds where hydroperoxy peroxy radicals are formed. We found that inclusion of the very fast H-shift reactions between the OO and OOH group suppresses or enhances the branching ratios. (4)

References

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