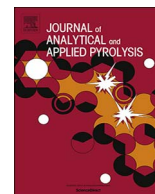




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Group additive modeling of cyclopentane pyrolysis

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ABSTRACT

The pyrolysis of cyclopentane is not well established although it is an abundant compound in typical naphtha feedstocks and can be considered a model compound for cyclic fuels. The studies in literature so far have focused primarily on the initial decomposition of cyclopentane in shock tubes. This article therefore explores the pyrolysis of cyclopentane in a continuous flow tubular reactor with pure cyclopentane feed at reactor conditions 0.17 MPa, 973–1073 K, and a residence time of 0.5s. Conversions of 5% to 75% were realized while the product concentrations were quantified using two dimensional gas chromatography. A mechanism composed of elementary high pressure limit reactions has been generated using the automatic network generation tool “Genesys”. Kinetics of the reactions originate from high level ab-initio calculations and new group additive values derived from ab-initio kinetic data in literature. Overall the Genesys model outperforms the models available in literature and there is a good agreement between model calculated mass fraction profiles and experimental data for 22 products ranging from hydrogen to naphthalene without any adjustments of the kinetic parameters. Reaction path analysis reveals that cyclopentane consumption is initiated by the unimolecular isomerization to 1-pentene, but overall dominated by hydrogen abstraction reactions by allyl radicals and hydrogen atoms to give cyclopentyl radicals, whose ring opening and further scissions lead to smaller molecules. Dominant routes for the major products are discussed.

1. Introduction

Research in pyrolysis of cyclic hydrocarbons is important for industrial processes like fast pyrolysis and steam cracking [1]. There is a huge pressure on the industry to produce fuels and lower olefins more economically than ever before. This implies more optimal operating conditions and using a cheaper feedstock. There is a limit to which the operating conditions can be optimized within the boundary conditions of metal corrosion and coke deposition [2]. The lucrative knob, which is also the topic of one of the most relevant research areas is to explore a cheaper feedstock. Typically, naphthenes and aromatics are undesirable feed components for pyrolysis, hence petrochemical cuts or other sources containing higher quantities of those components are cheap pyrolysis feeds. The tolerance toward naphthenes is relatively higher than for aromatics because of their lower coking tendency. At the same time, the pyrolysis of naphthenes is a relatively unexplored field compared to their linear and branched counterparts [3]. Among the simplest naphthenes, which are the single ring unsubstituted cycloalkanes, the ones most abundantly found in petrochemical feeds like light naphtha are cyclohexane and cyclopentane [4]. Out of these two, the pyrolysis of cyclohexane is a relatively mature research area [5–8].

Surprisingly, the one molecule whose pyrolysis behavior has not been studied in detail so far is cyclopentane. According to the authors’ knowledge, no previous work has been published related to the pyrolysis of cyclopentane, more so at steam cracking conditions.

The few literature studies involving pyrolysis of cyclopentane have focused on experimental investigation of auto-ignition and initial decomposition products in shock tubes [9–11]. In order to explain the ignition delay trends, kinetic models have been developed for cyclopentane oxidation. However, such models, though good for ignition delay time predictions, are generally not ideal for pyrolysis because they tend to focus on extremely short residence times, which implies that primarily the initial decomposition characteristics are well captured. Also, the hydrocarbon feed is highly diluted and this is an unrealistic representation of an industrial pyrolysis reaction as the polycyclic aromatic hydrocarbons are not formed at high dilutions and low residence times to the extent that are usually formed in steam cracking for example. Here we discuss a few relevant studies reported so far.

Around four decades ago, Tsang [11] did experiments to find out initial decomposition rates of cyclopentane in a comparative-rate single-pulse shock-tube. In this, the initial cyclopentane decomposition rate was established after comparing the experiment with that of a

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Nomenclature

List of symbols

$k_{rST}(T)$	Rate coefficient at temperature T , $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular, s^{-1} for unimolecular
$\chi(T)$	Quantum mechanical tunneling correction factor
k_B	Boltzmann's constant, $\text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$
h	Planck's constant, $\text{m}^2 \text{kg s}^{-1}$
$\frac{RT}{p}$	Molar volume at 1 atm, m^3
Δn	Molecularity of the reaction (2 for bimolecular, 1 for unimolecular reactions)
ΔG^\ddagger	Gibbs free energy difference between transition state and reactant(s) without the transitional mode, kJ
A	Pre-exponential factor $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular, s^{-1}

	for unimolecular
\tilde{A}	Single-event pre-exponential factor $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular, s^{-1} for unimolecular
E_a	Activation energy of a reaction, kJ/mol
$\Delta \text{GAV}^\circ(\log \tilde{A})$	Standard Δ group additive value for single-event pre-exponential factor
$\Delta \text{GAV}^\circ(E_a)$	Standard Δ group additive value for activation energy, kJ/mol
n_e	Number of single events
NNI	Non-nearest neighbor interaction (for $\log \tilde{A}$ and E_a)
exo	Exocyclic ring intra-molecular carbon centered radical addition
endo	Endocyclic ring intra-molecular carbon centered radical addition

standard reaction whose temperature decay characteristics were well known. This was the well-studied retro-Diels-Alder decomposition of cyclohexene feed giving ethylene and 1,3-butadiene. The residence time in the shock tube reached a maximum of 0.8 milli-second at temperatures 1000 K to 1200 K and pressures 2 bara to 6 bara with a maximum of 5% cyclopentane in feed. Cyclopentane conversions obtained were in the range of 0.01% to 1%. The main product detected was 1-pentene and based on product yields, the isomerization reaction of cyclopentane to give 1-pentene was hypothesized as the initial dominant decomposition step and a global rate coefficient for the same was proposed. The shock tube experiments also detected cyclopropane and a minor channel forming cyclopropane and ethylene from cyclopentane was proposed with a global rate coefficient, though at the temperatures of interest for steam cracking, the mass yield of cyclopropane was about 100–1000 times lower than that of 1-pentene. Tsang proposed a C5 biradical intermediate as the immediate product of cyclopentane decyclization. This biradical was suggested to form majorly 1-pentene through intra-molecular hydrogen abstraction, and minorly cyclopropane and ethylene by C–C beta scission.

About 30 years later, in 2006, Sirjean [12] did high level ab-initio CBS-QB3 calculations on ring opening of cycloalkanes. In that, cyclopentane was studied and a biradical C5 intermediate was envisaged, along the lines of Tsang [11]. Sirjean proposed CBS-QB3 based global rate coefficients for cyclopentane conversion to 1-pentene and that to cyclopropane and ethylene. The rate coefficient of the reaction forming 1-pentene matched well with that proposed by Tsang [11]. Cyclopropane was confirmed to be a minor product and the rate coefficient of the reaction forming cyclopropane and ethylene was about 1% of that forming 1-pentene at 1000 K. In this study, ab-initio calculations revealed that the C5 biradical has a bond rotation energy barrier equal to the activation energy for intra-molecular hydrogen abstraction to form 1-pentene. Hence, as soon as the cyclopentane ring opens to form C5 biradical, the C5-biradical undergoes bond rotation and a simultaneous and immediate conversion to 1-pentene. As a practical inference, for a complete cyclopentane pyrolysis model, the initiation step can be represented as a single elementary step isomerization to 1-pentene. Both Tsang [11] and Sirjean [12] studied the initial decomposition of cyclopentane and not its complete decomposition to smaller hydrocarbons and hydrogen nor the molecular growth to polycyclic aromatic hydrocarbons. Annesley and co-workers [13,14] measured cyclopentane ring opening kinetics in a Laser-Schlieren apparatus at 1500–2000 K at low pressures (total pressures 40–400 mbar), with cyclopentane partial pressures 0.1–20 mbar. The rate expression for cyclopentane isomerization to 1-pentene was derived from experiment and RRKM theory was applied to make an extrapolation to the high pressure limit. The rate coefficient determined by Annesley et al. [13,14] matches the ab-initio value of Sirjean et al. within 8% deviation at 1050 K. Therefore the value of Sirjean et al. was retained. The same authors also

concluded that no pressure dependence needs to be accounted for as pressure has a minimal effect on the rate coefficient for cyclopentane isomerization to 1-pentene. The rate coefficient at 40 mbar is only about 6% lower than the one at high pressure limit.

In 2015, Wang [15] proposed a comprehensive ab-initio based kinetic model for propylene pyrolysis with extensive potential energy surface scans of species including cyclopentane. This model predicts another initiation step for cyclopentane decomposition in addition to isomerization – that of C–H homolytic bond scission to give hydrogen atom and cyclopentyl radical. However, the rate coefficient for this reaction was found to be negligible (about 200 times smaller at 1000 K) compared to that of isomerization to 1-pentene. The Wang [15] model also contained some reactions involving cyclopentane and cyclopentyl radicals with ab-initio pressure dependent Chebyshev kinetics. Though originally intended for predicting propylene pyrolysis, it has the capability to attempt prediction of cyclopentane pyrolysis too. However, the model uses single-step lumped reactions to form aromatics like benzene, toluene, styrene, indene and naphthalene from 1,3-cyclopentadiene, so it is not a completely elementary reaction model. It has a mixture of pressure dependent kinetics, high pressure limit rate coefficients, for some reactions altered kinetic parameters and global lumped kinetics for aromatics formation. In spite of these features, it is the most relevant model in literature that comes close to meet our objective of describing the complete pyrolysis of cyclopentane and not just the initial decomposition trends. In addition, this model is also a source of ab-initio kinetic data especially of reactions involving cyclics whose group additive values are not yet reported, and whose rate parameters can be used to derive new group additive values for cyclic reactions. The model is also a source of ab-initio thermodynamics of cyclic species.

The other kinetic and thermodynamic data that may be required for the present study is that involving molecular growth to form aromatics and polycyclic aromatic hydrocarbons. These mechanisms involve many complex species, sometimes bicyclic and tricyclic molecules and may involve reaction families not usually relevant for pyrolysis of simple open chain molecules. It is generally believed that 1,3-cyclopentadiene is the precursor to the formation of aromatics and polyaromatics [16]. Cyclopentane and 1,3-cyclopentadiene being of similar skeletal structure, it is expected that a significant amount of 1,3-cyclopentadiene would be formed during cyclopentane pyrolysis which could in turn trigger aromatics formation and growth. Merchant's model [17] was reported to predict pyrolysis of 1,3-cyclopentadiene and ethylene feed by a model of more than 5000 elementary reactions forming benzene, toluene, styrene, indene and naphthalene. Merchant had done ab-initio investigation of kinetics of the most dominant pathways.

Among other studies on cyclopentane pyrolysis, Sirjean [10] did shock tube experiments with cyclopentane-oxygen-argon mixtures and

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