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

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Abstract

As a typical fossil fuel, coal is a major contributor to nitrogen oxide (NO\textsubscript{x}) pollution. The detailed mechanism of NO\textsubscript{x} generation from coal pyrolysis need to be clarified. Within this research, we used density functional theory (DFT) to investigate the formation mechanism of HCN as a NO\textsubscript{x} precursor during pyrolysis of pyrrole in the presence of hydrogen (H) radicals. Firstly, three different reaction positions for hydrogen radical attacking were compared. It was identified that hydrogen radical initially reacts with pyrrole at the location adjacent to N through a single elementary reaction step with an activation energy of 77.12 kJ/mol. Additionally, to examine the role of hydrogen radical in the pyrrole pyrolysis to form HCN, 12 subsequent reaction pathways were theoretically investigated. It was found that one of the pathway (Pathway a-4) involving hydrogen transfer followed by carbon-carbon cleavage processes is the route with the lowest energy barrier of all of the mechanisms reported, thus it plays an important role in the formation of HCN from the pyrrolic components of coal. These results further indicated that the hydrogen radicals significantly reduce the energy barrier of the pyrrole pyrolysis.

Keywords: NO\textsubscript{x}; hydrogen radicals; HCN; pyrrole; Density Functional Theory

1. Introduction

Coal combustion is a main source of nitrogen oxide (NO\textsubscript{x}) pollution in air [1]. NO\textsubscript{x} not only forms acid rain and photochemical smog, but also directly endangers human health [2]. At present, the mechanisms of NO\textsubscript{x} formation from coal are not well understood, and detailed elucidation of these formation mechanism plays an important role for efficient control of NO\textsubscript{x} 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.

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 accounts for 50–80 wt.% of total nitrogen [8]. Thus, the thermal decomposition of pyrrolic groups plays an essential role in NO$_x$ precursor formation. Among the many researchers who have studied the formation mechanisms of NO$_x$ precursors from pyrrole, it has been generally agreed that HCN is the primary N-containing product generated by pyrrole pyrolysis. For example, Martoprawiro et al. [9] proposed several reaction pathways for pyrrole pyrolysis with the major product being HCN. Zhai et al. [10] also investigated the reaction pathways of pyrrole pyrolysis to form HCN, and proposed a mechanism different from Martoprawiro’s work [9] for the formation of cis-crotonitrile and allyl cyanide. In addition, Bacska et al. [11] reported an optimal pathway with the lowest energy barrier (315.68 kJ/mol for the rate-determining step) for pyrrole pyrolysis to form HCN.

Pyrolysis of coal has been confirmed to involve radical reactions, and hydrogen (H) radicals are commonly generated during coal pyrolysis. During pyrolysis, coal is gradually heated, bond-breaking reactions within the network structure begin at 350-400°C, homolytic breaking of covalent bonds in the network structure generate reactive free radicals. In fact, the cracking of alkane and aromatics will break by C-C 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 radicals should exert significant effects on the formation of nitrogen-containing pollutants by reducing the activation energy of pyrrole pyrolysis to form HCN. For example, Mackie et al. [16] studied the pyrrole pyrolysis with hydrogen radical through experiments and molecular dynamics simulations, they found that the ring-opening of pyrrole is facilitated by hydrogen radical adsorption on it. Moreover, Zeng et al. [17] proposed a possible mechanism of hydrogen radical adsorption on pyrrole by quantum chemistry computation, theoretically confirming the hypothesis proposed by Mackie and co-workers.

However, it remains unclear how the hydrogen radical actually affects pyrrole pyrolysis to form HCN. To fill this research gap, in this work we use density functional theory (DFT) method to investigate the formation mechanism of HCN during pyrrole pyrolysis in the presence of hydrogen radicals and comprehensively examine the possible reaction pathways. These results will clarify the effects of hydrogen radicals on coal pyrolysis to form NO$_x$.

2. Methodology
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 combines the speed of density functional theory with the high accuracy of post-Hartree-Fock methods. It also helps alleviate the errors associated with truncated basis sets through extrapolation of energies to the complete basis set limit. In CBS-QB3 calculations, a geometry optimisation and frequency calculation are performed first at the B3LYP/6-311G(2d,d,p) level and then a subsequent frequency 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 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 errors of under 5 kJ/mol when tested against the G2/97 test set [20]. Furthermore, CBS-QB3 contains a correction for spin-contamination in radical species which further justifies its selection for this study.

3. Results and Discussion

There are three possible sites on the pyrrole that can be attacked by the hydrogen 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 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 attack on the nitrogen atom, is considerably less favourable, with an activation energy of 87.00 kJ/mol as well as being endothermic by 80.77 kJ/mol. The unpaired electron 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, which involves radical attack on the carbon atom opposite the nitrogen, is energetically similar to pri-a in that it has a low activation barrier of 16.06 kJ/mol and it is exothermic by 71.24 kJ/mol. Based on hydrogen radical attacking on each of the reaction site, the subsequent reaction pathways for HCN formation will be investigated and analysed.
Figure 1. Three sites for hydrogen radical attack on pyrrole.

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 involved 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 \( a-2-2m \), an 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.

A hydrogen abstraction from the nitrogen adjacent carbon to the terminal carbon of \( a-1-2m \) initiates pathway a-3 (green curve, Figure 2) and forms intermediate \( a-3-1m \). This species then undergoes a carbon-carbon cleavage to give the radical \( a-3-2m \) and the HCN isomer \( a-2-2m \), which again undergoes a hydrogen transfer to
yield HCN. The products of this route are significantly higher than those of path a-1 and a-2, suggesting a greater instability of the radical product a-3-2m.

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.

The last pathway considered is a-5 (red curve, Figure 2). In this route intermediate a-1-2m is converted directly to a-1-4m via a single transition state species a-5-1t. This transition state is lower in energy than a-1-3t by 36.97 kJ/mol, most likely due to the less sterically strained five member pericyclic transition state.
Figure 3. All the transition states of pyrolytic pathways following interaction at Pri-a. The blue spheres represent nitrogen atoms; the grey spheres represent carbon atoms; 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.

3.2. Reaction pathways following interaction at site Pri-b

Figure 4 shows two possible routes (b-1 and b-2) following hydrogen radical attack on the nitrogen (site Pri-b) and Figure 5 illustrates all the related transition states. The addition of the hydrogen radical on the nitrogen atom leads to the least 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 transfer of one hydrogen atom from the nitrogen to the terminal carbon radical is 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 pathway described previously. An alternative route is pathway b-2 (red curve, Figure 4). In this route, the hydrogen transfer occurs first and produces intermediate \(b-2-1m\).
This species is identical to \(a-1-1m\) and therefore proceeds to HCN in the same manner as outlined before.

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

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

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3.3. Reaction pathways following interaction at site Pri-c

Following the hydrogen radical addition on the non-nitrogen adjacent carbons (site Pri-c), an intermediate \(c-1-1m\) 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 shown in Figure 6 with the structure of key transition states shown in Figure 7. In 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 undergo a simultaneous hydrogen transfer and carbon-carbon bond breaking reaction to yield HCN and \(c-1-3m\), which is the same radical product as \(a-3-2m\). This reaction
requires a significantly large activation energy of 380.06 kJ/mol and is therefore the least facile of all the routes proposed in this work.

Figure 6. Pyrolytic pathways based on interaction Pri-c. The numerical values are energies in kJ/mol relative to that of pyrrole and hydrogen radical.

Figure 7. All the transition states of pyrolytic pathways following interaction at Pri-c. The blue spheres represent nitrogen atoms; the grey spheres represent carbon atoms; and the white spheres represent hydrogen atoms.
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 rise to intermediate c-2-1m which in turn will undergo a carbon-carbon bond breaking to yield c-2-2m, in which a CH$_2$ 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$_2$ to the 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 and c-2-4m. It is worth to note that the products of c-2-4m is the same as the products 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.

Route c-4 (yellow curve, Figure 6) is initiated from intermediate c-2-2m. Conversion to c-4-1m involves transfer of a hydrogen from the nitrogen-bound CH$_2$ to the terminal carbon. From c-4-1m, HCN is liberated through cleavage of a nitrogen-carbon bond, also yielding c-1-3m.

The last mechanism proposed at site Pri-c is route c-5 (green curve, Figure 6). In 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 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 c-2 of with an slight energy difference of 4.69 kJ/mol. Figure 8 outlines the structural differences mainly in the bond angle A(4C-5N-1C) and torsion angle A(3C-4C-5N-1C), respectively. These factors affect the distribution of electron density and are mainly responsible for the different activation energies. As c-5-1m is higher in energy than c-2-3m, the barrier height for this final reaction step is lower when compared to pathway c-2.
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.

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.

4. Conclusions

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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References


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.