**ABSTRACT**

  In this work, we have focused on the atmospheric reaction chemistry of two α-diketones 2,3- Pentanedione (2,3-PTD) and 2,3-hexanedione (2,3-HEX)withOH radical. The full reaction pathway was studied theoretically under H-atom abstraction reaction using density functional theory and wavefunction- based MP2 calculations. Single-point energy calculations were performed at CCSD(T) level of theory with 6–31+G(d,p) basis set. The H-atom abstraction from –CH2 group is the most dominant channel in both 2,3-PTD and 2,3-HEX with OH radical. The fate of secondary reactions of peroxy and alkoxy radical is studied in detail. The reaction force analysis shows that abstraction process is dominated by structural rearrangement than electronic reordering. The ETS-NOCV-based reaction scheme is studied in order to find out the pair wise interaction energy of the chemical bonding. The ETS-NOCV method for all the transition states shows π-bonding nature for the bond breaking (C–H) and bond formation (O–H) due to the presence of hydrogen bond. The theoretical rate constant value matches well with the experimental rate constant value for both α-diketones. Normal linear Arrhenius behaviour for all the pathways is found in the range of 278–350 K. The short atmospheric lifetime indicates the removal process of diketones with OH radical.