

Unusually Fast 1,6-H Shifts of Enolic Hydrogens in Peroxy Radicals: Formation of the First-Generation C₂ and C₃ Carbonyls in the Oxidation of Isoprene

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In a theoretical investigation using the CBS-QB3 // UB3LYP/6-31+G** method supported by higher-level computations such as CBS-QB3 // UQCISD/6-31+G**, the 1,6-H shifts of the enolic hydrogen in peroxy radicals of the type Z-HO-CH=CH-CH₂-OO• are found to face exceptionally low energy barriers of only about 11 kcal mol⁻¹ – *i.e.* 6 to 9 kcal mol⁻¹ lower than the barriers for similar shifts of alkanic hydrogens – such that they can proceed at unequaled rates of order 10⁵ to 10⁶ s⁻¹ at ambient temperatures. The unusually low barriers for enolic 1,6-H shifts in peroxy radicals, characterised here for the first, are rationalized. As cases in point, the *secondary* peroxy radicals Z-HO-CH=C(CH₃)-CH(OO•)-CH₂OH (Case A) and Z-HO-CH=CH-C(CH₃)(OO•)-CH₂OH (Case B) derived from the *primary* Z-δ-hydroxy-peroxy radicals in the oxidation of isoprene, are predicted to undergo 1,6-H shifts of their enolic hydrogens at TST-calculated rates in the range 270 to 320 K of $k(T)_A = 5.4 \times 10^{-4} \times T^{5.04} \times \exp(-1990/T) \text{ s}^{-1}$ and $k(T)_B = 109 \times T^{3.13} \times \exp(-3420/T) \text{ s}^{-1}$ respectively, *i.e.* $2.0 \times 10^6 \text{ s}^{-1}$ and $6.2 \times 10^4 \text{ s}^{-1}$, respectively, at 298 K, far outrunning in all relevant atmospheric and laboratory conditions their reactions with NO proposed earlier as dominant pathways.¹ These fast enolic-H shifts provide an explanation for the first-generation production of methylglyoxal + glycolaldehyde, and glyoxal + hydroxyacetone in isoprene oxidation at high-NO levels, recently determined by several groups.² However, under moderate- and low-NO atmospheric conditions, the fast interconversion and equilibration of the various thermally labile, initial peroxy conformers / isomers from isoprene and the isomerisation of the initial Z-δ-hydroxy-peroxy radicals, both recently proposed by us,³ are expected to substantially reduce the yields of the small carbonyls at issue.

References

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