

A DENSITY FUNCTIONAL THEORY STUDY ON THE PYROLYSIS MECHANISMS OF 2-PICOLINE

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Introduction

Heavy fuels such as coal and coal-derived liquids contain significant amount of chemically bound nitrogen. the combustion of these fuels, used as an energy source in many power plants, results in the formation of significant amounts of nitrogen oxides (NO_x). NO_x are environmental pollutants and lead to such hazards as acid rain and smog. Many methods have been proposed to reduce NO_x formation. But so far no completely satisfactory solution has been found. This is partly due to the fact that the complete combustion mechanism of heavy fuels is still not fully understood^[1, 2].

It is well-known that chemically bound nitrogen in coal and coal-derived liquids is predominantly in the form of heterocycles such as pyrrole and pyridine ring systems^[1-4]. Under combustion conditions these heterocycles may form nitrogen precursors of NO_x , and the rate of precursor formation may determine the rate of NO_x formation. Thus, it is important to understand the reaction mechanism and kinetics of these heterocycles at combustion temperatures. Contrary to the wide spread use of these fuels, there have been only a few detailed studies of pyrolysis reactions of pyrrole and pyridine rings. To date, the most comprehensive studies were carried out by Lifshitz et al^[5-8] and by Mackie et al^[9, 10], Zhai et al^[11] have investigated the pyrolysis mechanisms of pyrrole, Yoshihiko Ninomiya et al^[11] have used Semi-empirical PM3 molecular orbital calculations to study the reaction pathways of pyrolysis of pyridine, Zhou et al^[2] focused research on the pyrolysis mechanisms of indole yielding benzyl cyanide and *o*- and *m*-tolonitriles, and so on. From above studies, we can see that nitrogen-containing heterocyclic, which is separated from around state-selected nitrogen in coal macromolecule structure, can be used as local micro-structure model to illuminate the pyrolysis of related chemical bond. Because 2-Picoline not only contains conjugated six-membered ring representing coal aromaticity, but also includes methyl next to nitrogen denoting bridge bond and aliphatic branched chain in coal, it have been usually used as model compound to study the evolution from nitrogen in coal to precursors of volatile NO_x .

In this paper, to understand the details of major nitrogen-containing product formation under pyrolytic conditions, we carried out a detailed theoretical studies for pyrolysis mechanism of 2-Picoline via intermediate scheme of N-containing analogue of norbornadiene^[12] with a special emphasis on the differences and similarities with pyrrole, pyridine and indole.

Computational Details

All equilibrium and transition structure were optimized using density functional theory Dmol³ method. About the details of computing, different parameters were adopted according to the calculation tasks, purposes and molecular structures. More coarse parameters were used in Scan Potential Energy Surface and Transition State Search task by Local Density Approximation (LDA) method using Perdew-Wang-Ceperley functional (PWC) and MIN basis set. Owing to the needed of calculation efficiency, more precise parameters were used for intermediate and transition optimization, frequency analysis, electronic energy, thermodynamic parameters and structure microcosmic parameters calculation. In order to validate the

credibility of the above methods and parameters, the bond length of pyridine and IR spectrum of 2-Picoline were calculated, the calculation results qualitatively accord with the experimental results. All calculations were performed using the Cerius² program package.

Results and Discussion

Mechanism of pyrolysis. By iterative tentative calculation^[13] and precise calculation, we investigated the pyrolysis mechanism of 2-Picoline via intermediate scheme of N-containing analogue of norbornadiene. In a results, Five transition states (TS1, TS2, TS3, TS4 and TS5) and four intermediates (IM1, IM2, IM3 and $\cdot\text{HCNH}$) were determined, as shown in **Figure 1**. Meanwhile, Vibrational analysis was carried out for each structure to characterize it either as an equilibrium structure (no imaginary frequency) or a transition state (one imaginary frequency whose vibration mode corresponds to the reaction coordinate, see **Table 1**). Intrinsic reaction coordinate (IRC) calculation was implemented for most of the transition state structures to confirm whether they can lead to the desired reactants and products.

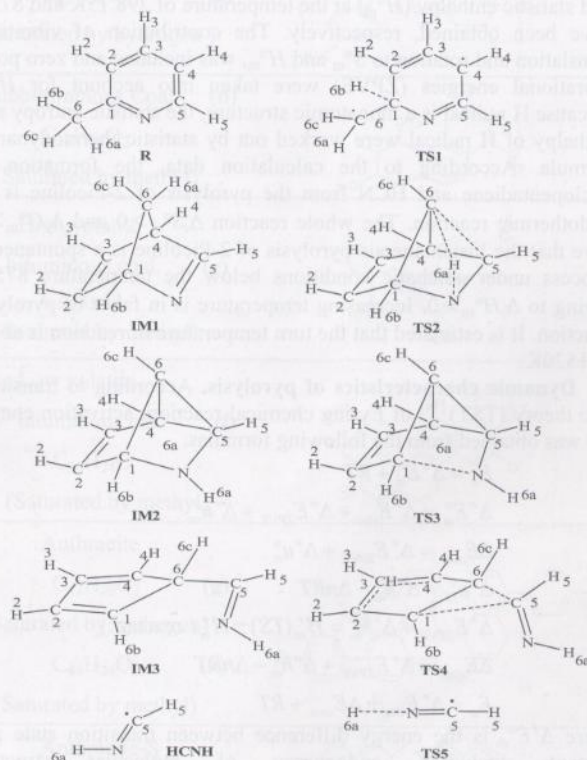


Figure 1 The critical structures along the proposed pyrolysis mechanisms of 2-Picoline via intermediate scheme of N-containing analogue of norbornadiene

Table 1 Imaginary frequency of each transition state and bond corresponding to relative normal vibration

Transition states	Imaginary frequency (cm^{-1})	Bond corresponding to normal vibration
TS1	198.90	C6-H6b-C1
TS2	1748.70	C6-H6a-N
TS3	454.30	C1-N
TS4	419.80	C6-C5-C1
TS5	842.50	N-H6a

Based on above analysis, we think that the pyrolysis mechanisms of 2-Picoline via intermediate scheme of N-containing analogue of Norbornadiene consists of the following six elementary reactions to produce mainly cyclopentadiene and hydrogen cyanide; the reactions are depicted in **Figure 2**.

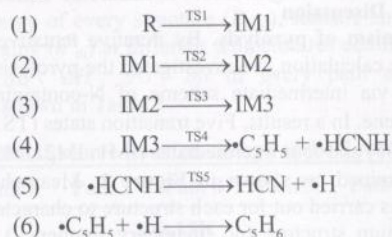


Figure 2 The elementary reaction of 2-Picoline pyrolysis via intermediate scheme of N-containing analogue of norbornadiene

Thermodynamic characteristics of pyrolysis. By calculation, the electronic energy of every structure (E_{elec}), statistic entropy (S_m°) and statistic enthalpy (H_m°) at the temperature of 298.15K and 875K have been obtained, respectively. The contribution of vibration, translation and rotation to S_m° and H_m° , was included and zero point vibrational energies (ZPVE) were taken into account for H_m° . Because H radical is a monatomic structure, the statistic entropy and enthalpy of H radical were worked out by statistic thermodynamic formula. According to the calculation data, the formation of cyclopentadiene and HCN from the pyrolysis of 2-Picoline is an endothermic reaction. The whole reaction $\Delta_r S_m^\circ > 0$ and $\Delta_r G_m^\circ > 0$ give that the instantaneous pyrolysis of 2-Picoline is a spontaneous process under adiabatic conditions below the temperature 875K. owing to $\Delta_r H_m^\circ > 0$, Increasing temperature is in favor of pyrolysis reaction. It is estimated that the turn temperature of reaction is about at 1520K.

Dynamic characteristics of pyrolysis. According to transition state theory (TST)^[14] of Eyring chemical reaction, activation energy (E_a) was obtained from the following formulas:

$$\begin{aligned}
 E_a &= \Delta^\ddagger E_m^\circ + RT \\
 \Delta^\ddagger E_m^\circ &= \Delta^\ddagger E_{elec} + \Delta^\ddagger E_{ZPVE} + \Delta^\ddagger u_m^\circ \\
 \Delta E_{coor}^\circ &= \Delta^\ddagger E_{ZPVE} + \Delta^\ddagger u_m^\circ \\
 \Delta^\ddagger u_m^\circ &= \Delta^\ddagger h_m^\circ - \Delta n RT \\
 \Delta^\ddagger E_{ZPVE} + \Delta^\ddagger h_m^\circ &= H_m^\circ(TS) - H_m^\circ(\text{reactant}) \\
 \Delta E_{coor}^\circ &= \Delta^\ddagger E_{ZPVE} + \Delta^\ddagger h_m^\circ - \Delta n RT \\
 E_a &= \Delta^\ddagger E_{elec} + \Delta E_{coor}^\circ + RT
 \end{aligned}$$

where $\Delta^\ddagger E_m^\circ$ is the energy difference between transition state and reactant, including endoenergy of molecular structure ($\Delta^\ddagger E_{elec} + \Delta^\ddagger E_{ZPVE}$) and statistic thermodynamic energy ($\Delta^\ddagger u_m^\circ$) of molecular vibration, transition and rotation; Zero point vibration energies (ZPVE) were taken into account for H_m° ; $\Delta^\ddagger h_m^\circ$ statistic enthalpy change; Δn the change number of molecule involved in reaction from reactants to complex product.

Figure 3 gives the energy relation of reaction process at the temperature of 298.15K; the energy change of over reaction process can be seen clearly.

The rate constant k was obtained from **Eq.1**, which can more accurately judge the rate-determining step of reactions.

$$k = \frac{k_B T}{h} \left(\frac{p^\circ}{RT} \right)^{1-n} \exp \left(\frac{\Delta_r S_m^\circ(p^\circ)}{R} \right) \exp \left(\frac{-\Delta_r H_m^\circ(p^\circ)}{R} \right) \quad (1)$$

Where T is reaction temperature, k_B , h , p° and R are Boltzmanns

constant, Planck constant, Standard atmospheric pressure and Gas constant, respectively.

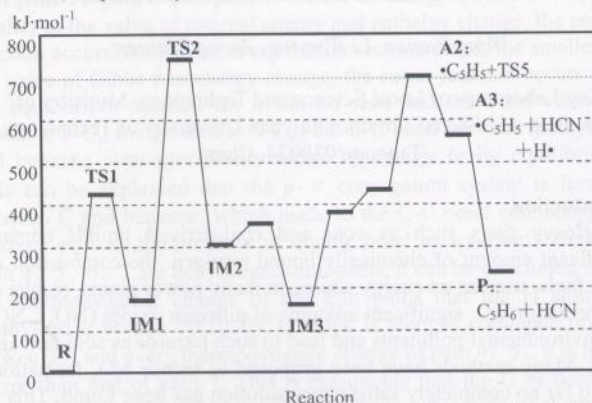


Figure 3 The energy relation of every stationary point during the pyrolysis of 2-Picoline (298.15K)

As what have been seen from **Figure 3**, the activation energy of elementary reaction 3 ($IM1 \rightarrow IM2$) is $E_a(298.15K) = 51.49 \text{ kJ} \cdot \text{mol}^{-1}$, $E_a(875K) = 28.84 \text{ kJ} \cdot \text{mol}^{-1}$, whose values are the smallest in overall reactions. Corresponding rate constant $\ln k_3(298.15K) = 9.944$ is the largest. Meanwhile, The activation energy of elementary reaction 2 ($IM1 \rightarrow IM2$) is the largest and the rate constant $\ln k_2(298.15K) = -199.289$, $\ln k_2(875K) = -46.720$ is the smallest in six elementary reactions. So the elementary reaction 2, a process of H atom migration, is confirmed to be rate-determining step in the pyrolysis process of 2-Picoline. Judged from rate constant of two different temperatures, the rate of 2-Picoline pyrolysis increases with increasing in reaction temperature, the effect of temperature on the formation of HCN is sufficiently obvious.

Acknowledgments

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References

- [1] Zhai L., Zhou X. F., Liu R. F. J. Phys. Chem. A, 1999, 103: 3917
- [2] Zhou X. F., Liu R. F. Journal of Molecular Structure (Theochem), 1999, 461-462: 569-579
- [3] Sneider, L.R., Buell, B. E., Howard, H. E. Anal. Chem. 1968, 40, 1303
- [4] Speers, G. C., Whitehead, E.V. In Crude petroleum in Organic Geochemistry; Eglington, G., Murphy, M.T.J, Eds.; Springer Verlag: Heidelberg, FRG, 1969; p638
- [5] Lifshitz, A., Tamburu, C et al. J. Phys. Chem. 1989, 93: 5802
- [6] Laskin, A., Lifshitz, A. J. Phys. Chem. 1997, 101, 7787
- [7] Laskin, A., Lifshitz, A. J. Phys. Chem. 1998, 102, 928
- [8] Lifshitz, A., Bidani, M., Agranat, A et al. J. Phys. Chem. 1987, 91: 6043
- [9] Mackie, J. C., Colket, M. B., Nelson, P. F., Esler, M. Int. J. Chem. Kinet. 1991, 23: 733
- [10] Mackie, J. C.; Colket, M. B et al. J. Phys. Chem. 1990, 94, 4099
- [11] Yoshihiko Ninomiya, Zhongbing Donga, Yoshizo Suzukib, Jugo Koketsua. Fuel, 2000, 79: 449-457
- [12] Terentis A., Doughty A., Mackle J. C. Journal of Physical Chemistry, 1992, 96: 10334-10339
- [13] Young D. C. New York: John Wiley & Sons, Inc., 2001, 147-157
- [14] Fu X. C., Shen W. X., Yao T. Y. Beijing: Higher education press, 1990, 798-812