**Study of the Formation of the First Aromatic Rings in the Pyrolysis of Cyclopentene**

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**Supplemental data**

**Figure S1: Schematic diagram of the instruments including the jet-stirred reactor and in (a) the synchrotron photoionization mass spectrometer and in (b) the laser photoionization mass spectrometer.**

|  |  |
| --- | --- |
| figure1  **I**: the differential pumped chamber with molecular-beam sampling system and **II** the photoionization chamber with the mass spectrometer: 1, VUV light; 2, to turbo molecular pumps; 3, molecular beam; 4, RTOF mass spectrometer; 5, ion trajectory; 6, microchannel plate detector; 7, quartz cone-like nozzle; 8, heated quartz jet-stirred reactor |  |

**Table S1: Adiabatic ionization energies calculated using software Gaussian [1]. Calculations were performed at the CBS-QB3 level of theory [2]. Comparison with literature data** [3]**.**

|  |  |  |  |
| --- | --- | --- | --- |
| **Species** | **Structure** | **Calculated AIEs (eV)** | **Literature data (eV)** |
| ***m/z* 65** |  |  |  |
| cyclopentadienyl radical |  | 8.73a, 8.48b | 8.41, 8.56, 8.7 |
| ***m/z* 78** |  |  |  |
| benzene |  | 9.26 | 9.24 |
| fulvene |  | 8.43 | 8.36 |
| 1,3-hexadiyne |  | 9.31 | 9.25, 9.41 |
| 1,4-hexadiyne |  | 9.66 | 9.50-9.75 |
| 1,5-hexadiyne |  | 9.97 | 9.9-10.0 |
| 2,4-hexadiyne |  | 8.82 | 8.9-9.0 |
| trans-1,3-hexadien-5-yne |  | 8.61 | 9.2-9.5 |
| cis-1,3-hexadien-5-yne |  | 8.65 | 9.2-9.5 |
|  |  |  |  |
| 1,5-hexadien-3-yne |  | 8.61 | 8.5 |

a singlet state for the cation. b triplet state for the cation.

**Table S2: Kinetic parameters used for the formation of toluene from the recombination of cyclopentadienyl and ethyl radicals as shown in Figure S2 (units: cm3, mol, s, cal).**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction | A | n | Ea | ref |
| ***Combination*** |  |  |  |  |
| C5H5 + C2H5 ECPD | 8.34×1015 | -0.70 | -0.50 | [[1]](#footnote-1) |
| ***Unimolecular Initiations*** |  |  |  |  |
| ECPD R1EACPD + H | 2.5×1015 | 0 | 78.7×103 | [[2]](#footnote-2) |
| R2ECPD + H ECPD | 1.00×1014 | 0 | 0 | [[3]](#footnote-3) |
| R3ECPD + H ECPD | 1.00×1014 | 0 | 0 | 3 |
| ***H-atom abstractions*** |  |  |  |  |
| ECPD + H R1ECPD + H2 | 1.4×1013 | 0 | 2.0×103 | [[4]](#footnote-4) |
| ECPD + H R2ECPD + H2 | 4.5×106 | 2 | 5.0×103 | [[5]](#footnote-5) |
| ECPD + H R3ECPD + H2 | 2.9×107 | 2 | 7.7×103 | 5 |
| ECPD + CH3 R1ECPD + CH4 | 590 | 2.9 | 5.06×103 | [[6]](#footnote-6) |
| ECPD + CH3 R2ECPD + CH4 | 1.0×1011 | 0 | 9.6×103 | 5 |
| ECPD + CH3 R3ECPD + CH4 | 0.75×10-7 | 6 | 5.8×103 | [[7]](#footnote-7) |
| ECPD + C3H5 R1ECPD + C3H6 | 96 | 3.14 | 11.5×103 | [[8]](#footnote-8) |
| ECPD + C3H5 R2ECPD + C3H6 | 4.0×101 | 3.3 | 18.17×103 | 5 |
| ECPD + C3H5 R3ECPD + C3H6 | 4.0×101 | 3.3 | 19.84×103 | 5 |
| ECPD + C5H5 R1ECPD + C5H6 | 96 | 3.14 | 11.5×103 | 7 |
| ECPD + C5H5 R2ECPD + C5H6 | 8.0×101 | 3.3 | 18.17×103 | 5 |
| ECPD + C5H5 R3ECPD + C5H6 | 8.0×101 | 3.3 | 19.84×103 | 5 |
| ***Isomerization*** |  |  |  |  |
| R1ECPD R2ECPD | 3.0×1013 | 0 | 50.4×103 | [[9]](#footnote-9) |
| R3ECPD R1ECPD | 1.92×109 | 1 | 32.5×103 | [[10]](#footnote-10) |
| ***Reactions of decomposition*** |  |  |  |  |
| R3ECPD C2H4 + C5H5 | 3.3×1013 | 0 | 22.5×103 | [[11]](#footnote-11) |
| R2ECPD R4ECPD | 1.4×1013 | 0 | 17.4×103 | [[12]](#footnote-12) |
| R2ECPD R4ECPD | 4.0×1013 | 0 | 35.5×103 | 5 |
| toluene + H R4ECPD | 3.2×1013 | 0 | 3.2×103 | [[13]](#footnote-13) |

**Table S3: Kinetic parameters used for the formation of toluene from the addition of the cyclopentadienyl radical to propene as shown in Figure S3 (units: cm3, mol, s, cal).**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction | A | n | Ea | ref |
| ***Addition*** |  |  |  |  |
| C5H5 + propene C5H5@C3H6l | 1.56×103 | 2.53 | 20.0×103 | [[14]](#footnote-14) |
| ***Cyclo-addition*** |  |  |  |  |
| C5H5@C3H6l C8H11-C4 | 3.10×1012 | 0 | 10.4×103 | [12] |
| reverse | 1.60×1013 | 0 | 27.1×103 | [12] |
| ***Decomposition*** |  |  |  |  |
| C8H11-C4 C8H11-C7 | 1.4×1013 | 0 | 24.6×103 | [12] |
| reverse | 2.7×1013 | 0 | 59.0×103 | [12] |
| C8H11-C7 C7H8-c7 + CH3 | 1.0×1013 | 0 | 31.0×103 | [[15]](#footnote-15) |
| ***Isomerization*** |  |  |  |  |
| R1ECPD R2ECPD | 3.0×1013 | 0 | 50.4×103 | [13] |

**Table S4: Kinetic parameters used for the formation of styrene from the cyclopentadienyl and allyl radicals as shown in Figure S4 (units: cm3, mol, s, cal).**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction | A | n | Ea | ref |
| ***Combination*** |  |  |  |  |
| C5H5 + C3H5 ACPD | 8.34×1015 | -0.70 | -0.50 | [[16]](#footnote-16) |
| ***Unimolecular Initiations*** |  |  |  |  |
| ACPD R1ACPD + H | 2.5×1015 | 0 | 78.7×103 | [[17]](#footnote-17) |
| ACPD R2ACPD + H | 1.26×1015 | 0 | 82.47×103 | [[18]](#footnote-18) |
| ***H-atom abstractions*** |  |  |  |  |
| ACPD + H R1ACPD + H2 | 1.4×1013 | 0 | 2.0×103 | [[19]](#footnote-19) |
| ACPD + H R2ACPD + H2 | 1.13×105 | 2.5 | 2.48×103 | [[20]](#footnote-20) |
| ACPD + CH3 R1ACPD + CH4 | 590 | 2.9 | 5.06×103 | [[21]](#footnote-21) |
| ACPD + CH3 R2ACPD + CH4 | 1.47 | 3.5 | 5.68×103 | [[22]](#footnote-22) |
| ACPD + C3H5 R1ACPD + C3H6 | 96 | 3.14 | 11.5×103 | [[23]](#footnote-23) |
| ACPD + C3H5 R2ACPD + C3H6 | 4.0×101 | 3.3 | 18.17×103 | [[24]](#footnote-24) |
| ACPD + C5H5 R1ACPD + C5H6 | 96 | 3.14 | 11.5×103 | 4 |
| ACPD + C5H5 R2ACPD + C5H6 | 8.0×101 | 3.3 | 18.17×103 | 7 |
| ***Isomerization*** |  |  |  |  |
| R1ACPD R2ACPD | 3.0×1013 | 0 | 50.4×103 | [[25]](#footnote-25) |
| ***Reactions of decomposition to styrene*** |  |  |  |  |
| R2ACPD R3ACPD | 1.4×1013 | 0 | 17.4×103 | [[26]](#footnote-26) |
| R2ACPD R3ACPD | 4.0×1013 | 0 | 35.5×103 | [[27]](#footnote-27) |
| Styrene + H R3ACPD | 3.2×1013 | 0 | 3.2×103 | [[28]](#footnote-28) |

**Table S5: Kinetic parameters used for the formation of naphthalene from the cyclopentadienyl radical (C5H5) as shown in Figure 8 (units: cm3, mol, s, cal).**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction | A | n | Ea | ref |
| ***Combination*** |  |  |  |  |
| C5H5 + C5H5 DCPD1 | 1.02×1013 | -0.26 | 0 | [8] |
| ***Unimolecular initiation*** |  |  |  |  |
| DCPD1 R1DCPD + H | 5.0×1015 | 0 | 78.7×103 | [16] |
| ***H-atom abstractions*** |  |  |  |  |
| DCPD1 + H R1DCPD + H2 | 2.8×1013 | 0 | 2.0×103 | [[29]](#footnote-29) |
| DCPD1 + CH3 R1DCPD + CH4 | 1180 | 2.9 | 5.06×103 | [[30]](#footnote-30) |
| DCPD1 + C3H5 R1DCPD + C3H6 | 191 | 3.14 | 11.5×103 | [[31]](#footnote-31) |
| DCPD1 + C5H5 R1DCPD + C5H6 | 191 | 3.14 | 11.5×103 | 3 |
| ***Reactions of decomposition to naphthalene*** |  |  |  |  |
| S1C10H9=>S2C10H9 | 1.26×109 | 0.90 | 10.7×103 | [17] |
| S2C10H9=>S1C10H9 | 7.95×109 | 1.03 | 1.8×103 | [17] |
| S2C10H9=>S3C10H9 | 7.42×109 | 1.02 | 19.3×103 | [17] |
| S3C10H9=>S2C10H9 | 1.81×108 | 1.34 | 32.7×103 | [17] |
| S3C10H9=>S4C10H9 | 8.13×109 | 0.90 | 13.1×103 | [17] |
| S4C10H9=>S3C10H9 | 2.11×1010 | 0.80 | 5.9×103 | [17] |
| S3C10H9=>S11C10H9 | 2.47×1011 | 0.72 | 24.9×103 | [17] |
| S11C10H9=>S3C10H9 | 2.23×1010 | 0.46 | 4.9×103 | [17] |
| S4C10H9=>S10C10H9 | 7.89×109 | 0.90 | 11.3×103 | [17] |
| S10C10H9=>S4C10H9 | 4.69×108 | 1.34 | 35.1×103 | [17] |
| S11C10H9=>S10C10H9 | 8.21×1010 | 0.28 | 3.3×103 | [17] |
| S10C10H9=>S11C10H9 | 6.09×1011 | 0.71 | 35.6×103 | [17] |
| S10C10H9=>naphthalene+R1H | 1.47×1010 | 0.96 | 14.0×103 | [17] |
| naphthalene+R1H=>S10C10H9 | 9.33×108 | 1.47 | 10.9×103 | [17] |

**Table S6: Kinetic parameters used for the formation of indene from the addition of the cyclopentadienyl radical (C5H5) to 1,3-butadiene as shown in Figure S6 (units: cm3, mol, s, cal).**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction | A | n | Ea | ref |
| ***Addition*** |  |  |  |  |
| C5H5 + C4H6 C5H5@C4H6 | 1.35×1000 | 3.01 | 6.4×103 | [[32]](#footnote-32) |
| ***Ring closure*** |  |  |  |  |
| C5H5@C4H6 C9H11@@1 | 1.00×1008 | 0.86 | 5.9×103 | [[33]](#footnote-33) |
| ***Isomerization*** |  |  |  |  |
| C9H11@@1 C9H11@@2 | 5.9×1012 | 0.00 | 28.9×103 | [[34]](#footnote-34) |
| C9H11@@2 C9H11@@1 | 4.1×1012 | 0.00 | 46.5×103 | 3 |
| ***Decomposition*** |  |  |  |  |
| C9H11@@2 => C9H10@@ + H | 4.50×1012 | 0.00 | 20.5×103 | [[35]](#footnote-35) |
| C9H10@@ + H => C9H11@@2 | 5.50×1012 | 0.00 | 7.0×103 | 4 |
| C9H11@@2 => indene + H2 | 2.29×1012 | 0.00 | 43.7×103 | [[36]](#footnote-36) |

**Figure S2: Reactions added in the model to account for the formation of toluene from the cyclopentadienyl radical. The scheme is based on the formalism proposed by [10] for the reaction of the methylcyclopentadienyl radical to benzene.**

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**Figure S3: Reactions added in the model to account for the formation of toluene from the reaction of the cyclopentadienyl radical and propene. The first steps are inspired from the study of Fascella et al. about the reaction of the cyclopentadienyl radical and acetylene [12].**

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**Figure S4: Reactions added in the model to account for the formation of styrene from the cyclopentadienyl radical.**

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**Figure S5: Mechanism proposed by Fascella et al. for the reaction of the cyclopentadienyl radical and acetylene to indene [12].**

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**Figure S6: Mechanism used for the formation of benzene from the addition of the cyclopentadienyl radical to 1,3-butadiene**

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**Figure S7: Comparison of the performance of the new model and of that previously published for ethyl‑benzene [21].**

|  |  |
| --- | --- |
| **New model** | **Previous model** |
|  |  |
| **Figure S7 (continued)** |  |
| **New model** | **Previous model** |
| **Figure S7 (continued)** |  |
|  |  |
| **New model** | **Previous model** |
| **Figure S7 (continued)** |  |
|  |  |
| **New model** | **Previous model** |
|  |  |

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1. as cyclopentadienyl + CH3 [4]. [↑](#footnote-ref-1)
2. as 1,3-cyclopentadiene = cyclopentadienyl + H [5], A /2. [↑](#footnote-ref-2)
3. Exgas correlation for recombination with H-atoms [6]. [↑](#footnote-ref-3)
4. as for 1,3-cyclopentadiene + H = cyclopentadienyl + H2 [7], A/2. [↑](#footnote-ref-4)
5. Exgas correlation for H-atom abstractions [6]. [↑](#footnote-ref-5)
6. as for 1,3-cyclopentadiene + CH3 = cyclopentadienyl + CH4 [8]. [↑](#footnote-ref-6)
7. as C2H6 + CH3 = C2H5 + CH4 [9], A/2. [↑](#footnote-ref-7)
8. as for 1,3-cyclopentadiene + H = cyclopentadienyl + H2 [7], A/2. [↑](#footnote-ref-8)
9. as for methylcyclopentadienyl radical = 5-methylene-1,3-cyclopentadiene radical [10]. [↑](#footnote-ref-9)
10. Exgas correlation for isomerizations [6]. [↑](#footnote-ref-10)
11. Exgas correlation for -scission [6] [↑](#footnote-ref-11)
12. as for 5-methylene-1,3-cyclopentadiene = 2,4-cyclohexadien-1-yl radical [10]. [↑](#footnote-ref-12)
13. as benzene + H = 2,4-cyclohexadien-1-yl radical [11]. [↑](#footnote-ref-13)
14. estimation from the addition of allyl to propene [8]. [↑](#footnote-ref-14)
15. Exgas correlation for -scission [6] [↑](#footnote-ref-15)
16. as cyclopentadienyl + CH3 [4]. [↑](#footnote-ref-16)
17. as 1,3-cyclopentadiene = cyclopentadienyl + H [5], A /2. [↑](#footnote-ref-17)
18. as 1-butene = but-3-en-1-yl + H [14]. [↑](#footnote-ref-18)
19. as for 1,3-cyclopentadiene + H = cyclopentadienyl + H2 [7], A/2. [↑](#footnote-ref-19)
20. as for propene + H = allyl + H2 [15], A\*2/3. [↑](#footnote-ref-20)
21. as for 1,3-cyclopentadiene + CH3 = cyclopentadienyl + CH4 [8]. [↑](#footnote-ref-21)
22. as for propene + CH3 = allyl + CH4 [15], A\*2/3. [↑](#footnote-ref-22)
23. as for 1,3-cyclopentadiene + allyl = cyclopentadienyl + propene [8]. [↑](#footnote-ref-23)
24. Exgas correlation for H-atom abstractions by allylic radicals [6] [↑](#footnote-ref-24)
25. as for methylcyclopentadienyl radical = 5-methylene-1,3-cyclopentadiene radical [10]. [↑](#footnote-ref-25)
26. as for 5-methylene-1,3-cyclopentadiene = 2,4-cyclohexadien-1-yl radical [10]. [↑](#footnote-ref-26)
27. Exgas correlation for -scission [6] [↑](#footnote-ref-27)
28. as benzene + H = 2,4-cyclohexadien-1-yl radical [11]. [↑](#footnote-ref-28)
29. as for 1,3-cyclopentadiene + H = cyclopentadienyl + H2 [7]. [↑](#footnote-ref-29)
30. as for 1,3-cyclopentadiene + CH3 = cyclopentadienyl + CH4 [8]. [↑](#footnote-ref-30)
31. as for 1,3-cyclopentadiene + allyl = cyclopentadienyl + propene [8]. [↑](#footnote-ref-31)
32. as for cyclopentadienyl + 1,3-cyclopentadiene = 8,9,10-trihydrofulvalenyl [18]. [↑](#footnote-ref-32)
33. as for hex-5-en-1-yl = cyclohexyl [19]. [↑](#footnote-ref-33)
34. as for C9H9-c5 => C9H9-c5t and C9H9-c5t => C9H9-c5 [12]. [↑](#footnote-ref-34)
35. as for C9H9-c5t => indene + H and indene + H => C9H9-ct [12]. [↑](#footnote-ref-35)
36. As for 1,3-cyclohexadiene => benzene + H2 [20]. [↑](#footnote-ref-36)