

Numerical Simulation of Reaction Mechanism of Ethane Pyrolysis to Form Benzene and Styrene

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ABSTRACT: Based on Materials Studio and Aspen Plus, the reaction mechanism of producing benzene and styrene from ethane steam heat lysis was investigated through the addition reaction of free radicals + alkenes or free radicals + alkynes to form large free radicals and then through the cyclization and dehydrogenation of large free radicals to form aromatic hydrocarbons. It was found the thermal cracking of ethane had 2 paths to form benzene and 1 path to form styrene. The 1st path to form benzene is that the product ethylene form $C_2H_3\bullet$ through a chain transfer, then $C_2H_3\bullet$ and ethylene additively react to form $1-C_4H_7\bullet-4$, which then reacts with ethylene to form $C_6H_{11}\bullet$, and finally, benzene is produced by dehydrogenation and transfer of $C_6H_{11}\bullet$. The 2nd path to form benzene is that acetylene is produced by dehydrogenation of $C_2H_3\bullet$, and then acetylene reacts via two sub-paths to form $1,3-C_4H_5\bullet-4$, which is cyclized to form $C_6H_9\bullet$, and finally, benzene is formed through dehydrogenation and transfer. The path to form styrene is that $1,3-C_4H_5\bullet-4$ and 1,3-butadiene are cyclized to form $C_8H_{11}\bullet$, and styrene is finally formed through dehydrogenation and chain transfer. Comparative analysis with industrial data showed there were 3 cycles in the ethane thermal cracking reaction network. The simulation data were well consistent with the industrial production data.

KEYWORDS: Ethane; Pyrolysis; Ethylene; Benzene; Styrene; Numerical simulation.

INTRODUCTION

Ethylene, propylene and butadiene (short as the three alkenes) are the basic raw materials of the petrochemical industry. The rapid development of the three major synthetic products has raised the increasing demand

for the three alkenes, which has resulted in the relative long-term shortage of vapor thermal cracker raw materials to production of the three alkenes. The problem of low three-alkenes yield is severe in China, which depends on heavy

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lysis raw materials. One excellent and low-cost solution is to optimize raw materials on process mathematical models. Thus, it is of great significance to build a hydrocarbon steam pyrolysis kinetic model with high prediction accuracy and adaptability to different industrial production materials. However, the research and establishment of thermal cracking reaction kinetic models is very difficult in the experimental research, owing to the short time of the free radical reaction, and the large variety and low concentrations of free radicals. Moreover, multiple reaction paths simultaneously compete for the same free radicals, and the small radicals, through chain transfer, re-form the micromolecular raw materials, which thereby affects the system balance. Therefore, it is difficult in experimental research to qualitatively or quantitatively judge whether each reaction path truly participates in the reaction and the degree of participation. In addition, differences in temperature and residence time from the wall to the center of the tube can lead to different depths of reaction, which result in differences in product distribution. Small-molecular olefins are more active than alkanes, and as the primary reaction proceeds, the small-molecular olefins such as ethylene and propylene will rapidly undergo secondary reactions to generate new small free radicals, which easily react with the raw materials and the olefin products. Although *Rice et al.* used experimental methods as early as 1931 to determine that the thermal cracking reaction obeys the free radical mechanism [1,2], the current research on the thermal cracking mechanism model of alkanes based on experimental methods is mostly focused on the primary reaction of small-molecular alkanes below C5 [3-9]. So far, the existing experimental methods cannot clarify the mechanism of free radical reaction of large molecules, and especially, there is no new and mature interpretation about the secondary reaction mechanism at large reaction depth. It is the multiple problems in hydrocarbon free radical mechanism experimental research that has driven many researchers to avoid the research on the reaction mechanism process, so there have emerged dynamic research methods such as empirical models [10], molecular models [11-13] and lumped models [14-15]. The limitation of these methods is that kinetic data are regressed from raw material composition and product analysis data, which has solved some practical problems, but can only adapt to specific raw material compositions, but not to all raw materials.

In other words, only the free radical mechanism model can be independent of the raw materials, cracking devices and cracking process conditions, and thus, only the free radical model has high adaptability and extension. Among the studies on the steam heat lysis process mechanism models, however, there is rare research about the side reaction network mechanism of the major lysis products -- ethylene, propylene and butadiene. There are only two studies on the mechanism of the primary and secondary radical reactions of ethane. *Maarten K. Sabbe et al.* simulated the primary and secondary reactions of ethane based on the first principle and gave the reaction network, found the path to form benzene was vinyl, butadiene, 1,4-hexadienyl, and finally benzene was formed by cyclohexenyl or cyclohexene, and compared the simulated data with industrial data [16]. *Goethem MWMV* calculated the maximum yield of ethylene by thermal cracking of ethane at different temperatures on SPYRO, and explained the effect of temperatures on ethylene yield from the perspective of reaction mechanism: ethylene first forms $C_2H_3\bullet$ and then from 1-butylene and then butadiene, and finally forms cyclopentadiene and benzol [17]. It was also believed benzol and $C_2H_3\bullet$ reacted at high temperature to form styrene [17]. It is clear the models above controversial whether the reaction mechanism of ethane thermal cracking reaction is free radical reaction, molecular reaction or both.

Through simulation on Materials Studio, we found in the primary and secondary reactions of ethane thermal cracking, the activation energy of chain propagation reaction of small radicals with the starting ethane and the main product ethylene is much smaller, so most of the small free radicals in the system can be obtained by chain propagation reaction. The addition reaction of small radicals + olefins or small radicals + alkyne is to form large radicals, and the cyclization and dehydrogenation of large radicals continue until benzene or styrene is formed, in which the required activation energy of each radical reaction is lower, which must be the easiest reaction route. Thus, in this study, we adopted the above reaction method, the reported numerical simulation technique [18] and the theory of free radical chain reaction and the primary reaction mechanism of ethane [18], and established the reaction network of benzene and styrene from ethane. The radical reactions in the free radical reaction network were simulated on Materials Studio to obtain the activation

energy (E_a) and pre-exponential factor (A) of each reaction. The above kinetic data were input as a mechanism model into the one-dimensional tubular reactor constructed on Aspen Plus for process simulation, which returned the product distributions of all paths. Since the products produced from different reaction paths were not completely identical, the amount of the same product in one path can be inferred by the amount of other products in other paths, and thereby the relationship between the amount of product generated by each path and total product amount can be clarified. For example, ethylene produced from ethane must be accompanied by 1:1 hydrogen generation, and there is definitely 1:1 methane formation in the ethylene produced by propane, so that ethylene formed from different raw materials can be separated according to the yields of hydrogen and methane. Thus, the reaction paths can be judged: the path that yields the largest amount of the target product must be the most active one among all paths. Through the amounts of products, we can clearly and quantitatively understand which reactions actually occurred and which reactions did not happen, which avoided artificial guesses, and thereby can accurately infer the reaction mechanism of the raw materials based on the product distribution [18]. Finally, the simulation results were compared with the literature [14] to verify the accuracy of the model.

THEORETICAL SECTION

Determination of kinetic parameters of ethane thermal cracking reaction network

The kinetic parameters of each elemental reaction were obtained on Materials Studio [19]. Firstly, the reactants, products and intermediates of each element reaction were geometrically optimized, and after virtual frequency was removed through frequency analysis, the energy stability point was identified. Then the transition state was searched via the LST/QST method and the transition state geometry was obtained. The frequency analysis showed only a single virtual frequency. The structure of the transition state was verified that the force matrix had one and the only negative eigenvalue. The vibration direction of the transitional virtual frequency pointed to the reactants and products, indicating the transition state was correct.

Finally, the kinetic parameters of each elementary reaction were obtained according to the transition state theory of chemical reaction proposed by Eyring *et al.* [20]. The activation enthalpy $\Delta_r H_m^\ddagger$ was calculated as follows:

$$\Delta_r H_m^\ddagger = H(TS) - H(R)$$

The activation energy E_a was computed as follows:

$$E_a = \Delta_r H_m^\ddagger + nRT$$

The pre-exponential factor A was computed as follows:

$$A = \frac{k_B T}{h} e^n \left(\frac{p^\theta}{RT} \right)^{1-n} \exp \left(\frac{\Delta_r S_m^\ddagger}{R} \right)$$

Where $\Delta_r H_m^\ddagger$ is the activation enthalpy of an elementary reaction; $H(TS)$ is the enthalpy at the Transition State (TS), $H(R)$ is the enthalpy of the reactant (R), E_a is the activation energy, n is the sum of molecular coefficients of all reactants, R is the ideal gas constant, T is the reaction temperature, k_B is the Boltzmann constant, h is the Planck constant, P^θ is the standard atmospheric pressure, and $\Delta_r S_m^\ddagger$ is the activation entropy of reaction. The calculation results are shown in Table 1.

As shown in Table 1, reactions 1-6 are the chain initiation reactions and primary reactions of ethane [18]; reactions 7-10 are chain initiation reactions and chain transfer reactions of ethylene. Clearly, ethylene is unlikely to undergo chain breakage of C-H bond, but the most likely reactions are the chain transfer reactions of small free radicals (e.g. H^\bullet , CH_3^\bullet , $C_2H_5^\bullet$) with ethylene to form $C_2H_3^\bullet$, and hydrogen and the corresponding hydrocarbons. Moreover, Reactions 11-16 are a reaction of form acetylene from $C_2H_3^\bullet$ and a possible secondary reaction of acetylene; Reactions 17-53 are the free radicals + olefins or free radicals + alkyne reactions such as cyclization and dehydrogenation reactions of $C_2H_3^\bullet$, C_2H^\bullet and other free radicals with small olefins such as ethylene and acetylene and alkyne, finally forming benzene and styrene.

After repeated calculations and comparison with the experimental data in the literature, we found 2 equilibrium reaction systems in the reaction network of ethane thermal cracking. The first one is formed by ethane, $C_2H_5^\bullet$ and ethylene. That is to say, ethane consists of the raw material ethane and the product ethane, and similarly, there is consumed ethylene and newly-formed ethylene in the reaction system. The reactions in the first equilibrium system are included in the above reactions. The second equilibrium reaction system consists of reactions 54-62. First, $C_4H_9^{\bullet-1}$ ('1' means carbon number 1 of $C_4H_9^{\bullet-1}$; the same below) is formed by addition reaction of C_2H_4 and $C_2H_5^\bullet$; CH_3^\bullet and propylene are formed by the isomerization reaction and the decomposition reaction of $C_4H_9^{\bullet-1}$; finally, $C_3H_7^{\bullet-1}$ is formed by the addition reaction of propylene and H^\bullet , and CH_3^\bullet and ethylene

Table 1: Ethane pyrolysis free radical reaction and kinetic parameters.

NO.	Reaction	E_a/ KJmol^{-1}	A/s^{-1} or $\text{Kmol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}$
1	$\text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{CH}_3^\bullet$	360	$9.12\text{E}+17$
2	$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}^\bullet$	449	$3.87\text{E}+16$
3	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}^\bullet$	160	$6.41\text{E}+13$
4	$\text{C}_2\text{H}_6 + \text{H}^\bullet \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$	30	$5.67\text{E}+13$
5	$\text{C}_2\text{H}_6 + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4$	37	$1.12\text{E}+13$
6	$\text{C}_2\text{H}_6 + \text{C}_2\text{H}_3^\bullet \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$	40	$5.38\text{E}+13$
7	$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{H}^\bullet$	497	$1.52\text{E}+16$
8	$\text{C}_2\text{H}_4 + \text{H}^\bullet \rightarrow \text{C}_2\text{H}_3 + \text{H}_2$	44	$1.10\text{E}+13$
9	$\text{C}_2\text{H}_4 + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_3 + \text{CH}_4$	61	$5.10\text{E}+14$
10	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3^\bullet \rightarrow \text{C}_2\text{H}_3 + \text{C}_2\text{H}_6$	72	$2.92\text{E}+12$
11	$\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}^\bullet$	185	$3.39\text{E}+15$
12	$\text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H}^\bullet$	525	$2.00\text{E}+17$
13	$\text{C}_2\text{H}_2 + \text{H}^\bullet \rightarrow \text{C}_2\text{H} + \text{H}_2$	58	$1.26\text{E}+14$
14	$\text{C}_2\text{H}_2 + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H} + \text{CH}_4$	68	$9.29\text{E}+12$
15	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3^\bullet \rightarrow \text{C}_2\text{H} + \text{C}_2\text{H}_4$	70	$2.91\text{E}+12$
16	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_5^\bullet \rightarrow \text{C}_2\text{H} + \text{C}_2\text{H}_6$	101	$1.36\text{E}+13$
17	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3^\bullet \rightarrow \text{Cyclopropene}^\bullet$	31	$8.02\text{E}+11$
18	$\text{C}_2\text{H}_4 + \text{H}^\bullet \rightarrow \text{C}_2\text{H}_5^\bullet$	8	$5.54\text{E}+13$
19	$\text{Cyclopropene}^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{Cyclopropyl}^\bullet$	52	$2.85\text{E}+13$
20	$\text{Cyclopropyl}^\bullet \rightarrow \text{Cyclopropene} + \text{H}^\bullet$	184	$3.16\text{E}+14$
21	$\text{Cyclopropene}^\bullet + \text{C}_2\text{H}_2 \rightarrow \text{Cyclopropyl}^\bullet$	57	$5.11\text{E}+12$
22	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3^\bullet \rightarrow \text{Cyclopropene}^\bullet$	34	$1.36\text{E}+12$
23	$\text{Cyclopropene}^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{Cyclopropyl}^\bullet$	62	$4.04\text{E}+12$
24	$\text{Cyclopropene}^\bullet + \text{C}_2\text{H}_2 \rightarrow \text{Cyclopropyl}^\bullet$	59	$1.72\text{E}+12$
25	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}^\bullet \rightarrow \text{Cyclopropene}^\bullet$	36	$1.51\text{E}+11$
26	$\text{Cyclopropene}^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{Cyclopropyl}^\bullet$	75	$1.01\text{E}+12$
27	$\text{Cyclopropyl}^\bullet \rightarrow \text{Cyclopropene}^\bullet$	176	$7.00\text{E}+12$
28	$\text{Cyclopropene}^\bullet + \text{C}_2\text{H}_2 \rightarrow \text{Cyclopropyl}^\bullet$	70	$1.07\text{E}+12$
29	$\text{Cyclopropyl}^\bullet \rightarrow \text{Cyclopropene}^\bullet$	138	$2.12\text{E}+12$
30	$\text{Cyclopropene}^\bullet \rightarrow \text{Cyclopropyl}^\bullet$	172	$1.11\text{E}+12$
31	$\text{Cyclopropyl}^\bullet \rightarrow \text{Cyclopropene}^\bullet$	110	$9.74\text{E}+13$

Table 1: Ethane pyrolysis free radical reaction and kinetic parameters. (Continued)

NO.	Reaction	Ea/ KJmol-1	A/s-1 or Kmol-1•m3•s-1
32	<chem>C1=CC=CC=C1.[H] >> C1=CC=CC=C1.[H]</chem>	333	4.23E+14
33	<chem>C1=CC=CC=C1.[H] >> C1=CC=CC=C1.H2</chem>	9	4.02E+12
34	<chem>C1=CC=CC=C1.C >> C1=CC=CC=C1.C</chem>	17	9.63E+13
35	<chem>C1=CC=CC=C1.CC >> C1=CC=CC=C1.CC</chem>	19	1.85E+12
36	<chem>C1=CC=CC=C1.CC >> C1=CC=CC=C1.CC</chem>	28	5.12E+14
37	<chem>C1=CC=CC=C1 >> C1=CC=CC=C1.[H]</chem>	180	2.12E+15
38	<chem>C1=CC=CC=C1 >> C1=CC=CC=C1.[H]</chem>	294	7.19E+15
39	<chem>C1=CC=CC=C1.[H] >> C1=CC=CC=C1.H2</chem>	7	3.36E+14
40	<chem>C1=CC=CC=C1.C >> C1=CC=CC=C1.C</chem>	14	3.19E+13
41	<chem>C1=CC=CC=C1.CC >> C1=CC=CC=C1.CC</chem>	16	7.62E+12
42	<chem>C1=CC=CC=C1.CC >> C1=CC=CC=C1.CC</chem>	32	6.12E+14
43	<chem>C1=CC=CC=C1 >> C1=CC=CC=C1.[H]</chem>	175	6.85E+14
44	<chem>C=CC >> C=CC.[H]</chem>	150	3.78E+16
45	<chem>C=CC >> C=CC.[H]</chem>	278	7.96E+12
46	<chem>C=CC + C=CC >> C=CC</chem>	38	7.64E+12
47	<chem>C=CC >> C=CC</chem>	17	3.17E+13
48	<chem>C=CC >> C=CC.[H]</chem>	177	4.69E+14
49	<chem>C=CC.[H] >> C=CC.H2</chem>	13	3.90E+14
50	<chem>C=CC.C >> C=CC.C</chem>	21	7.62E+13
51	<chem>C=CC.CC >> C=CC.CC</chem>	30	5.18E+13
52	<chem>C=CC.CC >> C=CC.CC</chem>	40	8.49E+13
53	<chem>C=CC >> C=CC.[H]</chem>	187	1.49E+15
54	<chem>C=CC >> C=CC</chem>	146	3.17E+13
55	<chem>C=CC >> C=CC</chem>	180	1.16E+13
56	<chem>C=CC >> C=CC</chem>	101	1.40E+14
57	<chem>C=CC >> C=CC</chem>	206	1.74E+13
58	<chem>C=CC >> C.C</chem>	151	1.04E+13
59	<chem>C=CC.[H] >> C=CC</chem>	6	2.52E+13
60	<chem>C=CC >> C.C</chem>	128	9.24E+13

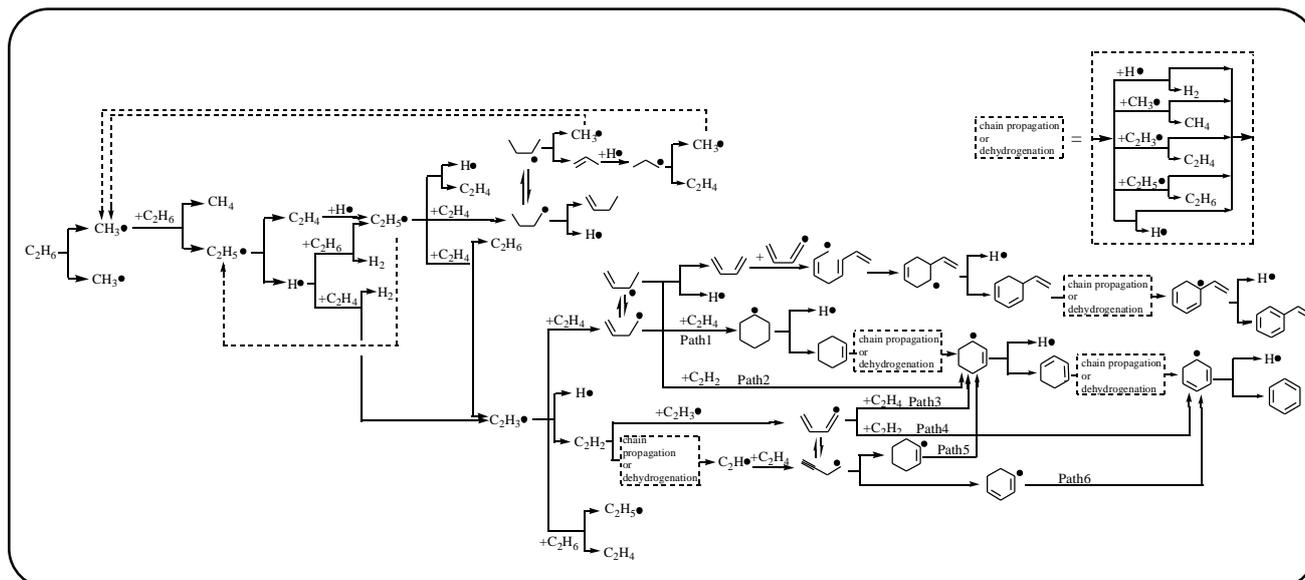


Fig 1. Reaction paths of ethane pyrolysis to form benzene and styrene

are formed by the decomposition reaction of $C_3H_7\cdot-1$, and $CH_3\cdot$ continues to circulate. If no complete equilibrium reaction system is established, the same product distribution as the experimental results cannot be obtained.

The total reaction path is shown in Fig. 1, in which the reaction network is formed by 62 elementary reactions. Clearly, there is only one path to generate styrene (path 1), and six paths to form benzene (paths 2-7) according to the reaction mode of the present invention (Fig. 1).

The kinetic data as-obtained were imported into a one-dimensional tube cracking furnace constructed on Aspen Plus to repeat simulation calculation. Various methods can be used to clarify which reactions have occurred and which have not. For example, a certain path can be deleted to see whether the product changes, and no change means this path is not involved in the reaction. The same product generated by different paths or in different ways can be regarded as different products [15]. A case is that benzene generated by 6 paths can be labeled as C_6H_6-1 to C_6H_6-6 , so as to distinguish benzene generated by different paths.

The calculation results show benzene is generated only by paths 2 and 4, and styrene is generated by path 1, and the yields are consistent with other studies. In addition, three chain transfer cycles were found in the simulation calculation:

(1) The ethane, $C_2H_5\cdot$ and ethylene circulation (cycle 1): After ethane chain initiation, methane and $C_2H_5\cdot$ are formed by the chain propagation reaction of ethane

and $CH_3\cdot$; then ethylene and $H\cdot$ are formed by the decomposition reaction of $C_2H_5\cdot$; $C_2H_5\cdot$ and hydrogen are formed by the chain propagation reaction of ethane and $H\cdot$ or other small free radicals.

(2) The addition and isomerization circulation of ethylene and $C_2H_5\cdot$ (cycle 2): $C_4H_9\cdot-1$ is formed by the addition reaction of ethylene and $C_2H_5\cdot$; then $C_4H_9\cdot-2$ is formed by the isomerization reaction of $C_4H_9\cdot-1$, and $CH_3\cdot$ and propylene are formed by the decomposition reaction of $C_4H_9\cdot-2$; methane and $C_2H_5\cdot$ are formed by the chain propagation reaction of ethane and $CH_3\cdot$; ethylene and $H\cdot$ are formed by the decomposition reaction of $C_2H_5\cdot$.

(3) circulation of propylene and hydrogen addition (cycle 3): $C_3H_7\cdot-1$ is formed by the addition reaction of propylene and $H\cdot$; $CH_3\cdot$ and ethylene are formed by the decomposition of $C_3H_7\cdot-1$; methane and $C_2H_5\cdot$ are formed by the chain propagation reaction of ethane and $CH_3\cdot$; ethylene and $H\cdot$ are formed by the decomposition reaction of $C_2H_5\cdot$.

The actual reaction path of ethane thermal cracking to produce benzene and styrene after simplification is shown in Fig. 2.

To fully understand the reaction mechanism of benzene to form benzene and styrene, we carried out material balance analysis by using the above reaction network (Table 2).

The first difficulty during material balancing is that if the product ethane was counted as another product,

Table 2: Material balance of ethane to form benzene and styrene.

Reaction	Yields/ mol %								
	Hydrogen	Methane	Ethyne	Ethene	Ethane	Propene	1,3-Butadiene	Benzene	Styrene
cycle 1	2.81	0.31		1.73					
cycle 2	25.35	2.82		22.52		0.67			
cycle 3	15.21	3.02		12.27					
Decomposition of C ₂ H ₅ •			0.03						
Decomposition of 1-C ₄ H ₇ •-4							0.28		
Path 1									0.03
Path 2								0.06	
Path 4								0.01	
Simulation data	43.37	6.51	0.03	36.52	10.29	0.67	0.28	0.07	0.03

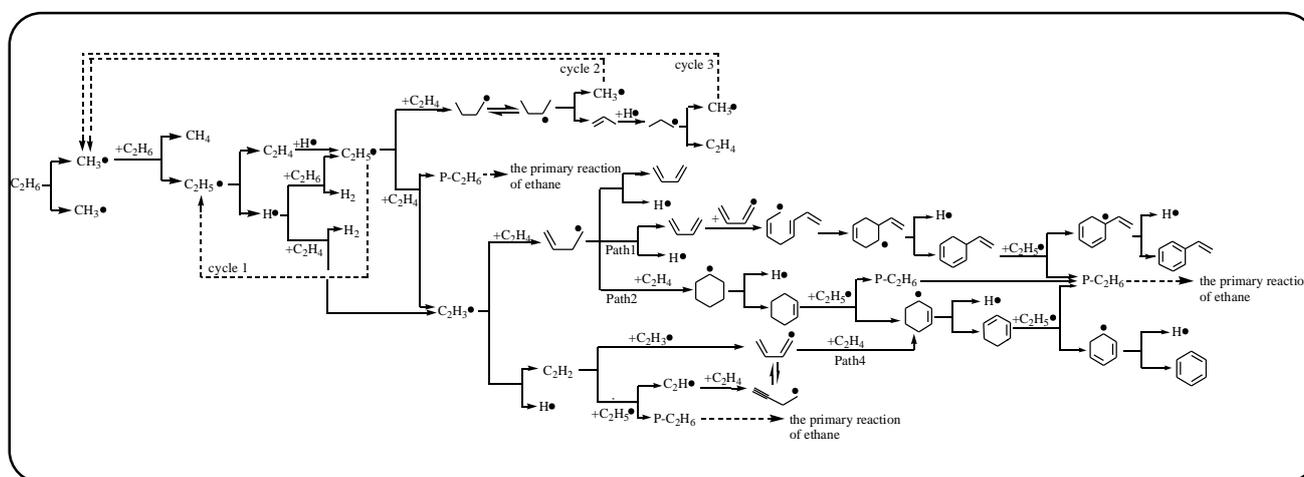


Fig. 2: Reaction mechanism of ethane pyrolysis to form benzene and styrene.

the product distribution will change largely. It is indicated that ethane, C₂H₅• and ethylene are an equilibrium reaction system, and if ethane is regarded as another product, the equilibrium of the system will be destroyed. Therefore, the product ethane with the raw material ethane can only be combined in the material balance. This is why there is only one composition of ethane in Table 2.

Due to the large amount of the raw material ethane, other small free radicals may preferentially undergo a chain transfer reaction with ethane to form C₂H₅•, which can participate in 3 types of reactions. Firstly, C₂H₅• is decomposed to form ethylene and H•, and due to the high activation energy (162 kJ/mol), the concentration of C₂H₅• in cycle 1 will increase due to accumulation. Secondly, C₂H₅• and different materials undergo the chain propagation reactions, activation energy of which varies

largely within 28-101 kJ/mol. Out calculation data show the concentration of C₂H₅• is 5 orders-of-magnitude higher than that of H• or CH₃•. Therefore, when the reaction depth is large, C₂H₅• will increase the rate of chain transfer reaction because the concentration of C₂H₅• is large. Thirdly, ethylene and C₂H₅• undergo addition reaction, activation energy of which is 32 kJ/mol, so C₂H₅• will preferentially react with the main product ethylene (cycle 2).

Based on the 3 cycles above, the reaction mechanism for the thermal cracking of ethane to benzene and styrene can be summarized as follows:

(1) The primary reaction of ethane pyrolysis is that two CH₃• parts are formed by the C-C breakage of ethane, then methane and C₂H₅• are formed by the chain propagation reaction of ethane and CH₃•; ethylene and H• are formed by the decomposition reaction of C₂H₅•; C₂H₅•

and hydrogen are formed by the chain propagation reaction of ethane and $\text{H}\cdot$ or $\text{CH}_3\cdot$, thus forming cycle 1.

(2) Ethylene is mainly derived from cycles 1, 2 and 3. As cycles 1, 2, and 3 continue, a large amount of $\text{C}_2\text{H}_5\cdot$ is generated in the system; ethylene and $\text{H}\cdot$ are formed by the decomposition reaction of $\text{C}_2\text{H}_5\cdot$, while $\text{C}_2\text{H}_5\cdot$ is continuously formed by the chain propagation reaction of ample ethane and active $\text{H}\cdot$. This process is performed again and again to generate a large amount of ethylene.

(3) Propylene is mainly derived from the decomposition of $\text{C}_4\text{H}_9\cdot$ -2 produced by $\text{C}_4\text{H}_9\cdot$ -1, but propylene reacts with $\text{H}\cdot$ to form $\text{C}_3\text{H}_7\cdot$ -1 by the addition reaction. Since the activation energy of this reaction is only 6 kJmol^{-1} , propylene will be consumed largely to produce ethylene and $\text{CH}_3\cdot$.

(4) Ethylene and small-molecule radicals are chain-transferred to form $\text{C}_2\text{H}_3\cdot$; $1\text{-C}_4\text{H}_7\cdot$ -4 is formed by the addition reaction of ethylene and $\text{C}_2\text{H}_3\cdot$, and $\text{C}_6\text{H}_{11}\cdot$ is formed by the cyclization reaction of ethylene and $1\text{-C}_4\text{H}_7\cdot$ -4. After dehydrogenation reaction and chain transfer reaction, benzene is finally formed (path 2). The path 2 is the main path to generate benzene. $1,3\text{-C}_4\text{H}_5\cdot$ -4 is formed by the addition reaction of acetylene and $\text{C}_2\text{H}_3\cdot$. $\text{C}_2\text{H}_3\cdot$ decomposes to form acetylene, and $\text{C}_2\text{H}\cdot$ is formed by the chain propagation reaction of acetylene and other material. $1\text{-C}_4\text{H}_5\cdot$ -4 is formed by the addition reaction of ethylene and $\text{C}_2\text{H}\cdot$, and $1,3\text{-C}_4\text{H}_5\cdot$ -4 is formed by the isomerization reaction of $1\text{-C}_4\text{H}_5\cdot$ -4. $\text{C}_6\text{H}_9\cdot$ is formed by the cyclization reaction of ethylene and $1,3\text{-C}_4\text{H}_5\cdot$ -4, and after dehydrogenation reaction and chain transfer reaction, benzene is finally formed (path 4).

(5) $\text{C}_8\text{H}_{11}\cdot$ is formed by the cyclization reaction of $1,3\text{-C}_4\text{H}_5\cdot$ -4 and 1,3-butadiene. After dehydrogenation reaction and chain transfer reaction styrene is finally formed. This is the only way to generate styrene (path 1).

(6) 1,3-butadiene, acetylene, the by-product hydrogen, and methane are derived from the decomposition of $1\text{-C}_4\text{H}_7\cdot$ -4, the decomposition of $\text{C}_2\text{H}_3\cdot$, the chain transfer of $\text{H}\cdot$ with C_2H_6 and C_2H_4 , and the $\text{CH}_3\cdot$ chain transfer reaction with C_2H_6 respectively. And $\text{CH}_3\cdot$ has 3 main sources: the decomposition of $1\text{-C}_4\text{H}_9\cdot$ -2, the decomposition of $1\text{-C}_3\text{H}_7\cdot$ -2, and the chain initiation reaction between $\text{CH}_3\cdot$ (which is formed from the chain initiation of C_2H_6) and ethane.

Comparison between simulated data and literature data

Table 4 compares the simulated data with the industrial data and simulated data in literature [16]. Clearly, our simulation data are well consistent with the industrial production data. Since only the reaction of ethylene to form benzene and styrene was considered, but other secondary reactions such as secondary reaction of propylene were ignored, the propylene yield is slightly higher and the benzene yield is slightly lower.

CONCLUSIONS

(1) The theoretical calculation method for studying the mechanism of hydrocarbon pyrolysis reaction with Materials Studio and Aspen plus was proposed, and the free radical + olefin or free radical + alkynes are the reaction methods with the minimum activation energy was presented.

(2) A reaction network for the thermal cracking of ethane to form benzene and styrene was established by the above method. Firstly, the kinetic constants of 62 free radical reactions in the network were calculated on Materials Studio. Seven reaction paths for the formation of benzene and styrene from ethane were obtained from these reactions. Secondly, the one-dimensional tubular reactor constructed on Aspen Plus was repeatedly used for simulation calculation, and two paths for benzene and one path for formation of styrene were obtained.

(3) There are not only sequential reactions in the thermal cracking reaction of ethane, but also three reaction cycles. Firstly, after $\text{CH}_3\cdot$ is formed by the chain initiation reaction of ethane, methane and $\text{C}_2\text{H}_5\cdot$ are formed by the chain propagation reaction of ethane and $\text{CH}_3\cdot$; then ethylene and $\text{H}\cdot$ are formed by the decomposition reaction of $\text{C}_2\text{H}_5\cdot$. $\text{C}_2\text{H}_5\cdot$ and hydrogen are formed by the chain propagation reaction of ethane and $\text{H}\cdot$ or other small free radicals (cycle 1). Secondly, $\text{C}_4\text{H}_9\cdot$ -1 is formed by the addition reaction of ethylene and $\text{C}_2\text{H}_3\cdot$; $\text{C}_4\text{H}_9\cdot$ -2 is formed by the isomerization reaction of $\text{C}_4\text{H}_9\cdot$ -1, and $\text{CH}_3\cdot$ and propylene are formed by the decomposition reaction of $\text{C}_4\text{H}_9\cdot$ -2; while Methane and $\text{C}_2\text{H}_5\cdot$ are formed by the chain propagation reaction of ethane and $\text{CH}_3\cdot$, and finally ethylene and $\text{H}\cdot$ are formed by the decomposition reaction of $\text{C}_2\text{H}_5\cdot$ (cycle 2). Thirdly, $\text{C}_3\text{H}_7\cdot$ -1 is formed by the addition reaction of propylene and $\text{H}\cdot$. $\text{CH}_3\cdot$ and ethylene are formed by the decomposition reaction of $\text{C}_3\text{H}_7\cdot$ -1; methane and $\text{C}_2\text{H}_5\cdot$ are formed by the chain propagation

Table 3: Comparison with industrial data and simulation data.

Item	Yields /wt%							
	Hydrogen	Methane	Ethyne	Ethene	Ethane	Propene	1,3-Butadiene	Benzene
Industrial data in paper[16]	3.06	2.2	0	41.5	48.85	0.89	0.58	0.3
Simulation data in paper[16]	3.10	3.00	0.3	42.21	48.32	0.6	1.16	0.4
Simulation data in this paper	3.26	1.8	0	42.23	48.4	1.16	0.34	0.14

the reaction of ethane and CH_3^\bullet , and ethylene and H^\bullet are formed by the decomposition reaction of $\text{C}_2\text{H}_5^\bullet$ (cycle 3).

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