Experimental and theoretical investigations for the gas-phase reactions of OH radical with α-pinene and β-pinene.

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OH radicals play an important role in the chemistry of biologically emitted volatile hydrocarbons in the troposphere. α-pinene and β-pinene are the two most abundant monoterpenes emitted in to the troposphere by coniferous trees.[1] The rate coefficients for the gas-phase reactions of OH radicals with α-pinene and β-pinene have been determined at 298 K and 800 Torr of N_2 using the relative rate method, with propylene as a reference compound. The OH radicals were generated by UV photolysis of hydrogen peroxide (H_2O_2) at 254 nm. A gas chromatograph equipped with a flame ionization detector (GC-FID) was used for quantitative analysis of the reactants. To gain a deeper insight into the reaction mechanism theoretical calculations were also carried out for these reactions. The rate coefficients of OH radical with α-pinene and β-pinene were computed using conventional transition state theory (CTST) coupled meta-hybrid density functional theory (DFT).[2] Structures of the reactants, transition states and products were optimized at M06-2X/6-31G* and M06-2X/6-311++G** level of theories. Energies are obtained by single-point calculation at the above structures using M06-2X/Aug-cc-pVTZ to produce the potential energy surface. Both addition and abstraction channels were explored elaborately. The theoretically computed rate coefficients were compared with experimental results. The OH-driven atmospheric lifetimes of α-pinene and β-pinene were calculated using both experimentally and theoretically determined rate coefficients.

References

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