

Potential Energy Surface for Oxidation of Indenyl C₉H₇

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Abstract—Ab initio calculations were performed to obtain local energy extrema, including an effect of reagents, intermediates, and reaction products on the potential energy surface for the C₉H₇+O₂ reaction, playing a significant role in oxidation of polycyclic aromatic hydrocarbons at combustion conditions. The final products, determined as a result of the calculations are styrenyl radical C₈H₇+CO₂, ortho-vinyl phenyl radical C₈H₇+CO₂ and 1-H-inden-1-one C₉H₆O+OH, which is predicted to be the prevailing reaction product.

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Polycyclic aromatic hydrocarbons (PAH), which are produced in incomplete combustion of fossil fuels and biomass from natural processes, are considered among the most abundant pollutants and soot precursors, which exert a great impact on environment and health. The chemical mechanisms for PAH formation and degradation in combustion are presented by a large variety of reactions between molecules and radicals in different isomeric forms [1–5]. The process of enlarging the simplest aromatic hydrocarbons is an important link in the formation of large PAHs. With the increase of molecular weight of PAHs, their toxicity generally increases [4]. Simultaneously with the molecular PAH growth, the degradation reactions take place at the edges of PAHs and soot, due to the presence of such common oxidants as O₂, O, and OH abundant in the combustion environment [2, 3]. The significant role of indenyl radical C₉H₇ in the process of PAH formation is identified [4]. Besides its ability to combine with abundant cyclopentadienyl, C₅H₅ radical to form carcinogenic phenanthrene, indenyl radical, consisting of two aromatic rings, causes a toxic effect by itself. Still, the information about the oxidation pathways of the indenyl radical with molecular oxygen present in combustion environment is scarce. That is why the aim of this paper is to map out the potential energy surface (PES) of the C₉H₇+O₂ reaction using ab initio calculations.

In order to develop reliable kinetic models for the formation and degradation of PAH and soot in combustion, detailed information is required on the mechanism, rate constants, and product branching ratios of elementary chemical reactions involved in these processes [6]. Rate constant calculations in turn require accurate energies and structures and molecular parameters (rotational constants and vibrational frequencies) for reaction intermediates (W), transition states (TS), and products of reaction (P), which were computed using the Gaussian 09 [7] and MOLPRO 2010 [8] program packages. Geometries were optimized at the density functional B3LYP/6-311G(d,p) level of theory. Vibrational frequencies were computed at the same theoretical level and were used to evaluate zero-point vibrational energy corrections (ZPE). Intrinsic reaction coordinate (IRC) calculations were performed to confirm connections between transition states and local minima. For C₉H₇O₂ species, the refinement of single-point energies was carried out employing the modified G3(MP2,CC)//B3LYP [9, 10] composite scheme where the energies were computed as

$$E_0[G3(MP2,CC)] = E[(CCSD(T)/6-311G^{**})] + \Delta E_{MP2} + E(ZPE). \quad (1)$$

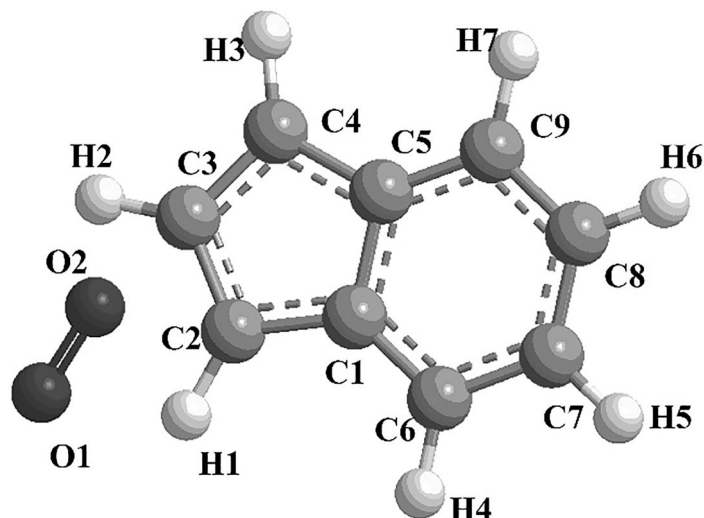


Fig. 1. Designation of atoms in the chemical structure of indenyl+O₂.

Here $\Delta E_{\text{MP2}} = E[\text{MP2}/\text{G3Large}] - E[\frac{\text{MP2}}{6} - 311\text{G}^{**}]$ is a correction for the superposition error of the basis set and $E(\text{ZPE})$ is the zero-point energy. In the CCSD(T) and MP2 calculations for open-shell species, the energies were computed from restricted RHF-RCCSD(T) and unrestricted UMP2 energy values, respectively, where RHF-RCCSD(T) here denotes partially spin-adapted open-shell coupled cluster singles and doubles theoretically augmented with a perturbation correction for triple excitations starting from molecular orbitals, obtained from restricted open shell Hartree-Fock (ROHF) calculations.

The initial structure of the reactants – the indenyl radical and molecular oxygen are shown in Fig. 1. After the initial attachment of O₂ to the C2 position in the five-membered ring of indenyl, forming intermediate W1 via a low barrier of 2.8 kcal/mol (all the energies are given relatively the initial reactants), three possible pathways were found – the first one (Fig. 2) – where the O atom of O₂, which is not connected to C2, migrates toward C3 to form intermediate W2.

The obtained compound isomerizes through ring opening C2–C3 via a barrier of 23.5 kcal/mol at transition state TS2-3, producing W3, residing in a deep potential well of 81.5 kcal/mol. After this critical barrier is overcome, the reaction easily proceeds via closure of a six-membered ring containing an oxygen atom (W4), H migration from C2 to the out-of-ring O atom (W5), ring opening (W6), and H migration from OH to the C₂H₂ side chain (W7). At the G3(MP2,CC) level of theory energy values give the information about the instability of the W6 isomer, hence the resulting potential curve of this pathway can exclude the TS5-6 barrier and W6 formation, and the reaction proceeds from W5 isomer to W7 through TS6-7 of –50.2 kcal/mol. Finally, isomer W7 dissociates to ortho-vinyl phenyl radical and CO₂. Relative energies (in kcal/mol) are indicated for both CCSD(T)/6-311G(d,p) (the first bold number) and G3(MP2,CC) (the second italic number) methods (Fig. 2).

The second reaction pathway is initiated by attachment of O₂ in C2 position as well, but after isomerization to W1 the O atom adds to C1 position in the ring (Fig. 2) through TS1-9 via a barrier of 18.6 kcal/mol, which is 5 kcal/mol higher than that at TS1-2. After intermediate W8 is formed, it rearranges, through C1–C2 bond cleavage, to isomer W9 which is located in a deep potential well (–63.7 kcal/mol). The further mechanism of the reaction is similar to the first pathway – the closure of the ring by placing the O atom in the bridging position (W10) through a low barrier at TS10-11 of 18.5 kcal/mol, and then the migration of the H atom from C2 to O, which demands a 49.5 kcal/mol barrier at TS11-12. Subsequent ring opening (via TS12-13 of 26 kcal/mol) leads to the formation of W12, and further sequence of low-barriers- fast reaction steps includes migration of the H atom followed by dissociation to styrenyl radical C₈H₇ and CO₂.

On the third two-step pathway the reaction of indenyl+O₂ leads to the 1-H-inden-1-one C₉H₆O product, through OH elimination (Fig. 2). This way includes formation of W1 isomer similarly to the

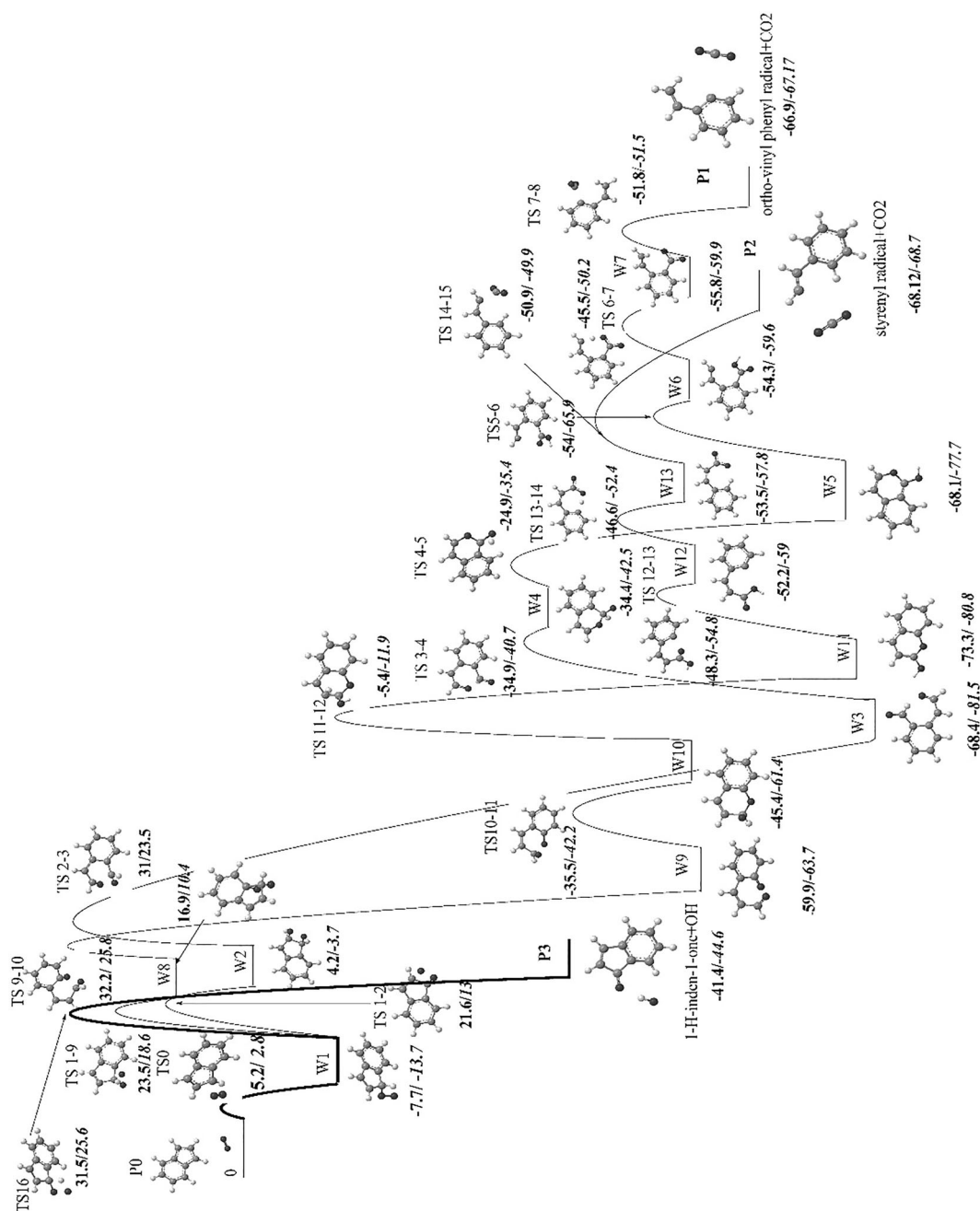


Fig. 2. The $C_9H_7+O_2$ reaction pathways leading to the formation of the ortho-vinyl phenyl radical $C_8H_7+CO_2$, styrenyl radical $C_8H_7+CO_2$, and 1-H-inden-1-one C_9H_6O+OH .

pathways described above. IRC calculations were performed and they confirmed the formation of the 1-H-inden-1-one C_9H_6O product through a 25.6 kcal/mol barrier at TS16.

As a result of the present study of the $C_9H_7+O_2$ reaction, three products were detected by means of ab initio calculations – ortho-vinyl phenyl radical C_8H_7 , styrenyl C_8H_7 , and 1-H-inden-1-one C_9H_6O , obtained in the course of multistep reaction pathways by elimination of the CO_2 and OH fragments. The pathway to 1-H-inden-1-one formation seems to be more efficient because the product is formed as a result of only a two-step mechanism. The performing both CCSD(T)/6-311G(d,p) and MP2 calculations gives chemically accurate values of energy.

The obtained energy scheme shown in Fig. 2 displays three possible pathways for the $C_9H_7+O_2$ reaction. The most efficient way of reaction is the formation 1-H-inden-1-one radical via OH de-

tachment from intermediate $C_9H_7O_2$. The other products are styrenyl and ortho-vinyl phenyl radicals. The consequent steps beyond the PES obtained in the present investigation will be the search of the additional reaction pathways from the deep potential wells W3 and W9 – the probability of existing of some additional energy efficient pathways for the $C_9H_7+O_2$ reaction may be quite high.

Further, all of the obtained energy values and zero-point vibrational energy corrections (ZPE) will be used in Rice–Ramsperger–Kassel–Marcus Master Equation (RRKM-ME) calculations of temperature- and pressure-dependent rate constants for this reaction.

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REFERENCES

1. A. R. Ghildina, A. D. Oleinikov, V. N. Azyazov, and A. M. Mebel, *Combust. and Flame* **183**, 181 (2017).
2. M. Frenklach, *Phys. Chem. Chem. Phys.* **4**, 2028 (2002).
3. B. S. Haynes and H. G. Wagner, *Z. Phys. Chem.* **133**, 201 (1982).
4. L. Zhu, X. Shi, Y. Sun, and Q. Zhang, *Chemosphere* **189**, 265 (2017).
5. I. Tokmakov, G.-S. Kim, V. V. Kislov, et al., *J. Phys. Chem. A* **109**, 6114 (2005).
6. A. D. Oleinikov, V. N. Azyazov, and A. M. Mebel, *Combust. and Flame* **191**, 309 (2018).
7. M. J. Frisch, G. W. Trucks, and H. B. Schlegel, *GAUSSIAN 09 Revision A.1* (Gaussian, Inc., Wallingford, CT, 2009).
8. H.-J. Werner, P. J. Knowles, G. Knizia, et al., *MOLPRO*, version 2010.1, a package of ab initio programs, <http://www.molpro.net>.
9. A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
10. L. A. Curtiss, K. Raghavachari, P. C. Redfern, et al., *Chem. Phys. Lett.* **314**, 101 (1999).

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