Kinetics of the Benzyl + HO₂ and Benzoxyl + OH Barrierless Association Reactions: Fate of the Benzyl Hydroperoxide Adduct under Combustion and Atmospheric Conditions

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Figure S1 shows the M06-L/cc-pvtz geometries that resemble the transition state of reactions R1 (panel a) and R2 (panel b) at 300 K. Radical-radical association reactions do not have a well-defined saddle point that can be fully optimized as it is the case in reactions with a barrier height. These two geometries were obtained by dissociation of the adduct benzylhydroperoxide along the C–O (a) and O–O (b) bond distances, which adopt values of 2.6 Å and 2.3 Å, respectively. These bond distances were found to minimize the reactive flux at 300 K, and therefore the rate constants, of reactions R1 and R2 in our VRC-TST calculations, and can be thereby considered as an accurate approach to the their transition states at that temperature.



Figure S1. Transition states found for the reactions R1 (a) and R2 (b) at 300 K at the M06-L/cc-pvtz level. The eigenvector of the imaginary frequency, 162i cm⁻¹ and 258i cm⁻¹ for the transition states of reactions R1 and R2, respectively, are shown by the blue arrows.

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The potential energy profile with the stationary points on the potential energy surface of reactions R1– R5 is shown on Figure S2 at the M06-2X/cc-pvtz level.



Figure S2. M06-2X/cc-pvtz potential energy profile connecting the stationary points on the potential energy surface of reactions R1–R5. The stationary points of the reactions whose rate constants have been calculated in this work, that is, R1 and R2, are highlighted in bold font.