

Hydrogen shift reactions in four methyl-buten-ol (MBO) peroxy radicals and its impact on the atmosphere

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Methyl-buten-ol (MBO) molecules are emitted from many different natural sources. The most important biogenic emitted MBO is the 2-methyl-3-buten-2-ol (MBO232), with an estimated global emission around 1.6-2.2 Tg yr⁻¹.(1) The oxidation of MBO232 produces secondary organic aerosols (SOA), when the NO concentration is low.(2) It is proposed, that the possible formation of the SOA is due to the production of C₅-triols. Recently, it is suggested, that an internal hydrogen transfer reaction (H-shift) from an alcohol group could lead to the formation of epoxides.(3) Current results suggest that epoxides might be an important SOA precursor, that could contribute to SOA production in forest regions.(4)

We investigate the possible hydrogen shift (H-shift) reactions in the peroxy radicals derived from four different MBOs; 2-Methyl-3-buten-2-ol (MBO232), 2-Methyl-3-buten-1-ol (MBO231), 3-Methyl-3-buten-2-ol (MBO332) and 3-Methyl-3-buten-1-ol (MBO331), with quantum mechanical calculations. The rate constants of the forward 1,5 H-shift reactions in all four MBO peroxy radicals are greater than the rate constant of the forward 1,4 or 1,6 H-shift reactions. The rate constants for the 1,5 H-shift reaction from a CH group or OH group are approximately 1 s⁻¹ and 10⁻³ s⁻¹, respectively. The atmospheric impact of OH oxidation of MBO232 is investigated. The major atmospheric reactions of the MBO232 peroxy radical are the reactions with NO and HO₂, with reaction yield of 85 % and 13 %, respectively. The H-shift reactions of MBO232 peroxy radical play a minor role with a total yield of about 2 %. The production of epoxides from the atmospheric oxidation of MBO232 is unlikely, since the barrier height for the epoxide formation is high and hence the formation of the epoxide is very slow.

References

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