Formation of two-ring PAHs in circumstellar envelopes of asymptotic giant-branch stars
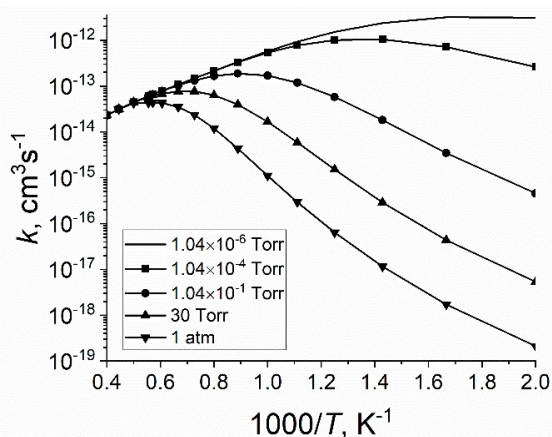
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It is known, that PAHs can form from the growth of small aromatic molecules such as benzene and toluene in the shells of carbon-rich AGB stars and planetary nebulae. Methyl-substituted and, more generally, alkylated PAHs, the prototype molecule of which is toluene, can play a special role in the growth of PAHs. In high-temperature environments, for example, in circumstellar envelopes or during combustion, they can be formed as a result of methylation/alkylation processes, that is, as a result of CH_3/alkyl radical-to-H exchange reactions, which require significant barriers. The benzyl radical is formed from toluene by abstraction of an H atom from the methyl group. The present study revisited the mechanism and kinetics of the $C_7H_7 + C_3H_3$ reaction using advanced methods of transition state theory to evaluate critical rate constants of barrierless entrance and exit reaction channels. The calculations uphold the reaction mechanism proposed in the earlier work by Matsugi and Miyoshi[1], but provide new quantitative details. The final energy refinement was based on a modified combined scheme: $E[G3] = E[CCSD(T)/6-311G^{**}] + E[MP2/G3Large] - E[MP2/6-311G^{**}] + E(ZPE)$, where CCSD(T) is the coupled cluster method with the $6-311G^{**}$ basis, and MP2 is the Möller-Plesset second-order perturbation theory method with the $6-311G^{**}$ and G3Large basis sets. The reaction mechanism includes several biradical compounds (singlets with open shells), for which geometry optimization and vibration frequency calculations were performed using the unrestricted $UB3LYP/6-311G^{**}$ approach, and the total energies were refined using the composite triplet-singlet-gap method[2]: $E^S = E^T[G3(MP2,CC)] + \Delta E^{S-T}(CASPT2(10,10)/cc\text{-}pVTZ) + ZPE^S$, where $E^T[G3(MP2,CC)]$ is the G3(MP2,CC) energy of the triplet state without ZPE with an optimized open-shell geometry, $\Delta E^{S-T}(CASPT2(10,10)/cc\text{-}pVTZ)$ is the difference between the singlet and triplet states calculated using the second-order multiconfiguration perturbation theory method CASPT2 with an active space consisting of 10 electrons distributed over 10 orbitals and with the basis cc-PVTZ. It is shown that at high temperatures about 2500 K, the constant rates of formation methyleneindanyl radicals for the measured pressure values in the AGB stars are at the level of about 2.31×10^{-14} cm^3 s^{-1}. However, with a decrease in temperature and the rate of formation (p9+p10) + H increase by orders of magnitude, which interrupts the apparent weakening of the appearance of the initial complexes and an increase in the yield of bicyclic reaction products.

Picture 1 – Constant rates of the reaction $C_7H_7 + C_3H_3 \rightarrow (p9 + p10) + H$ expected at various pressures

References
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2. J. A. Miller, S. J. Klippenstein, Y. Georgievskii, L. B. Harding, W. D. Allen, A. C. Simmonett, J. Phys. Chem. A **114**, 4881 (2010).