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1 Theoretical Study of the Effect of Hydrogen Radicals 2 on the Formation of HCN from Pyrrole Pyrolysis

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12 Abstract

13 As a typical fossil fuel, coal is a major contributor to nitrogen oxide (NO_x) pollution.
14 The detailed mechanism of NO_x generation from coal pyrolysis need to be clarified.
15 Within this research, we used density functional theory (DFT) to investigate the
16 formation mechanism of HCN as a NO_x precursor during pyrolysis of pyrrole in the
17 presence of hydrogen (H) radicals. Firstly, three different reaction positions for
18 hydrogen radical attacking were compared. It was identified that hydrogen radical
19 initially reacts with pyrrole at the location adjacent to N through a single elementary
20 reaction step with an activation energy of 77.12 kJ/mol. Additionally, to examine the
21 role of hydrogen radical in the pyrrole pyrolysis to form HCN, 12 subsequent reaction
22 pathways were theoretically investigated. It was found that one of the pathway
23 (Pathway a-4) involving hydrogen transfer followed by carbon-carbon cleavage
24 processes is the route with the lowest energy barrier of all of the mechanisms reported,
25 thus it plays an important role in the formation of HCN from the pyrrolic components
26 of coal. These results further indicated that the hydrogen radicals significantly reduce
27 the energy barrier of the pyrrole pyrolysis.

28 **Keywords:** NO_x; hydrogen radicals; HCN; pyrrole; Density Functional Theory

29 1. Introduction

30 Coal combustion is a main source of nitrogen oxide (NO_x) pollution in air [1].
31 NO_x not only forms acid rain and photochemical smog, but also directly endangers
32 human health [2]. At present, the mechanisms of NO_x formation from coal are not
33 well understood, and detailed elucidation of these formation mechanism plays an
34 important role for efficient control of NO_x emission during coal utilization [3,4].

35 It has been identified that HCN and NH₃, which are generated during coal
36 utilization under high temperature, are the main precursors of NO_x [5,6]. Therefore,
37 the thermal decomposition of N-containing model compounds to NH₃ and HCN is
38 important for understanding NO_x formation.

39 Three types of N-containing compounds exist in coal: pyrrole-N, pyridine-N, and
40 quaternary-N [7]. The dominant nitrogen source in coal is the pyrrole type, which
41 accounts for 50–80 wt.% of total nitrogen [8]. Thus, the thermal decomposition of
42 pyrrolic groups plays an essential role in NO_x precursor formation. Among the many
43 researchers who have studied the formation mechanisms of NO_x precursors from
44 pyrrole, it has been generally agreed that HCN is the primary N-containing product
45 generated by pyrrole pyrolysis. For example, Martoprawiro et al. [9] proposed several
46 reaction pathways for pyrrole pyrolysis with the major product being HCN. Zhai et al.
47 [10] also investigated the reaction pathways of pyrrole pyrolysis to form HCN, and
48 proposed a mechanism different from Martoprawiro's work [9] for the formation of
49 cis-crotonitrile and allyl cyanide. In addition, Bacskay et al. [11] reported an optimal
50 pathway with the lowest energy barrier (315.68 kJ/mol for the rate-determining step)
51 for pyrrole pyrolysis to form HCN.

52 Pyrolysis of coal has been confirmed to involve radical reactions, and hydrogen
53 (H) radicals are commonly generated during coal pyrolysis. During pyrolysis, coal is
54 gradually heated, bond-breaking reactions within the network structure begin at
55 350-400°C, homolytic breaking of covalent bonds in the network structure generate
56 reactive free radicals. In fact, the cracking of alkane and aromatics will break by C-C
57 and C-H homolysis in a long chain reaction, as the temperature rises, C-H homolysis
58 will occur competitively to form hydrogen radicals [12–15]. Therefore, hydrogen
59 radicals should exert significant effects on the formation of nitrogen-containing
60 pollutants by reducing the activation energy of pyrrole pyrolysis to form HCN. For
61 example, Mackie et al. [16] studied the pyrrole pyrolysis with hydrogen radical
62 through experiments and molecular dynamics simulations, they found that the
63 ring-opening of pyrrole is facilitated by hydrogen radical adsorption on it. Moreover,
64 Zeng et al. [17] proposed a possible mechanism of hydrogen radical adsorption on
65 pyrrole by quantum chemistry computation, theoretically confirming the hypothesis
66 proposed by Mackie and co-workers.

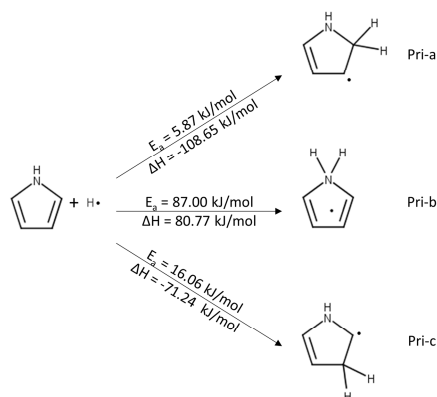
67 However, it remains unclear how the hydrogen radical actually affects pyrrole
68 pyrolysis to form HCN. To fill this research gap, in this work we use density
69 functional theory (DFT) method to investigate the formation mechanism of HCN
70 during pyrrole pyrolysis in the presence of hydrogen radicals and comprehensively
71 examine the possible reaction pathways. These results will clarify the effects of
72 hydrogen radicals on coal pyrolysis to form NO_x.

73 2. Methodology

74 All calculations were carried out in Gaussian 16 [18], using the CBS-QB3
75 method of Petersson and co-workers [19]. CBS-QB3 is a composite method that
76 combines the speed of density functional theory with the high accuracy of
77 post-Hartree-Fock methods. It also helps alleviate the errors associated with truncated
78 basis sets through extrapolation of energies to the complete basis set limit. In
79 CBS-QB3 calculations, a geometry optimisation and frequency calculation are
80 performed first at the B3LYP/6-311G(2d,d,p) level and then a subsequent frequency
81 analysis is carried out at the B3LYP/CBSB7 level. Following this, single point energy
82 calculations at the CCSD(T)/6-31+G9d') and MP4SDQ/CBSB4 level are performed
83 and the energy is obtained at the complete basis set limit through extrapolation at the
84 MP2/CBSB3 level. This method has been shown to be highly accurate, with mean
85 errors of under 5 kJ/mol when tested against the G2/97 test set [20]. Furthermore,
86 CBS-QB3 contains a correction for spin-contamination in radical species which
87 further justifies its selection for this study.

88 3. Results and Discussion

89 There are three possible sites on the pyrrole that can be attacked by the hydrogen
90 radical, which we have termed Pri-a, Pri-b and Pri-c as shown in Figure 1. Interaction
91 at site Pri-a involves the radical reacting with the carbon atom that is adjacent to the
92 nitrogen. This is the reaction site with the lowest energy barrier, at 5.87 kJ/mol, and
93 the greatest exothermicity, releasing 108.65 kJ/mol. At site Pri-b, a hydrogen radical
94 attack on the nitrogen atom, is considerably less favourable, with an activation energy
95 of 87.00 kJ/mol as well as being endothermic by 80.77 kJ/mol. The unpaired electron
96 is located at the centre of the ring in this representation as it will be distributed
97 throughout the pyrrole ring through resonance structures. Interaction at site Pri-c,
98 which involves radical attack on the carbon atom opposite the nitrogen, is
99 energetically similar to pri-a in that it has a low activation barrier of 16.06 kJ/mol and
100 it is exothermic by 71.24 kJ/mol. Based on hydrogen radical attacking on each of the
101 reaction site, the subsequent reaction pathways for HCN formation will be
102 investigated and analysed.



103

104 *Figure 1. Three sites for hydrogen radical attack on pyrrole.*

105 3.1. Reaction pathways following interaction at site Pri-a

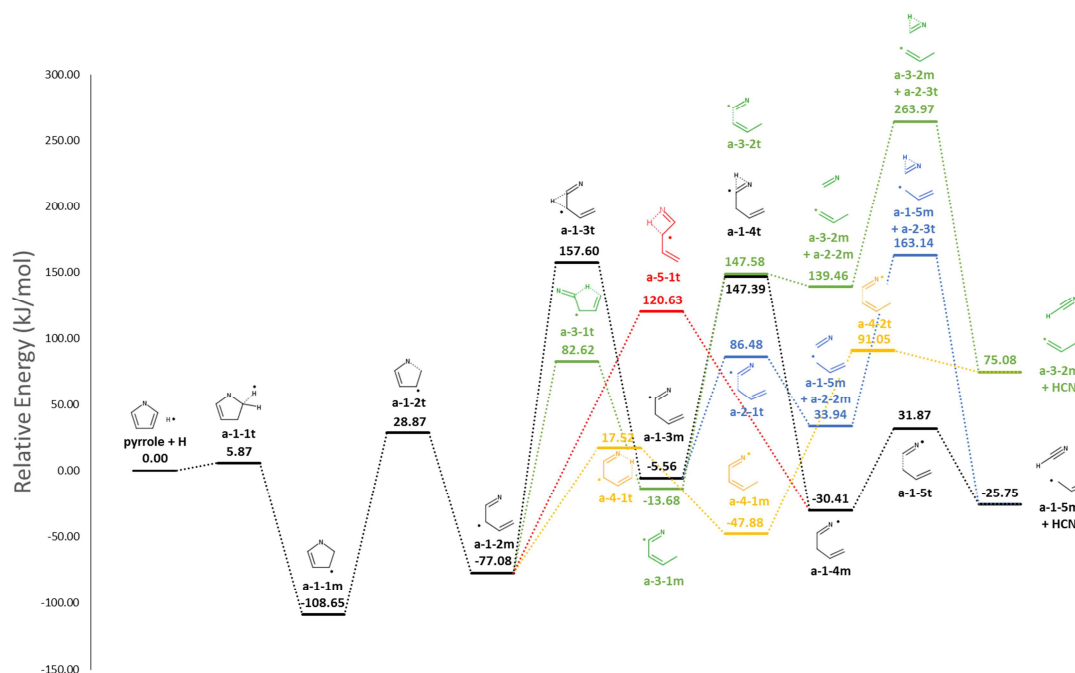
106 Following the hydrogen radical addition at the nitrogen adjacent carbon, five
 107 possible pathways (a-1, a-2, a-3, a-4, and a-5) for HCN formation were investigated.
 108 These pathways, as outlined in Figure 2, are all initiated through a ring opening step
 109 from *a-1-1m* to *a-1-2m* with an activation barrier of 137.52 kJ/mol. The molecular
 110 structures of the related transition states involved in these pathways are shown in
 111 Figure 3.

112 In the first route (a-1) of these pathways (black curve in Figure 2), a hydrogen
 113 transfer step occurs from the nitrogen bound carbon to the adjacent carbon atom,
 114 converting *a-1-2m* to *a-1-3m*. The reaction proceeds through *a-1-3t* with a barrier
 115 height of 234.68 kJ/mol. This allows for the nitrogen-bound hydrogen to transfer to
 116 the newly formed carbon radical to give intermediate *a-1-4m*. From here, a low
 117 energy cleavage reaction (62.28 kJ/mol) occurs to yield HCN and the radical species
 118 *a-1-5m*.

119 In the alternative a-2 route (blue curve in Figure 2), the carbon-carbon cleavage
 120 occurs in intermediate *a-1-3m* to give the radical *a-1-5m* and *a-2-2m*, a HCN isomer.
 121 Conversion of *a-2-2m* to HCN involves a nitrogen to carbon hydrogen transfer, with
 122 an activation energy of 129.20 kJ/mol and gives the same products as reaction
 123 pathway a-1.

124 A hydrogen abstraction from the nitrogen adjacent carbon to the terminal carbon
 125 of *a-1-2m* initiates pathway a-3 (green curve, Figure 2) and forms intermediate
 126 *a-3-1m*. This species then undergoes a carbon-carbon cleavage to give the radical
 127 *a-3-2m* and the HCN isomer *a-2-2m*, which again undergoes a hydrogen transfer to

128 yield HCN. The products of this route are significantly higher than those of path a-1



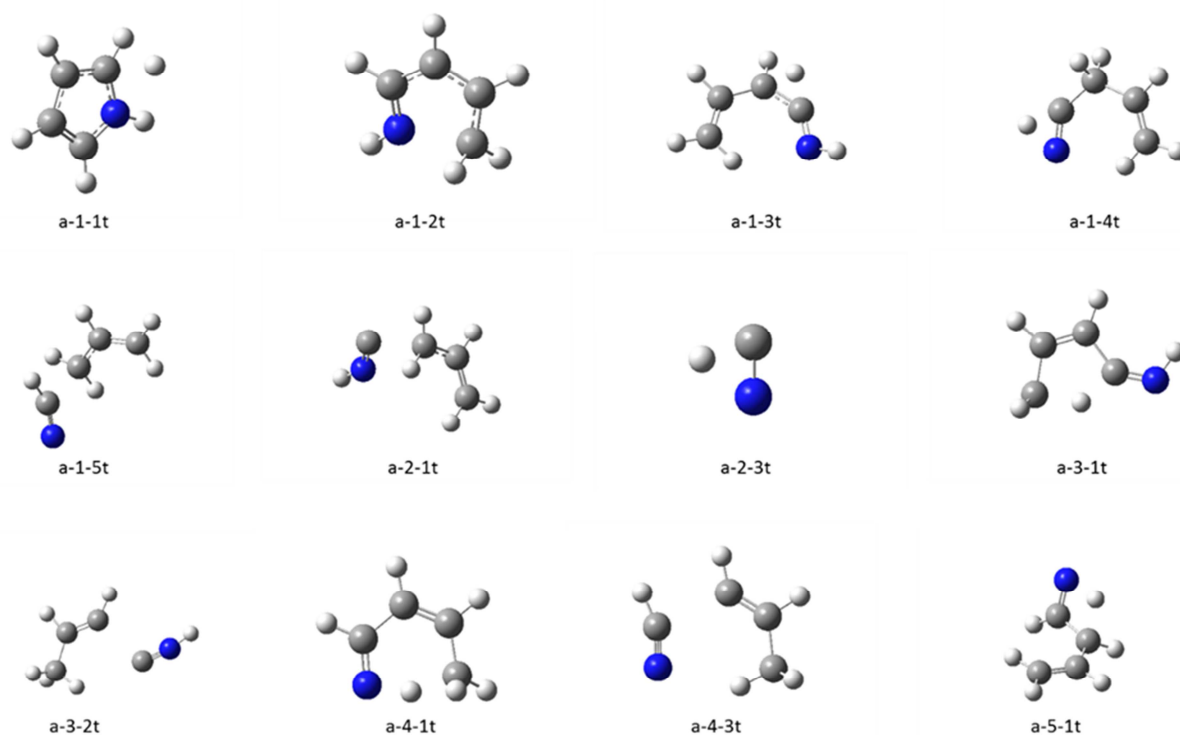
129 and a-2, suggesting a greater instability of the radical product *a-3-2m*.

130

131 *Figure 2. Pyrolytic pathways following interaction Pri-a. The numerical values are*
 132 *energies in kJ/mol relative to that of pyrrole and hydrogen radical.*

133 Pathway a-4 (yellow curve, Figure 2) is the most energetically facile of the five
 134 routes following interaction at site Pri-a. The intermediate *a-1-2m* is converted to
 135 *a-4-1m* through a hydrogen transfer from the nitrogen to the terminal carbon atom.
 136 The energy barrier for this is relatively low at 94.60 kJ/mol, most likely owing to the
 137 6 membered pericyclic transition state *a-4-1t*. The intermediate *a-4-1m* is converted to
 138 products *a-3-2m* and HCN through a carbon-carbon cleavage, with a barrier height of
 139 138.93 kJ/mol.

140 The last pathway considered is a-5 (red curve, Figure 2). In this route
 141 intermediate *a-1-2m* is converted directly to *a-1-4m* via a single transition state
 142 species *a-5-1t*. This transition state is lower in energy than *a-1-3t* by 36.97 kJ/mol,
 143 most likely due to the less sterically strained five member pericyclic transition state.



144

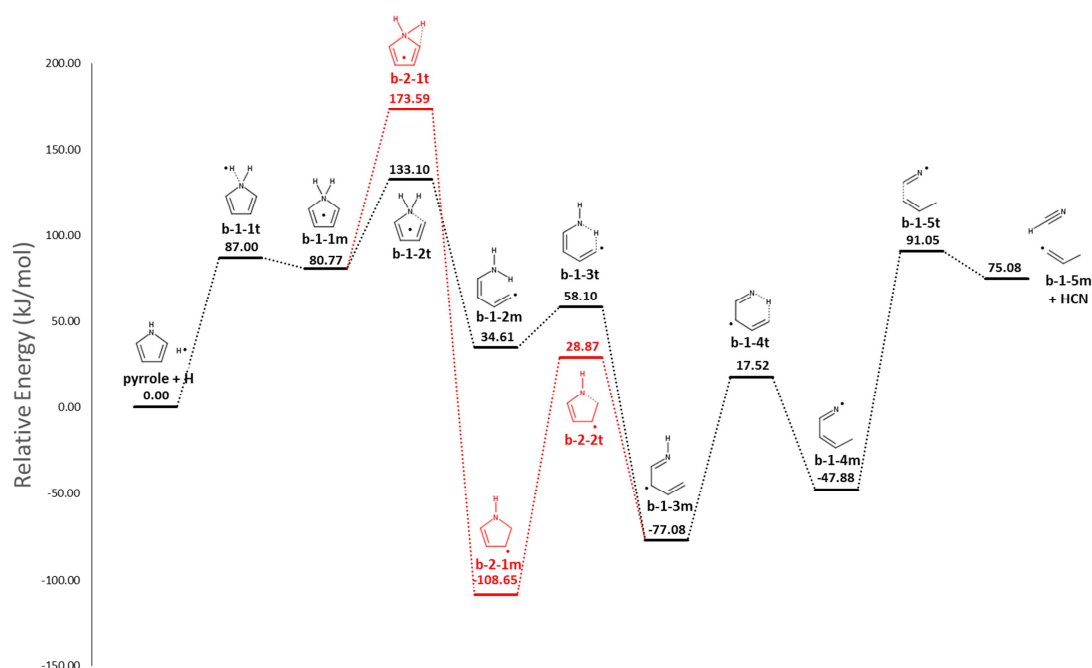
145 *Figure 3. All the transition states of pyrolytic pathways following interaction at Pri-a.*
 146 *The blue spheres represent nitrogen atoms; the grey spheres represent carbon atoms;*
 147 *and the white spheres represent hydrogen atoms.*

148 As a summary of all pathways following site Pri-a, pathway a-4 is the most facile
 149 in terms of activation enthalpy, with a barrier height of 91.05 kJ/mol. However, this
 150 pathway leads to the final product pair that is higher in energy and exothermic by
 151 75.08 kJ/mol. The alternative pathway of a-5, whilst having a greater energy barrier of
 152 120.63 kJ/mol, leads to more favourable products. This pathway is exothermic, with a
 153 relative energy of -25.75 kJ/mol. It can be concluded that pathway a-4 is the most
 154 facile kinetic route, whilst pathway a-5 is the lowest energy thermodynamic route.

155 3.2. Reaction pathways following interaction at site Pri-b

156 Figure 4 shows two possible routes (b-1 and b-2) following hydrogen radical
 157 attack on the nitrogen (site Pri-b) and Figure 5 illustrates all the related transition
 158 states. The addition of the hydrogen radical on the nitrogen atom leads to the least
 159 stable cyclic pyrrole radical, intermediate *b-1-1m*. A facile cleavage of a
 160 nitrogen-carbon bond can occur to yield intermediate *b-1-2m*. Following this, a
 161 transfer of one hydrogen atom from the nitrogen to the terminal carbon radical is
 162 easily achieved with a barrier height of just 23.49 kJ/mol and yields intermediate
 163 *b-1-3m*. This intermediate is analogous to *a-1-2m* and proceeds to HCN via the same
 164 pathway described previously. An alternative route is pathway b-2 (red curve, Figure
 165 4). In this route, the hydrogen transfer occurs first and produces intermediate *b-2-1m*.

166 This species is identical to *a-1-1m* and therefore proceeds to HCN in the same manner



167 as outlined before.

168 *Figure 4. Pyrolytic pathways following interaction Pri-b. The numerical values are*
 169 *energies in kJ/mol relative to that of pyrrole and hydrogen radical.*



170

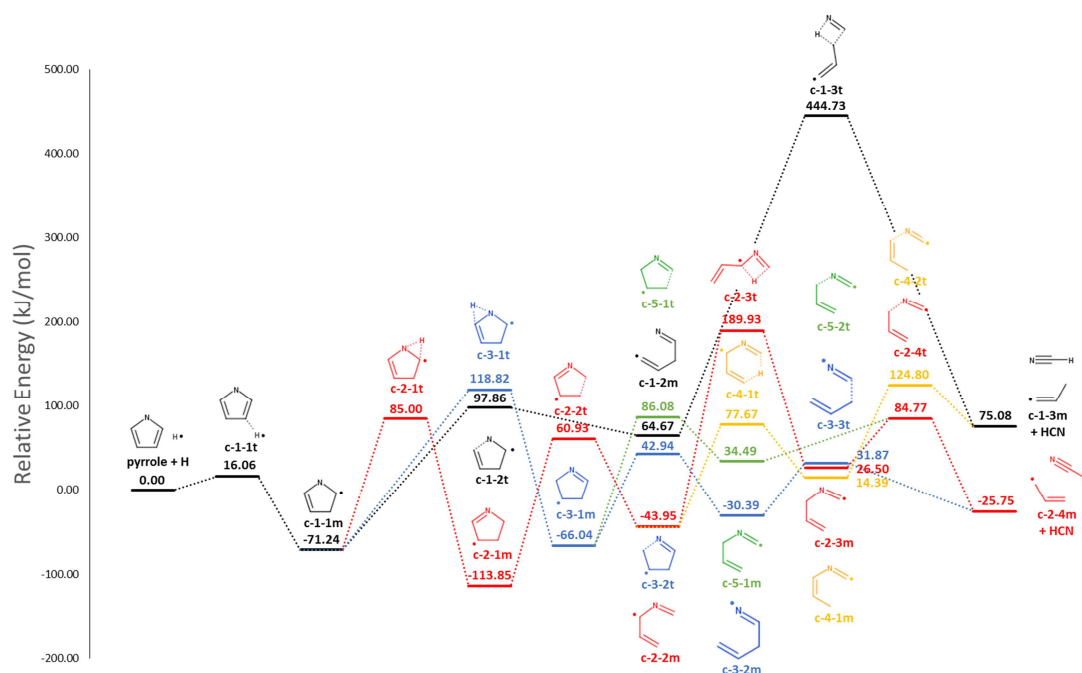
171 *Figure 5. All the transition states of pyrolytic pathways following interaction at Pri-b.*
 172 *The blue spheres represent nitrogen atoms; the grey spheres represent carbon atoms;*
 173 *and the white spheres represent hydrogen atoms.*

174 3.3. Reaction pathways following interaction at site Pri-c

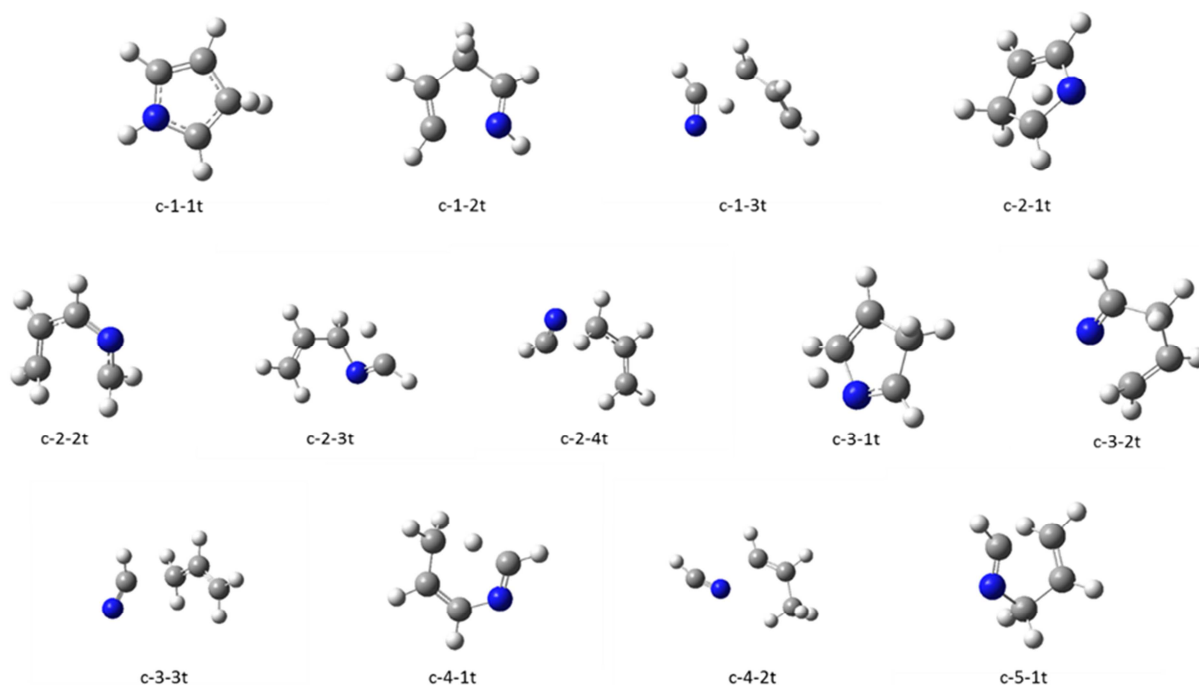
175 Following the hydrogen radical addition on the non-nitrogen adjacent carbons (site
 176 Pri-c), an intermediate *c-1-1m* was formed at an initial stage. Following this, five
 177 possible routes (c-1, c-2, c-3, c-4, and c-5) to HCN formation were investigated as
 178 shown in Figure 6 with the structure of key transition states shown in Figure 7. In
 179 pathway c-1 (black curve, Figure 6), intermediate *c-1-1m* undergoes a carbon-nitrogen
 180 cleavage to yield intermediate *c-1-2m* via transition state *c-1-2t*. This species can then
 181 undergo a simultaneous hydrogen transfer and carbon-carbon bond breaking reaction
 182 to yield HCN and *c-1-3m*, which is the same radical product as *a-3-2m*. This reaction

183 requires a significantly large activation energy of 380.06 kJ/mol and is therefore the
 184 least facile of all the routes proposed in this work.

185 *Figure 6. Pyrolytic pathways based on interaction Pri-c. The numerical values are*



186 *energies in kJ/mol relative to that of pyrrole and hydrogen radical.*



187

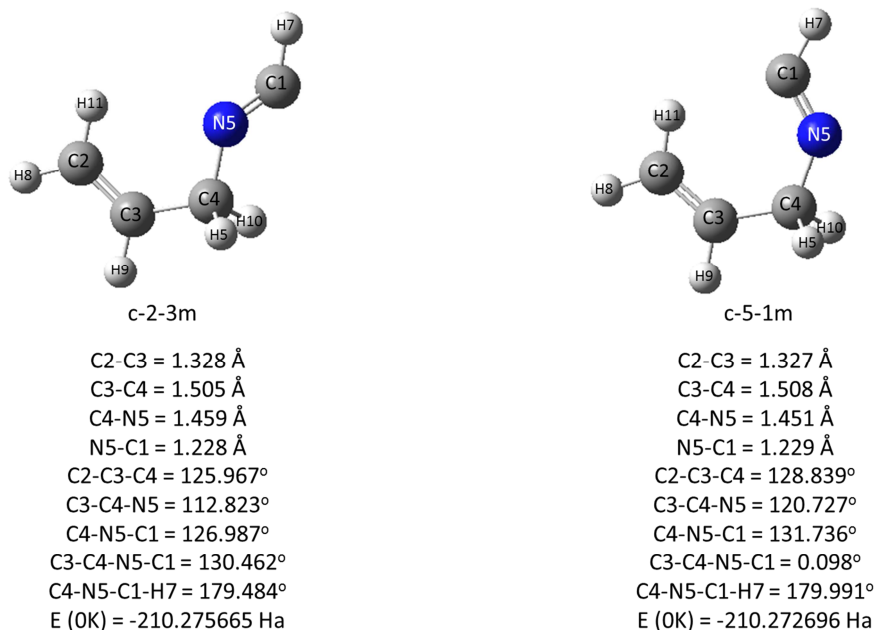
188 *Figure 7. All the transition states of pyrolytic pathways following interaction at Pri-c.*
 189 *The blue spheres represent nitrogen atoms; the grey spheres represent carbon atoms;*
 190 *and the white spheres represent hydrogen atoms.*

191 Alternatively, a hydrogen transfer can take place from the nitrogen atom to the
192 adjacent carbon radical position as in pathway c-2 (red curve, Figure 6). This gives
193 rise to intermediate *c-2-1m* which in turn will undergo a carbon-carbon bond breaking
194 to yield *c-2-2m*, in which a CH₂ group is double bonded to the nitrogen atom. The
195 conversion of *c-2-2m* to *c-2-3m* involves transfer of a hydrogen from this CH₂ to the
196 other nitrogen bonded carbon atom. From this intermediate, there is a low energy
197 barrier (58.27 kJ/mol) transition state for the carbon-nitrogen cleavage to give HCN
198 and *c-2-4m*. It is worth to note that the products of *c-2-4m* is the same as the products
199 of *a-1-5m* obtained from pathway a-1.

200 Intermediate *c-1-1m* can convert to *c-3-1m* through a transfer of the hydrogen
201 from the nitrogen to the non-radical neighbouring carbon and formation of a
202 nitrogen-carbon double bond, this pathway is called as c-3 (blue curve, Figure 6). The
203 barrier height of *c-3-1t* is the greatest of the possible reactions for *c-1-1m* at 190.06
204 kJ/mol. Breaking of the nitrogen-carbon single bond to open the pyrrole ring gives
205 intermediate *c-3-2m*. From here, a low energy carbon-carbon bond rupturing yields
206 HCN and *c-2-4m*, with a activation barrier of 62.26 kJ/mol.

207 Route c-4 (yellow curve, Figure 6) is initiated from intermediate *c-2-2m*.
208 Conversion to *c-4-1m* involves transfer of a hydrogen from the nitrogen-bound CH₂ to
209 the terminal carbon. From *c-4-1m*, HCN is liberated through cleavage of a
210 nitrogen-carbon bond, also yielding *c-1-3m*.

211 The last mechanism proposed at site Pri-c is route c-5 (green curve, Figure 6). In
212 this route, intermediate *c-3-1m* undergoes a carbon-carbon bond breakage to yield
213 *c-5-1m*. This intermediate is structurally isomeric with compound *c-2-3m* and
214 proceeds to *c-2-4m* and HCN via the same transition state. It is noted that the
215 intermediate *c-5-1m* of pathway c-5 is an isomer of intermediate *c-2-3m* of pathway
216 c-2 of with a slight energy difference of 4.69 kJ/mol. Figure 8 outlines the structural
217 differences mainly in the bond angle A(4C-5N-1C) and torsion angle
218 A(3C-4C-5N-1C), respectively. These factors affect the distribution of electron
219 density and are mainly responsible for the different activation energies. As *c-5-1m* is
220 higher in energy than *c-2-3m*, the barrier height for this final reaction step is lower
221 when compared to pathway c-2.



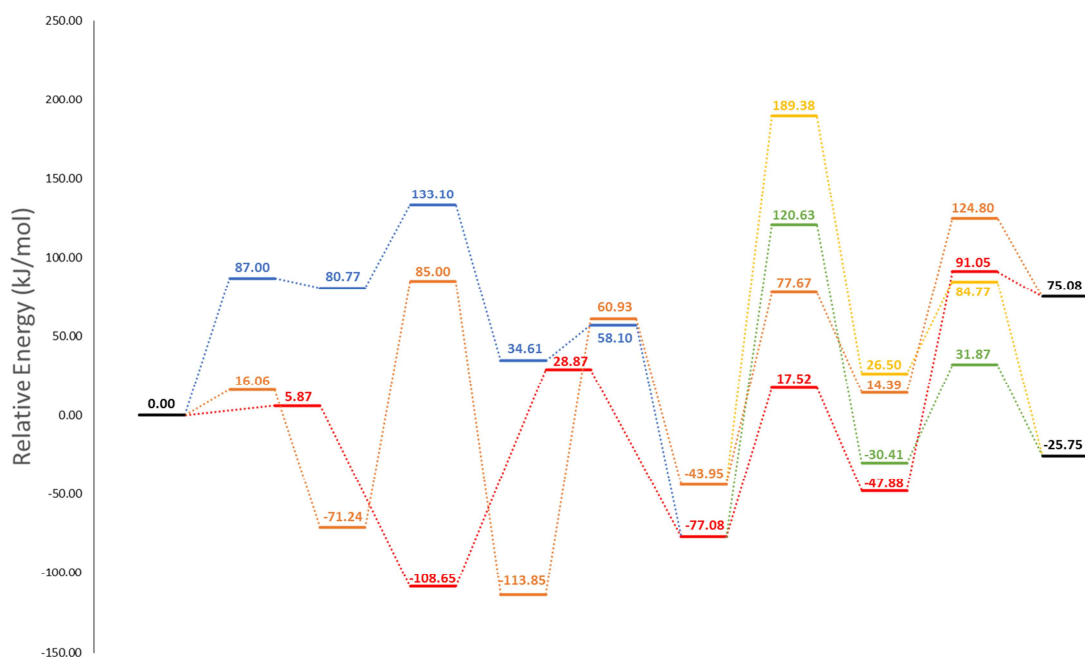
222

223 *Figure 8. Comparison of structures of intermediates c-2-3m and c-5-1m.*

224 As a summary of all pathways following interaction site Pri-c, it has two low
 225 energy routes of interest similar with the case of site Pri-a. It was found that the route
 226 with the lowest activation energy, pathway c-4, leads to the higher energy products.
 227 The more feasible mechanism for formation of the low energy products is through
 228 pathway c-2, with an energy barrier of 189.38 kJ/mol. We can therefore assign
 229 pathway c-4 as the kinetic pathway and c-2 as the thermodynamic route.

230 3.4. Comparison of all the optimal pathways from each interaction sites

231 Considering the fact that it is difficult to identify the reaction routes of hydrogen
 232 radicals reacting with pyrrole experimentally, thus within this work, all the
 233 theoretically proposed pathways were compared. Figure 9 shows five key routes of
 234 interest based on the previous discussion on each interaction sites: pathways a-4 (red),
 235 a-5 (green), b-1 (blue), c-2 (yellow) and c-4 (orange). The relative energies of each
 236 pathway, with 189.38 kJ/mol being the maximum, can be considered quite facile in
 237 the high temperature conditions of coal pyrolysis.



238

239 *Figure 9. Key pyrolytic pathways for HCN formation from pyrrole pyrolysis: a-4*
 240 *(red), a-5 (green), b-1 (blue), c-2 (yellow) and c-4 (orange).*

241 Pathway a-4 is the route with the lowest activation energy of all of the
 242 mechanisms reported herein and as such, we suspect it plays an important role in the
 243 formation of HCN from the pyrolysis of pyrrolic components from coal.

244 4. Conclusions

245 Three different interactions between the hydrogen radical and pyrrole, and twelve
 246 subsequent reaction pathways were theoretically investigated in this work to examine
 247 the role of hydrogen radical in the pyrrole pyrolysis to form HCN.

248 It was shown that pyrrole is susceptible to hydrogen radical attack, particularly on
 249 the carbon atoms, where the addition of the radical is not only notably exothermic, but
 250 also proceeds via a very low energy transition state. The instability of the intermediate
 251 formed following radical attack on the nitrogen atom leads invariably to conversion to
 252 intermediates of Pri-a.

253 After comparing with all the twelve pathways proposed for hydrogen radical
 254 interaction with each reaction site, the route a-4 following hydrogen radical attacking
 255 the site Pri-a, has been identified as the optimal reaction route for HCN formation
 256 from pyrrole pyrolysis. This optimal pathway will play an important role for
 257 comprehensive understanding of the HCN and further NO_x formation during coal
 258 pyrolysis.

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ACCEPTED MANUSCRIPT

1. The HCN formation mechanism during coal pyrolysis was investigated theoretically.
2. Pyrrole was selected as coal compound and the influence of H radicals were studied.
3. H will attack the carbon adjacent to N in pyrrole at the initial reacting stage.
4. An optimal pathway was found for HCN formation from pyrrole pyrolysis.