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# Accepted Manuscript

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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

As a typical fossil fuel, coal is a major contributor to nitrogen oxide  $(NO_x)$  pollution. 13 14 The detailed mechanism of NO<sub>x</sub> generation from coal pyrolysis need to be clarified. 15 Within this research, we used density functional theory (DFT) to investigate the formation mechanism of HCN as a NO<sub>x</sub> precursor during pyrolysis of pyrrole in the 16 presence of hydrogen (H) radicals. Firstly, three different reaction positions for 17 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<sub>x</sub>; 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<sub>x</sub> not only forms acid rain and photochemical smog, but also directly endangers 32 human health [2]. At present, the mechanisms of NO<sub>x</sub> 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<sub>x</sub> emission during coal utilization [3,4].

It has been identified that HCN and  $NH_3$ , which are generated during coal utilization under high temperature, are the main precursors of  $NO_x$  [5,6]. Therefore, the thermal decomposition of N-containing model compounds to  $NH_3$  and HCN is important for understanding  $NO_x$  formation.

39 Three types of N-containing compounds exist in coal: pyrrole-N, pyridine-N, and quaternary-N [7]. The dominant nitrogen source in coal is the pyrrole type, which 40 41 accounts for 50-80 wt.% of total nitrogen [8]. Thus, the thermal decomposition of 42 pyrrolic groups plays an essential role in NO<sub>x</sub> precursor formation. Among the many researchers who have studied the formation mechanisms of NO<sub>x</sub> precursors from 43 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 cis-crotonitrile and allyl cyanide. In addition, Bacskay et al. [11] reported an optimal 49 pathway with the lowest energy barrier (315.68 kJ/mol for the rate-determining step) 50 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 gradually heated, bond-breaking reactions within the network structure begin at 54 350-400℃, homolytic breaking of covalent bonds in the network structure generate 55 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 will occur competitively to form hydrogen radicals [12-15]. Therefore, hydrogen 58 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 through experiments and molecular dynamics simulations, they found that the 62 ring-opening of pyrrole is facilitated by hydrogen radical adsorption on it. Moreover, 63 Zeng et al. [17] proposed a possible mechanism of hydrogen radical adsorption on 64 65 pyrrole by quantum chemistry computation, theoretically confirming the hypothesis proposed by Mackie and co-workers. 66

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 method of Petersson and co-workers [19]. CBS-QB3 is a composite method that 75 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 calculations at the CCSD(T)/6-31+G9d') and MP4SDQ/CBSB4 level are performed 82 83 and the energy is obtained at the complete basis set limit through extrapolation at the MP2/CBSB3 level. This method has been shown to be highly accurate, with mean 84 85 errors of under 5 kJ/mol when tested against the G2/97 test set [20]. Furthermore, CBS-QBS contains a correction for spin-contamination in radical species which 86 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 at site Pri-a involves the radical reacting with the carbon atom that is adjacent to the 91 92 nitrogen. This is the reaction site with the lowest energy barrier, at 5.87 kJ/mol, and the greatest exothermicity, releasing 108.65 kJ/mol. At site Pri-b, a hydrogen radical 93 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 throughout the pyrrole ring through resonance structures. Interaction at site Pri-c, 97 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 investigated and analysed. 102



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

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

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

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

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

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

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





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.* 

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

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

Figure 4 shows two possible routes (b-1 and b-2) following hydrogen radical 156 attack on the nitrogen (site Pri-b) and Figure 5 illustrates all the related transition 157 158 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 nitrogen-carbon bond can occur to yield intermediate b-1-2m. Following this, a 160 161 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 b-1-3m. This intermediate is analogous to a-1-2m and proceeds to HCN via the same 163 164 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.





- 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.



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 radial addition on the non-nitrogen adjacent carbons (site 176 Pri-c), an intermediate *c*-1-1*m* was formed at an initial stage. Following this, five possible routes (c-1, c-2, c-3, c-4, and c-5) to HCN formation were investigated as 177 178 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 cleavage to yield intermediate c-1-2m via transition state c-1-2t. This species can then 180 undergo a simultaneous hydrogen transfer and carbon-carbon bond breaking reaction 181 to yield HCN and c-1-3m, which is the same radical product as a-3-2m. This reaction 182

- 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.



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 adjacent carbon radical position as in pathway c-2 (red curve, Figure 6). This gives 192 193 rise to intermediate *c*-2-1*m* which in turn will undergo a carbon-carbon bond breaking 194 to yield c-2-2m, in which a CH<sub>2</sub> group is double bonded to the nitrogen atom. The conversion of c-2-2m to c-2-3m involves transfer of a hydrogen from this CH<sub>2</sub> to the 195 196 other nitrogen bonded carbon atom. From this intermediate, there is a low energy barrier (58.27 kJ/mol) transition state for the carbon-nitrogen cleavage to give HCN 197 198 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.

Intermediate c-1-1m can convert to c-3-1m through a transfer of the hydrogen from the nitrogen to the non-radical neighbouring carbon and formation of a nitrogen-carbon double bond, this pathway is called as c-3 (blue curve, Figure 6). The barrier height of c-3-1t is the greatest of the possible reactions for c-1-1m at 190.06 kJ/mol. Breaking of the nitrogen-carbon single bond to open the pyrrole ring gives intermediate c-3-2m. From here, a low energy carbon-carbon bond rupturing yields 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 CH<sub>2</sub> 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 c-5-1m. This intermediate is structurally isomeric with compound c-2-3m and 213 214 proceeds to c-2-4m and HCN via the same transition state. It is noted that the intermediate c-5-1m of pathway c-5 is an isomer of intermediate c-2-3m of pathway 215 c-2 of with an slight energy difference of 4.69 kJ/mol. Figure 8 outlines the structural 216 217 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*-5-1*m* 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.



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

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

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



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

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

### 244 **4.** Conclusions

238

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

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

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

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- 320

- 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.