The reaction of 2-naphthyl with 1,3-butadiene: a theoretical study

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Abstract. This work is devoted to a theoretical study of the 2-naphthyl + 1,3-butadiene reaction aimed at understanding the hydrogen-loss mechanism in the reactions of n-naphthyl (n=1,2) with 1,3-butadiene. All intermediates and transition states, their vibrational frequencies and zero-point vibrational energies, and the potential energy diagram were calculated at the G3(MP2,CC)//B3LYP/6-311G** theoretical level. The estimate of the reaction rate constant gives the order of 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at temperatures below 500 K.

1 Introduction

A great amount of theoretical and experimental research in the field of polycyclic aromatic hydrocarbons (PAH) growth and soot formation have been reported in last decades. These investigations demonstrated harmful effects of PAH on the environment and human health [1-3]. Due to high thermal stability of aromatic radicals and resonantly stabilized free radicals the following mechanisms are considered important in the PAH and soot precursor formation: hydrogen abstraction–acetylene addition (HACA) [4–6], phenyl addition–cyclization [7, 8], and ethynyl addition [9]. However, more complex PAH such as three-ring phenanthrene and anthracene could not be formed through HACA-based mechanisms. In this article, the addition of a 1,3-butadiene molecule is proposed as a key step in the formation of a third aromatic ring.

Recently obtained experimental and theoretical results on the reaction of 1-naphthyl with 1,3-butadiene defy the thesis that PAH growth is predominantly a high temperature phenomenon [10] and a further support for this conclusion is provided here for the analogous reaction of 2-naphthyl.

2 Methods

Optimization of geometry of reactants, products, intermediates, and transition states, and zero-point vibrational energy calculations were performed by using DFT calculations at the B3LYP/6-311G** level. Single point energies were refined by using higher level of theory methods and calculated using the following scheme: E_0 [G3(MP2, CC)] = E

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[CCSD(T) /6 − 311G**] + ΔEMP2 + E(ZPE), where ΔEMP2 = E[MP2/G3Large] – E[MP2/6 − 311G**] is a basis set correction and E(ZPE) is the zero-point energy. The calculations were performed by using the GAUSSIAN 09 [2] and MOLPRO 2010 packages [3].

Reaction rate constants for all reaction steps were computed by solving one-dimensional master equation using Rice-Ramsperger-Kassel-Marcus theory. The harmonic approximation was applied to calculate partition functions using B3LYP/6-311G** frequencies.

3 Results

Quantum chemical calculations at the theory level described above provide information about five hydrogen loss channels in the bimolecular reaction of 2-naphthyl with 1,3-butadiene. All the investigated species and intermediates are represented in Figure 1 with relative energies given in kcal mol^{-1} with respect to the reactants. The first channel leading to P4 + H products starts with a small barrier (TS0-4) 3.87 kcal mol^{-1} above the reactants. This is a formation of a bond between the radical site in 2-naphthyl and a second C atom in 1,3-butadiene leading to intermediate W4 located in a potential well 32.78 kcal mol^{-1} below the reagents. The further development of this channel passes through a hydrogen loss barrier TS4-P4 from the attacked carbon in 1,3-butadiene. The barrier height is 32.59 kcal mol^{-1} and the channel forms the P4 species that is 7.36 kcal mol^{-1} lower in energy than the separated reagents. The initial reactants also have a second channel leading to the P1, P2, P3 and P6 products presented in Figure 1. This channel starts with a van der Waals complex W0 located at -1.72 kcal mol^{-1} that represents a barrier-free entry into the reaction channel. After that a bond is formed between the radical site in 2-naphthyl and the terminal carbon atom of 1,3-butadiene via the transition state TS0-1 (-1.07 kcal mol^{-1}) descending into a potential well W1 at -46.82 kcal mol^{-1}. Hydrogen loss from C1 in 1,3-butadiene represents the reaction channel from W1 to the P1 + H products (at -8.98 kcal mol^{-1}) via the transition state TS1-P1 located at -5.91 kcal mol^{-1}. The reaction can also continue from W1 (-46.82 kcal mol^{-1}) to W2 (-46.26 kcal mol^{-1}) intermediates that are close in energy and the linking transition state TS1-2 at -32.67 kcal mol^{-1} is a trans-cis rearrangement in the 1,3-butadiene side chain. The next endoergic hydrogen loss from C1-carbon in butadiene pathway leads to the P2 + H products at -6.04 kcal mol^{-1} via transition state TS2-P2 at -2.95 kcal mol^{-1}. Other two pathways lead to P3 (1,4-dihydrophenanthrene) and P6 (1,4-dihydroanthracene). Both mechanisms involve ring closure. The channel to P3 passes via TS2-3 (-27.29 kcal mol^{-1}) to W3 (-52.23 kcal mol^{-1}) with ring closure on the C1-carbon of the former 2-naphthyl reactant and after that proceeds via hydrogen loss from the C1-carbon via transition state TS3-P3 (-25.26 kcal mol^{-1}) and gives the product P3 + H at -25.05 kcal mol^{-1}. The last reaction channel has the similar mechanism but the ring closure in TS2-6 (-26.24 kcal mol^{-1}) occurs on the C3-carbon in 2-naphthyl. After that reaction goes through intermediate W6 (-46.97 kcal mol^{-1}) and hydrogen-loss transition state TS6-P6 (-18.11 kcal mol^{-1}) and finds its end in the product P6 + H located at -24.26 kcal mol^{-1}.

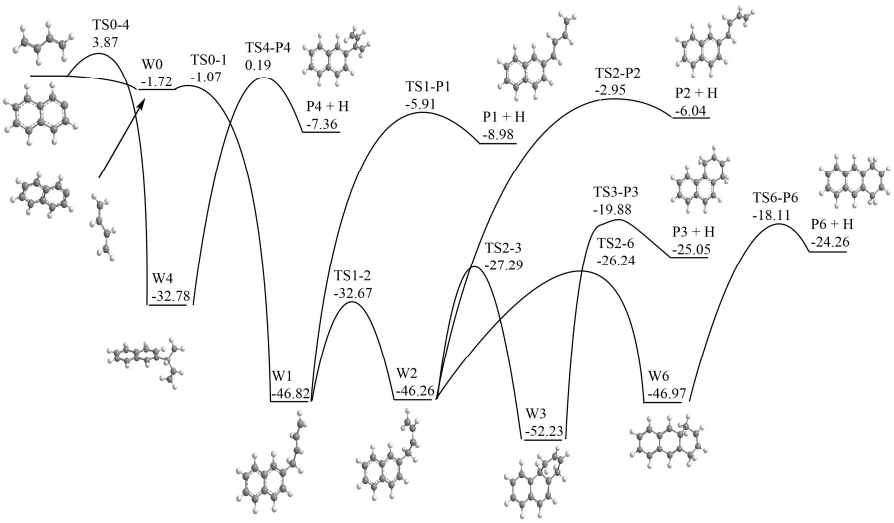

Fig. 1. Potential energy diagram for the reaction of 2-naphthyl with 1,3-butadiene; the energies are given in kcal mol^{-1} relative to the separated reactants.

RRKM-Master Equation calculations were exploited to obtain reaction rate constants for five pressures indicated in Fig. 2 in the range of temperature from 300 to 2500 K. The calculated temperature-dependent reaction rate constants for pressures 0.01, 0.1, 1, 10, 100 atm and the high pressure limit are presented in Figure 2. The curves behaviour below 700 K is similar and coincides with the HP limit. Some small decrease could be seen for all finite pressures at higher temperatures and after that the rate constants merge in one curve again.

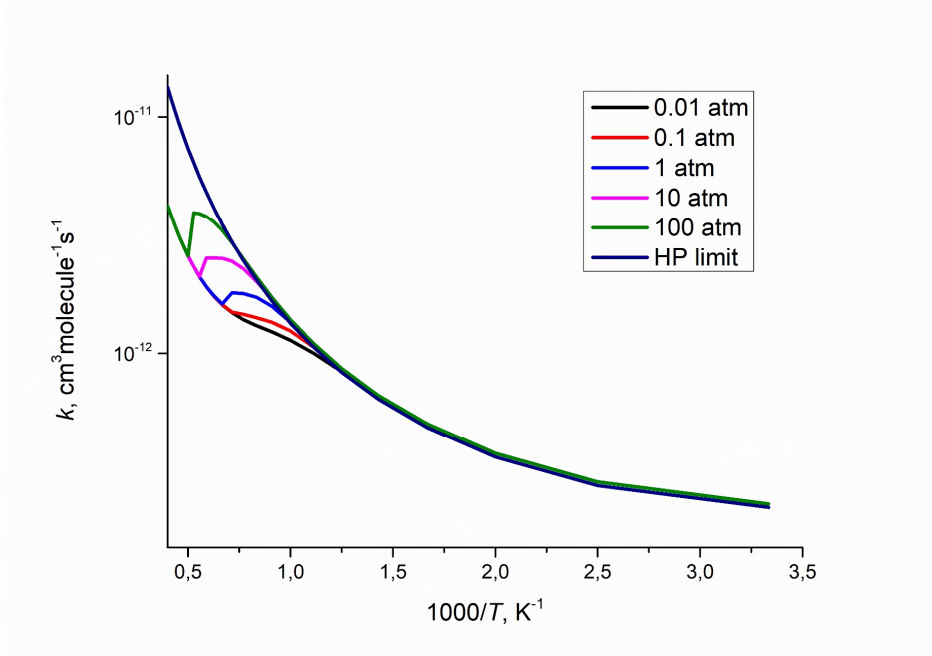

Fig. 2. Reaction rate constants for all investigated pressures and at the high pressure limit.

The analysis of the branching ratios allows us to conclude that the channels leading P1 and P2 plus H would be the main channels in the reaction at high temperatures, whereas the three-ring products dihydrophananthrene P3 and dihydroanthracene P6 show significant yields in the 1200-2000 K range. The reaction shows low pressure dependence and the product branching ratios for P1-P6 are presented in Table 1. For the temperatures below 1200 K, W1 and W2 complexes get collisionally stabilized and the resulting contributions are presented in Table 2.

Table 1. Branching ratios of the reaction of 2-naphthyl with 1,3-butadiene for pressure 1 atm.

T, K	P1	P2	P3	P4	P6
1200	3,08%	1,44%	4,13%	0,02%	2,93%
1300	28,89%	14,39%	32,61%	0,27%	22,87%
1400	35,98%	19,47%	25,38%	0,62%	18,56%
1500	41,30%	24,01%	19,28%	0,81%	14,60%
1600	45,09%	27,91%	14,61%	1,00%	11,38%
1700	47,64%	31,16%	11,14%	1,17%	8,89%
1800	49,26%	33,82%	8,60%	1,33%	6,99%
1900	50,25%	36,00%	6,72%	1,47%	5,56%
2000	50,79%	37,79%	5,34%	1,60%	4,48%
2100	51,05%	39,27%	4,30%	1,72%	3,65%
2200	51,13%	40,51%	3,51%	1,84%	3,01%
2300	51,10%	41,54%	2,91%	1,94%	2,51%
2400	51,01%	42,40%	2,44%	2,04%	2,12%
2500	50,88%	43,12%	2,06%	2,13%	1,80%

Table 2. Branching ratios of the W1 and W2 intermediates at the low temperatures for 1 atm.

T, K	W1	W2
300	34,91%	65,05%
400	33,36%	66,49%
500	32,73%	66,79%
600	29,82%	69,08%
700		98,21%
800		97,72%
900		97,40%
1000		96,30%
1100		93,76%
1200		88,25%

4 Conclusion

The mechanism of the 2-naphthyl + 1,3-butadiene reaction has been proposed in this study. The potential energy diagram and reaction rate constants with branching ratios were obtained in a broad set of pressures and temperatures. This study is important to complement the assumption PAH generation is not only a high-temperature phenomenon. P1 and P2 with hydrogen are concluded to be the main products at high temperatures but the three-ring products dihydrophenanthrene and dihidroanthracene can also be readily formed at certain conditions. The calculated reaction rate constants show low pressure dependence at pressures above 0.01 atm.

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References

1. B.S. Haynes, H.G. Wagner, Prog. Energy Combust. Sci. **7** (1981).
2. M. Frenklach, Phys. Chem. Chem. Phys. **4** (2002).
3. H. Richter, J.B. Howard, Prog. Energy Combust. Sci. **26** (2000).
4. M. Frenklach, E. D. Feigelson, Astrophys. J. **341** (1989).
5. M. Frenklach, H. Wang, Symp. (Int.) Combust. **23** (1991).
6. I. Cherchneff, J. R. Barker, A. G. G. M. Tielens, Astrophys. J. **401** (1992).
7. B. Shukla, M. Koshi, Combust. Flame **158** (2011).
8. B. Shukla, K. Tsuchiya, M. Koshi M. 2011. J. Phys.Chem. A **115** (2011).
9. A. M. Mebel, V. V. Kislov, R. I. Kaiser. 2008 J. Am. Chem. Soc. **130** (2008).
10. A. M. Thomas, M. Lucas, T. Yang, R. I. Kaiser, L. Fuentes, D. Belisario-Lara, A. M. Mebel, ChemPhysChem **18**, 15 (2017).
11. M.J. Frisch et al. *GAUSSIAN 09*, Revision A.1 (Gaussian, Inc., Wallingford, CT, 2009).
12. *MOLPRO*, version 2010.1, a package of ab initio programs, H.J.Werner and others, see http://www.molpro.net.