Reaction mechanism for the oxidation of $C_{15}H_9$ with hydroxyl

Galimova G.R.[1,2], Azyazov V.N.[1,2], Mebel A.M.[1,3]

[1]*Samara National Research University (34, Moskovskoye Shosse, Samara, Russia, 443086)*
[2]*Lebedev Physical Institute (221, Novo-Sadovaya, Samara, Russia, 443011)*
[3]*Florida International University (SW 8th St, Miami, 33199, USA)*

The $C_{15}H_9$ molecule is invoked as a soot surface site bearing five-member ring for modeling of the oxidation of soot[1]. Here we report the potential energy surfaces for the oxidation reaction of $C_{15}H_9$ by OH calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. Fig. 1 exhibits the calculated most likely configurations resulting from the interaction of $C_{15}H_9$ with OH.

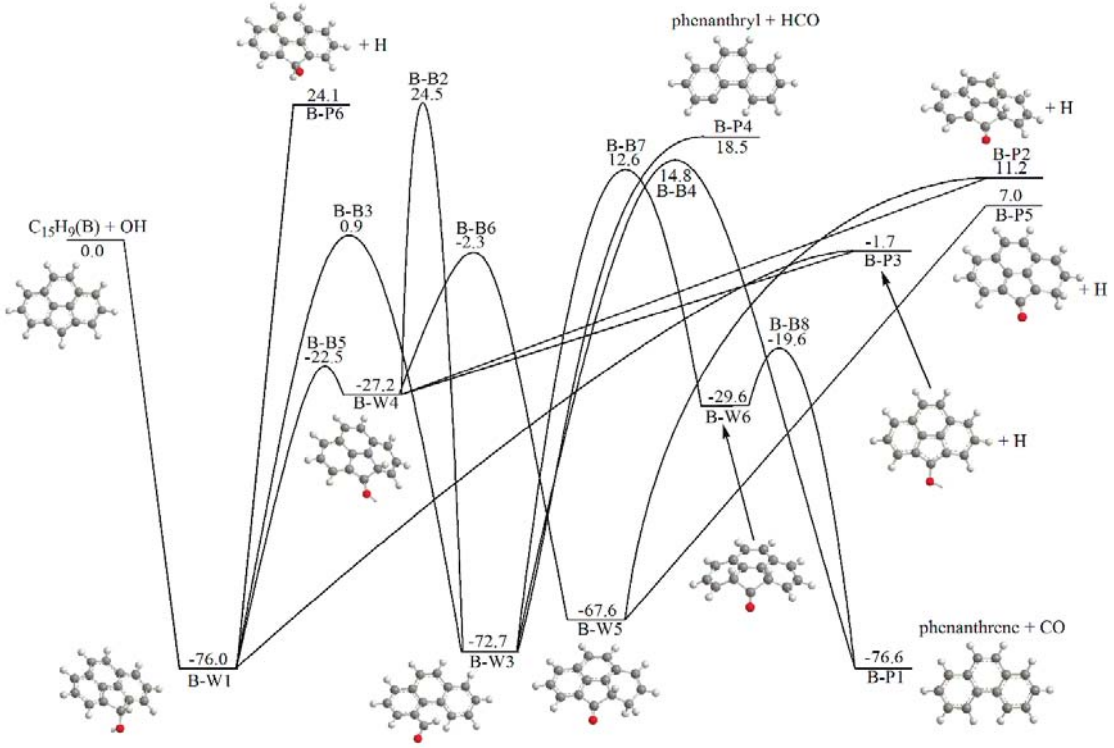

Fig. 1 Possible pathways for the $C_{15}H_9$ + OH reaction. The relative energies of stable species, intermediates, and transition states are depicted with italic numbers (in kcal/mole).

The $C_{15}H_9$(B) + OH reaction is found to predominantly proceed by the stabilization/dissociation channel forming $C_{15}H_{10}O$ (B-W1), which the further dissociates to $C_{15}H_8OH$ + H (B-P3) or back to the $C_{15}H_9$(B) + OH reactants, whereas the pathway producing B-P6 directly is only minor. Removal of CO is unlikely; because the degree of embedding of a five-membered ring is deep (the five-membered ring has three common edges with the surrounding six-member rings).

The presentation will also address the reaction of $C_{15}H_9$(A) where the embedded five-member ring has two common edges with the surrounding six-member rings, as well as oxidation reactions of $C_{15}H_9$(A) and $C_{15}H_9$(B) with atomic oxygen.

References

[1] Galiya R. Galimova, Valeriy N. Azyazov, Alexander M. Mebel, Reaction mechanism, rate constants, and product yields for the oxidation of cyclopentadienyl and embedded five-member ring radicals with hydroxyl, Combust. Flame 187 (2018), 147-164.