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Understanding the mechanism of radical reactions in 1-hexene pyrolysis

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ABSTRACT

The pyrolysis of 1-hexene was investigated at 873, 923 and 973 K, and interpreted in a chain mechanism of free radical reactions. The experimental data fit the reaction kinetic model adequately. The rate constant of 1-hexene overall conversion increases from 0.0312 to 0.116 to 0.453 s⁻¹ with increasing temperature from 873 to 923–973 K, leading to the apparent activation energy of 188.7 ± 1.0 kJ mol⁻¹. Primary products consist of C₁–C₃ paraffins, C₂–C₄ olefins, butadiene, cyclopentane, cyclopentene, coke and hydrogen. The quantitative analysis of product selectivity shows that various products are formed through different elementary reactions with varying reaction path probability (RPP). Rising temperature promotes homolysis of feed molecule (chain initiation), recombination of radicals (chain termination), and coke formation. The average reaction chain length (KCL) decreases from 5.86 to 5.19 with increasing temperature from 873 to 973 K.

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1. Introduction

Production of light olefins such as ethylene by thermal cracking of large hydrocarbons is one of important processes in petrochemical industry. Many attempts have been made to investigate the process of hydrocarbons pyrolysis experimentally and theoretically. Over the past 30 years, the studies on the mechanism and kinetics of hydrocarbon pyrolysis have become deeper and wider progressively (Sundaram and Froment, 1978; Willems and Froment, 1988; Fake et al., 1997; Norinaga and Deutschmann, 2007).

When many studies were carried out on the pyrolysis of alkanes (Khan et al., 2008; Ziegler et al., 2005; Mallinson et al., 1992; Dominé et al., 1990; Watanabe et al., 2000; Aribike and Susu, 1988), relatively few were conducted on the pyrolysis of alkenes. It is commonly accepted that pyrolysis of hydrocarbons proceeds through a free-radical chain mechanism (Bounaceur et al., 2002; Franz et al., 2000; Xiao et al., 1997; Zdeněk and Josef, 1992; Pant and Kunzru, 1996), mainly including: homolysis of hydrocarbon to form free radicals (initiation), β-decomposition of free radicals or H-abstraction of radicals from hydrocarbons (propagation), radical isomerization, and

recombination or disproportionation of radicals (termination). With using thermochemical data such as enthalpy and bond dissociation energy (Blanksby and Ellison, 2003; McMillen and Golden, 1982), researchers were able to generate the mechanistic model of hydrocarbon pyrolysis including all possible elementary reactions. For a complex system of hydrocarbon pyrolysis involving various radicals (reactive intermediates), such mechanistic model could contain a huge number of elementary reactions. In *n*-hexane pyrolysis, for example, several kinetic models including more than 200 elementary reactions have been developed (Bounaceur et al., 2002). Obviously, all the reactions may be thermodynamically possible, but only parts of them are kinetically feasible. Kinetic modeling based on thermochemical data could give the information of thermodynamic possibility to predict if a reaction could take place, but could not verify if a reaction has been feasibly carried out. For a practical application, the mechanism from thermochemical analysis has to be optimized or simplified in view of reaction feasibility, and the kinetic model has to be validated by experimental investigation.

As a large family, hydrocarbons include various alkanes, alkenes, cyclanes, cyclenes, aromatics, etc. Among them,

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alkenes are present in gasoline up to 20% (Yahyaoui et al., 2005). As a member of alkene group, 1-hexene is important intermediate specie in the oxidation of cyclohexane which is a common surrogate for cycloalkane fuels (Kiefer et al., 2009). For the pyrolysis of 1-hexene at high temperature, Wang et al. (2004) reported that the major reaction paths were those to produce C_3H_4 at temperature below 1273 K and to produce $C_3H_3^*$ at temperature above 1273 K. Kiefer et al. (2009) investigated cyclohexane and 1-hexene decomposition over the temperature range 1300–2000 K and found that cyclohexane simply isomerized to 1-hexene, and this then dissociated almost entirely by a more rapid C–C scission to allyl and *n*-propyl radicals. Tsang (1978) determined the thermal stability of cyclohexane and 1-hexene and revealed that the 1-hexene bond-breaking reaction led to an allylic resonance energy of 42.7 kJ and a heat of formation of allyl radicals of 176.6 kJ. Yahyaoui et al. (2005) conducted experimental and modeling study of 1-hexene oxidation in the temperature between 1270 and 1700 K at a pressure of about 0.2 MPa, and determined that the apparent activation energy, E_a , was approximately equal to 230 kJ mol⁻¹ at high temperature (>1400 K) and strongly decreased to about 120 kJ mol⁻¹ at low temperature (<1400 K). Ranzi et al. (2001) presented a wide range kinetic modeling study on oxidation and combustion of the *n*-hexene isomers and concluded that isomerization reactions of the hexenyl radicals were found to play a significant role in the chemistry and interactions of the three *n*-hexene isomers.

In the present work, the pyrolysis of 1-hexene was investigated with a plug-flow tube reactor at 873, 923–973 K. Based on the experimental data, a chain mechanism was first established, and then a quantitative interpretation to the details of reaction kinetics and selectivity was presented. We have also discussed the influence of temperature on kinetics and selectivity in terms of reaction path probabilities by using the chain mechanism postulate.

2. Materials and methods

2.1. Materials

The feedstock, 1-hexene of 99+% purity, was obtained from the China Petrochemical Corporation Hangzhou Refinery and used without further purification.

2.2. Apparatus

The apparatus consists of three major units: injector, reactor and collector. The injector is a syringe driven by a variable speed motor (SAGE INSTRUMENTS model 355). The reactor, a Quartz tube with 35 cm length by 1.5 cm internal diameter, has an independently controlled two-zone heater. The upper part (20' 1.5 cm i.d.) packed with 0.25 cm ceramic rings acts as preheating section, and the lower part (15' 1.5 cm i.d.) filled with inert silica sand (40–60 mesh) serves as reaction section. The collector is composed of a water-cooled condenser, a glass pot inserted in an ice bath followed by a glass finger immersed in dry ice, and a gas buret.

2.3. Experimental procedure

The pyrolysis of 1-hexene was investigated at 873, 923 and 973 K, and the reaction time was adjusted by changing the feed rate while keeping the total amount of feed-delivered constant. Prior to each run, the reactor was pre-purged for 20 min

with nitrogen (~ 200 cm³ min⁻¹), in situ. In a typical run, the feed was first pumped into the preheating zone, vaporized, and then entered the reaction zone. During the reaction, the outlet vapor was passed through the condenser to the pot, to the cold finger and finally to the buret. The liquid constituents in the output were collected in the pot and finger, while the gaseous products were collected in the buret by the downward displacement of a saline solution. At the end of each run, reactor purged with dry nitrogen at 150 cm³ min⁻¹ for 20 min, and then washed by toluene. The residues insoluble to toluene were regarded as coke. To quantify the amount of coke formed during a run, carbon dioxide-free air was passed through the reactor (~ 150 cm³ min⁻¹) at 1073 K for 6 h. All water produced was trapped in two drierite tubes in series, while the carbon dioxide was trapped in two ascarite tubes. The amount and composition (H/C ratio) of coke were determined from the weight of water and carbon dioxide collected.

The fluctuation of temperature between inlet and outlet of reactor was determined to be in the range of ± 3 K. Mass balance was performed on the input and output streams. Experimental runs with mass balances ± 2 wt% were rejected. This level of accuracy was adequate for the data interpretation.

2.4. Analysis

All products were identified using an Agilent 5973 GC/MS. Gaseous products were analyzed by an Agilent 6820 gas chromatograph. Liquid products were analyzed by an Agilent 2010 gas chromatograph with a 60-m SE54 capillary column and a flame ionization detector. Products were eluted at 283 K followed by a temperature program of 5 K/min up to 573 K.

3. Results and discussion

3.1. Initial selectivity of products

Selectivity data could be useful in evaluating the quantitative aspects of the cracking reaction mechanism. An effective methodology for determining the selectivities of primary products from experimental yield and conversion data was well established (Zhao et al., 1993). For each product, the time-averaged yield sampled from $t=0$ to t_f is plotted against the time-averaged conversion of feed. Each of the plots is enveloped by a single curve, the optimum performance envelope (OPE). The initial selectivities of primary products in 1-hexene pyrolysis at various temperatures were determined from the slopes of OPE curves at $t \rightarrow 0$, and presented in Table 1. The primary products included C₁–C₄ paraffins, C₂–C₄ olefins, butadiene, cyclopentane, cyclopentene, coke and hydrogen, while trace amounts of C₅ olefin or diolefin as well as benzene or toluene were found only as secondary products at higher conversion of feed. Among these primary products, the ethylene has the highest weight selectivity greater than 22.8%, while the selectivity of butanes was near to zero. The selectivity distribution of primary products varied with the reaction temperature. For examples, the weight selectivity of ethane decreased from 10.2% to 9.2% and that of coke increased from 10.1% to 12.3% with increasing temperature from 873 to 973 K.

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