Theoretical study of 1-acenaphthyl oxidation with molecular oxygen

Alina Kuznetsova[1,2], Denis Porfiriev[1], Valery Azyazov[1]

[1] Lebedev Physical Institute, Samara Branch, 221 Novo-Sadovaya str., Samara, Russia, 443011
[2] Samara National Research University, 34, Moskovskoye shosse, Samara, Russia, 443086
malina-jun@yandex.ru

A pressing issue is the formation of soot and polycyclic aromatic hydrocarbons (PAHs) during incomplete combustion of hydrocarbon fuels, since they are chemical compounds harmful to humans and the environment [1,2]. Reducing unwanted emissions is possible by switching to cleaner and more efficient fuel combustion systems. Designing such equipment requires the use of more advanced kinetic models of PAH oxidation, since large PAH molecules are used as model molecules in studies of chemical interactions on soot [3–6].

Previous theoretical [7] and experimental works [8] have determined that acenaphthylene occupies an important place in the mechanism of PAH and soot growth according to HACA. Further studies [9, 10] have shown that, due to the peculiarities of the edge structure, the rate constants of addition to the five-membered ring of acenaphthylene are the highest. The latter circumstance has created interest in studying the mechanism of oxidation of 1-acenaphthyl by molecular oxygen.

Molecular parameters and relative energies were obtained using the composite calculation scheme G3(MP2,CC)//B3LYP/6-311G(d,p), providing chemical accuracy. The connectivity of the stationary states through the corresponding transition states was confirmed by IRC calculations. The values of the rate constants and relative yields of the reaction products were calculated for different conditions within the RRKM-ME theory with kinetic accuracy.

Potential energy surface (PES) analysis revealed that the most energetically favorable reaction channels are those leading to O atom abstraction and CO abstraction. The reaction kinetics and relative yields were studied for the 0.01-100 atm pressure range and 500–2500 K temperature range. Competitive behavior of the reaction products was found at low pressure. At high temperatures and low pressures, the O abstraction channel dominates, while at low temperatures and pressures, the CO abstraction channel dominates. The relative yields of the products are equal at a temperature of ≈ 77 K.

This work was supported by the Ministry of Higher Education and Science of the Russian Federation under Grant No. 075-15-2021-597 "Origin and evolution of organic molecules in our Galaxy".

References

1. H. N. Sharma et al., *Energy & Fuels* **2012**, 26, 9.
2. A. Raj, G. R. da Silva, S. H. Chung, *Combustion and flame* **2012**, 159, 11.
3. K. Sendt, B. S. Haynes, *Combustion and flame* **2005**, 143, 4.
4. M. S. Celnik et al. *Proceedings of the Combustion Institute* **2009**, 32, 1.
5. M. Frenklach et al. *Symposium (International) on Combustion* **1985**, 20, 1.
6. M. Frenklach *Physical chemistry chemical Physics* **2002**, 4, 11.
7. V. V. Kislov, A. I. Sadovnikov, A. M. Mebel *The Journal of Physical Chemistry A* **2013**, 117, 23.
8. D. S. N. Parker et al. *Angewandte Chemie International Edition* **2015**, 54, 18.
9. P. Liu et al. *Combustion and Flame* **2019**, 199.
10. P. Liu, Z. Li, W. L. Roberts *Combustion and Flame* **2021**, 230.