Fluorene formation in the reaction of phenyl and benzyl radicals theoretical study

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Up to nowadays combustion reactions of various hydrocarbons is still remaining as a main source of energy. Due to inefficient conditions of the process, in flames appear products of incomplete combustion, such as polycyclic aromatic hydrocarbons (PAH), that eventually lead to soot formation — a strong pollutant. The key for the solution of this problem is to understand properly the mechanisms that lie behind the PAHs formation and growth. As so, the possible mechanism for third ring formation by addiction of phenyl and benzyl radicals was suggested.

The study of this reaction was performed by using ab initio methods of quantum chemistry. The geometries of reagents, intermediates, transition states and products were calculated using the B3LYP/6-311G**. At the same level of theory the values of vibrational frequencies and zero vibration energies, as well as the estimated energies of the molecular systems entering the reaction, were obtained. The refinement of energies to achieve chemical accuracy is carried out by G3(MP2, CC)//B3LYP composite method.

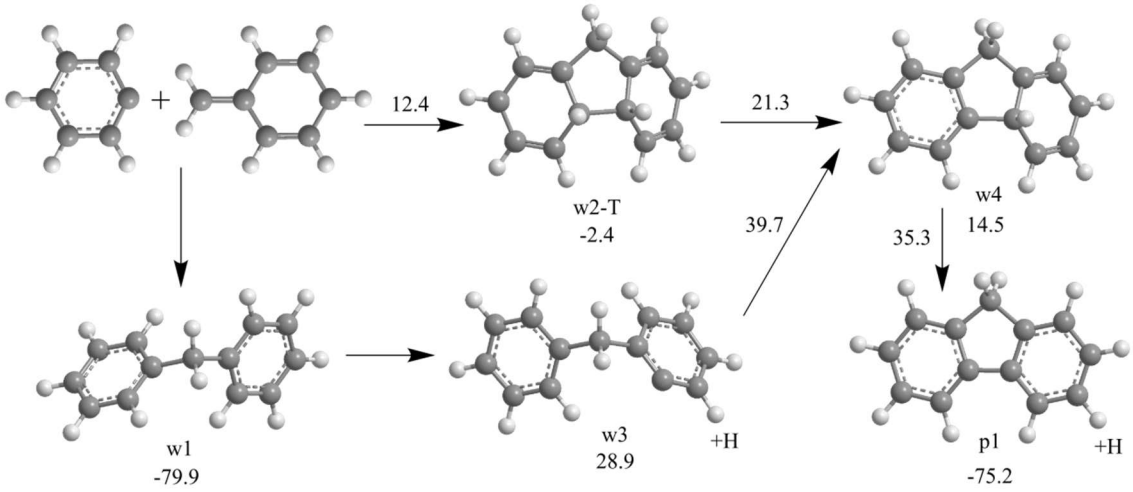

Figure 1 — one of the possible reaction's pathways. Energies is listed in Kcal/mol relative to the ones of the reagents

The path through w1 implies the usual barrier-free connection of reagents with further step-by-step separation of atomic hydrogen and closure into a ring. The separation of molecular hydrogen at once is expected to be less profitable, due to a higher barrier. Alternatively, the case when the reagents are combined in a triplet state (w2-T) is also possible. This way is more profitable because of lower barriers, as well as fewer intermediate steps, since the closure of the ring goes immediately.