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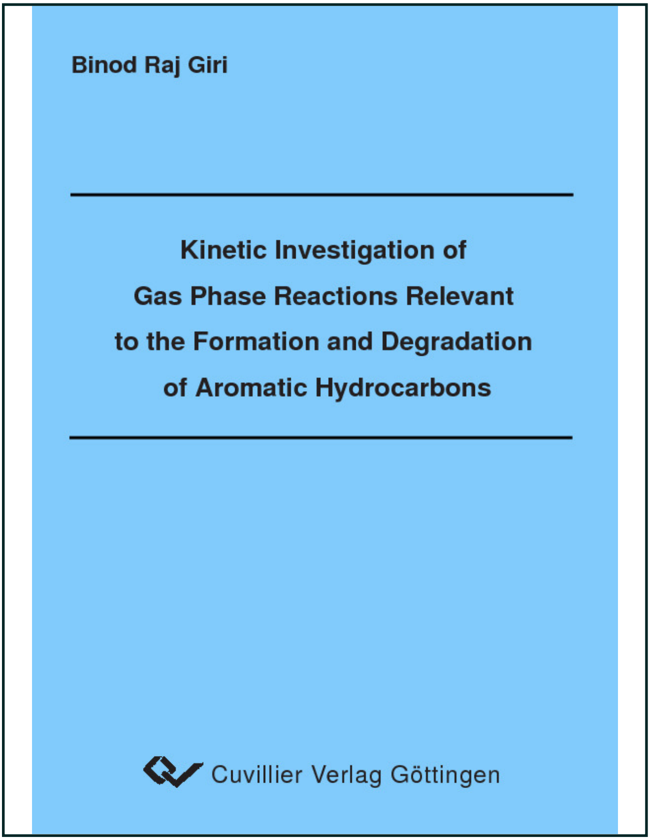
Kinetic Investigation of Gas Phase Reactions Relevant to the Formation and Degradation of Aromatic Hydrocarbons



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Chapter 1

Summary

This work mainly focuses on the kinetic investigation for the formation of the first aromatic ring and its degradation at combustion relevant conditions. The reactions involving aromatic species play a crucial role in the combustion chemistry for the formation of polyaromatic hydrocarbons (PAH, the precursors to soot). In this work, two different setups were used: laser flash photolysis followed by UV-absorption, and shock tube technique combined with **A**tomic **R**esonance **A**bsorption **S**pectroscopy (ARAS) to detect H-atoms.

For the investigation of the recombination reaction of propargyl radicals (C_3H_3) dipropargyl oxalate (DPO) was introduced as a new, halogen-free photolytic source for propargyl radicals. Experiments were carried out at conditions T = 375 - 520 K and p = 1 - 140 bar. The recombination rate coefficients were found to be pressure independent and slightly temperature dependent. Existing discrepancies regarding the UV-absorption of propargyl radical were resolved with the use of DPO as a propargyl radical source. The absorption spectrum for propargyl radical between 295 - 355 nm reported in recent works was confirmed, whereas an absorption of C_3H_3 near 240 nm discussed in earlier works could not be confirmed.

The unimolecular decompositions of allene (a-C_3H_4) and propyne (p-C_3H_4) were studied behind reflected shock waves at conditions, T = 1470 -

2150 K, p = 0.25 - 4 bar. A significant pressure dependence was observed for their dissociation rates. For both isomers, the rate coefficients showed virtually identical pressure and temperature dependence, indicating a fast mutual isomerization. A detailed kinetic analysis showed that CH bond fission is the dominant process. The present experimental observations are in accordance with a recent theoretical prediction. The experimentally observed p- and T-dependences were well reproduced by master equation analysis.

Benzene (c-C_6H_6) and phenyl radical (c-C_6H_5) pyrolysis were studied in a shock tube behind reflected shock waves using ARAS technique at $p = 0.25$ - 1.2 bar and $T = 1600$ - 2300 K, for phenyl pyrolysis temperature ranged between 1430 K and 2380 K. A significant pressure dependence was observed for both cases. The experimental observations showed that CH bond scission leading to a phenyl radical and an H-atom is the dominating initial step for the benzene pyrolysis. The further dissociation of phenyl radicals was interpreted in terms of the recently revised Bauer-Aten mechanism which considers the more energetically favored route leading to *ortho*-benzyne (o-C_6H_4) + H. On the basis of this mechanism, the experimental results on the benzene and phenyl pyrolysis were adequately reproduced.

Furthermore, the reactions that build up and consume aromatic species govern the kinetics of soot formation. Hence, the rate coefficients for the reactions c-C_6H_5 + H $\rightarrow$ products, c-C_6H_6 + H $\rightarrow$ c-C_6H_5 + H_2 and c-C_6H_5 + C_2H_2 $\rightarrow$ c-$C_6H_5C_2H$ + H were also investigated using shock tube/H-ARAS technique for varying experimental conditions. The kinetic data obtained in this work are parameterised for combustion modeling.

Zusammenfassung

Die vorliegende Arbeit beschäftigt sich mit kinetischen Untersuchungen zur Bildung und Abbau des ersten aromatischen Rings unter verbrennungsrelevanten Bedingungen. Die entsprechenden Reaktionen spielen in der Verbrennungschemie eine entscheidende Rolle bei der Bildung polyaromatischer Kohlenwasserstoffe und damit von Ruß. Es wurden zwei unterschiedliche Messanordnungen verwendet: Laserblitzlichtphotolyse mit anschließender Messung der UV-Absorption sowie der Stoßwellentechnik kombiniert mit **A**tom-**R**esonanz-**A**bsorptions-**S**pektroskopie (ARAS) zur Detektion von H-Atomen.

Um die Rekombination von Propargylradikalen zu untersuchen, wurde erstmalig Diprogargyloxalat (DPO) als halogenfreie photolytische Quelle für Propargylradikale verwendet. Die Experimente wurden im Temperaturbereich von 375 - 520 K und bei Drücken von 1 - 140 bar durchgeführt. Für die Geschwindigkeitskonstanten der Rekombination wurde eine leichte Temperaturabhängigkeit, aber keine Druckabhängigkeit gefunden. Frühere Diskrepanzen hinsichtlich der UV-Absorption von Progargylradikalen wurden durch Verwendung des neuen Radikalvorläufers DPO beseitigt. Eine Absorptionsbande des Propargylradikals im Bereich von 295 - 355 nm wurde im Einklang mit neuren Arbeiten anderer Autoren gefunden, während eine früher diskutierte Absorption um 240 nm nicht bestätigt werden konnte.

Die unimolekularen Zerfälle von Allen (a-C_3H_4) und Propin (p-C_3H_4) wurden bei Temperaturen von 1470 - 2150 K und Drücken von 0,25 - 4 bar hinter reflektierten Stoßwellen untersucht. Die Geschwindigkeitskonstanten zeigten eine deutliche Druckabhängigkeit. Für beide Isomere wurden praktisch gleiche Geschwindigkeitskonstanten gefunden, was auf eine schnelle wechselseitige Isomerisierung hinweist. Eine detaillierte kinetische Analyse zeigte, daß der CH-Bindungsbruch der dominierende Schritt ist. Die Ergeb-

nisse dieser Arbeit stimmen mit theoretischen Vorhersagen überein und die experimentell gefundenen p- und T-Abhängigkeiten lassen sich durch eine Mastergleichungsanalyse reproduzieren.

Die Zerfälle von Benzol (c-C_6H_6) und Phenyl (c-C_6H_5) wurden in einem Stoßrohr hinter reflektierten Stoßwellen mit Hilfe der ARAS-Technik bei p = 0,25 bis 1,2 bar und T = 1600 bis 2300 K (Benzol) bzw. T = 1430 bis 2300 K (Phenyl) untersucht. In beiden Fällen wurde eine deutliche Druckabhängigkeit der Reaktionsgeschwindigkeit beobachtet. Bei der Benzolpyrolyse ist der CH-Bindungsbruch zu Phenylradikalen und H-Atomen der dominierende Einleitungsschritt. Die weitere Dissoziation des Phenylradikals wurde mit einem jüngst vorgeschlagenen Mechanismus interpretiert, welche die Bildung von *ortho*-Benzin (o-C_6H_4) postuliert. Auf der Grundlage dieses Mechanismus konnten die experimentellen Ergebnissen der Benzol- und Phenyl-Pyrolyse konsistent reproduziert werden.

Weiterhin wurden die Geschwindigkeitskonstanten für die Reaktionen c-$C_6H_5 + H \rightarrow$ Produkte, c-$C_6H_6 + H \rightarrow$ c-$C_6H_5 + H_2$ und c-$C_6H_5 + C_2H_2 \rightarrow$ c-$C_6H_5C_2H + H$ mit Hilfe der Stoßwellentechnik und ARAS-Detektion bei verschiedenen experimentellen Bedingungen bestimmt. Alle in dieser Arbeit erhaltenen kinetischen Daten wurden für kinetische Modellierungen anwenderfreundlich parametrisiert.

Chapter 2

General Introduction

Commercial fuels contain about 40% cyclic and aromatic hydrocarbons - they are used to increase the octane number. The reactions involving the aromatic hydrocarbons and their radicals play a pivotal role in the combustion chemistry. The formation and degradation of aromatic hydrocarbons are often discussed with a big concern in the hydrocarbon combustion chemistry since these processes govern the kinetics for the formation of polyaromatic hydrocarbons (PAH's), the precursors of soot.

The combustion products from transportation, industries and power generation are the major sources of airborne pollution which are directly associated with human health. The fine particles (d $\leq$ *1* μm) emitted directly by the combustion devices can easily be inhaled. These particles are thought to pose a great risk to human health causing lethal disease like lung cancer. To minimize the environmental impact as well as for the better utilization of fossil energy, more efficient and economic combustion devices have to be developed. For the development of such devices, a better understanding of the mechanisms of PAH and soot formation processes during hydrocarbon combustion is essential. Therefore, theoretical as well as experimental studies on the kinetics of elementary reactions involved in the combustion and pyrolysis processes are of crucial importance.

In recent years, considerable efforts have been made in order to understand the PAH and soot formation processes [1–16]. It has been suggested that once the aromatic rings are formed, the ring growth leading to PAH occurs *via* a repetitive reaction sequence of two steps (see Fig. 2.1), *i.e.*,

i) H-atom abstraction from an aromatic species (A_i) by H-atom:

$$A_i + H \quad \Rightarrow \quad A^{\bullet}{}_i + H_2 \qquad\qquad R_{2.1}$$

followed by

ii) an addition of acetylene to the radical site of the aromatic species ($A^{\bullet}{}_i$):

$$A^{\bullet}{}_i + C_2H_2 \quad \Rightarrow \quad A_iCHC^{\bullet}H \qquad\qquad R_{2.2}$$

This reaction sequence for an aromatic ring growth is termed as **HACA** "**H**-**A**bstraction-$\mathbf{C}_2H_2$-**A**ddition" mechanism which was proposed by Wang and Frenklach [3–5]. Before dealing with the aromatic ring growth, the reaction routes leading to the first aromatic ring from small aliphatics have to be explored.

Generally, two different reaction pathways have been suggested for the formation of aromatic species from the aliphatic compounds [6, 10, 12–17]:

i) reaction pathways involving C_2- and C_4-hydrocarbons [6, 15, 17]:

$$HC{\equiv}C^{\bullet} + HC{\equiv}CH \quad \Rightarrow \quad HC{\equiv}C\text{-}CH{=}C^{\bullet}H \qquad R_{2.3}$$

$$HC{\equiv}C\text{-}CH{=}C^{\bullet}H + HC{\equiv}CH \quad \Rightarrow \quad c\text{-}C_6H_5 \qquad R_{2.4}$$

$$H_2C{=}C^{\bullet}H + HC{\equiv}CH \quad \Rightarrow \quad H_2C{=}CH\text{-}CH{=}C^{\bullet}H \qquad R_{2.4}$$

$$H_2C{=}CH\text{-}CH{=}C^{\bullet}H + HC{\equiv}CH \quad \Rightarrow \quad \text{c-}C_6H_6 + H \qquad R_{2.5}$$

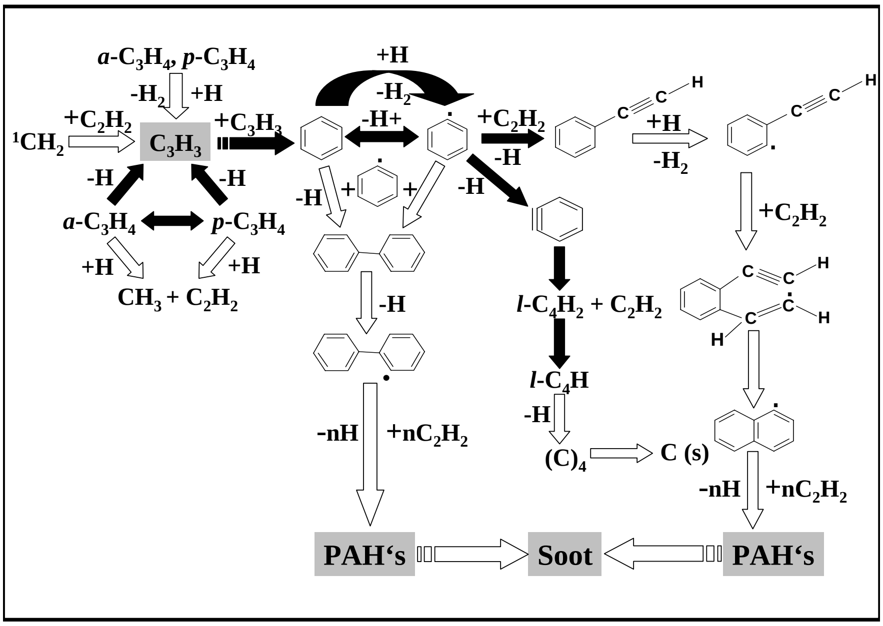

Figure 2.1: Reaction scheme showing the formation of the first aromatic ring, its degradation and growth leading to polyaromatic hydrocarbons (PAH's).

ii) reaction pathways involving C_3 hydrocarbons (in particular propargyl radicals) [6,12,13]:

$$
\begin{array}{llll}
{}^1CH_2 + HC{\equiv}CH & \Rightarrow & {}^\bullet CH_2\text{-}C{\equiv}CH + H & R_{2.6} \\
{}^\bullet CH_3 + HC{\equiv}CH & \Rightarrow & CH_3\text{-}C{\equiv}CH + H & R_{2.7} \\
{}^\bullet CH_2\text{-}C{\equiv}CH + {}^\bullet CH_2\text{-}C{\equiv}CH & \Rightarrow & c\text{-}C_6H_5 + H & R_{2.8} \\
{}^\bullet CH_2\text{-}C{\equiv}CH + {}^\bullet CH_2\text{-}C{\equiv}CH & \Rightarrow & c\text{-}C_6H_6 & R_{2.9}
\end{array}
$$

iii) a coupling of these two reaction sequences *via* reactions of the cyclopentadienyl radical (c-C_5H_5) [6,16]:

$$
\begin{array}{llll}
{}^\bullet CH_2\text{-}C{\equiv}CH + HC{\equiv}CH & \Rightarrow & c\text{-}C_5H_5 & R_{2.10} \\
{}^\bullet CH_3 + c\text{-}C_5H_5 & \Rightarrow & c\text{-}C_6H_6 + 2H & R_{2.11} \\
c\text{-}C_5H_5 + c\text{-}C_5H_5 & \Rightarrow & c\text{-}C_{10}H_8 + 2H & R_{2.12}
\end{array}
$$

Among the different routes suggested, the self-reaction of propargyl radicals (C_3H_3) is regarded as a key step for the formation of the first aromatic ring during the combustion processes [10–14,18–21]. Propargyl radical is the smallest resonantly stabilized free radical with a resonance stabilization energy of about 50 kJ/mol [22]. Due to its thermal stability, the self-reactions of propargyl radicals becomes a major channel for propargyl radical loss at combustion relevant temperatures. For this reason, the knowledge of rate coefficients for the reactions that produce C_3H_3 radicals and consume them are very important from the combustion point of view.

C_3H_3 radicals can be formed by either direct dissociation of C_3H_4 isomers or by H-abstraction from these precursors in an H-abundant atmosphere. The kinetic investigations on C_3H_4 isomers are important from theoretical and practical aspects as well. On one hand, they are important precursors for propargyl radicals while on the other hand, they are produced in the thermal decomposition of propylene and propane under combustion conditions. Moreover, the potential energy surface (PES) of C_3H_4 reaction is very complex having multiple wells and channels [23–28] which may lead to a complex pressure and temperature dependence of the rate coefficients. The rate data existing in the literature on the thermal dissociation of propyne (p-C_3H_4) and allene (a-C_3H_4) are partly contradictory [12, 29–32] and the discrepancies regarding the competition between the isomerization and the decomposition of C_3H_4 isomers still exist.

Over the past decades, numerous experimental studies on the self-reaction of propargyl radicals have been contributed [29,33–39]. However, kinetic data for this reaction at high pressures are still scarce. Furthermore, the spectrum of the propargyl radicals is discussed contradictorily in the literature. The use of halogenated propargyl precursors e.g., C_3H_3Cl, C_3H_3Br and C_3H_3I often obscured the spectroscopic features of propargyl radicals due to the formation of an adduct radical $C_3H_3X_2$ (X = Cl, Br, I). It is discussed that the adduct radical is formed by the reaction of halogen atom with the precursor molecule [36].

Despite numerous efforts [5,40–55] on the kinetic investigations of C_6 hydrocarbons e.g., benzene (c-C_6H_6) and phenyl radicals (c-C_6H_5), the mechanism for their dissociation is still under discussion. In most of the earlier studies, CH bond fission was considered to be the dominant process in the benzene pyrolysis. However, it was discussed that CC bond fission leading to C_4H_4 + C_2H_2 substantially contribute to the benzene pyrolysis at $T \geq 2000$ K [50,56] whilst at lower temperatures Mebel *et al.* [55] pointed out that the isomerization of c-C_6H_6 leading to open chain C_6H_6 (l-C_6H_6) is dominating and suggested that the isomerization channel should be included for combustion modeling. Likewise, the mechanism for phenyl radical decompostion is also under discussion. In earlier studies [40–42,46,49–52,54], the results were interpreted assuming that the phenyl decomposition occurs *via* ring opening into an open-chain intermediate (l-C_6H_5). Recently, a more energetically favoured channel *via* *ortho*-benzyne (o-C_6H_4) has been proposed [43,57] for c-C_6H_5 dissociation.

In this work, the self-reaction of propargyl radicals was investigated at high pressures and at elevated temperatures. Dipropargyl oxalate ($HCCCH_2O(O)C$-$C(O)OCH_2CCH$, DPO) as a new photolytic source for propargyl radicals was introduced for the first time. The dissociation rates for a-C_3H_4, p-C_3H_4, c-C_6H_6 and c-C_6H_5 were determined, and in addition to this, a detailed picture on the kinetic model for a-C_3H_4, p-C_3H_4, c-C_6H_6 and c-C_6H_5 pyrolysis was provided. The reactions that build up and consume aromatic species govern the kinetics of soot formation. Keeping this fact in view, the rate parameters for i) c-C_6H_5 + H → products ii) c-C_6H_6 + H → c-C_6H_5 + H_2 iii) c-C_6H_5 + C_2H_2 → c-C_6H_5CCH + H were also determined for varying experimental conditions. Important reactions governing the balance for the formation and degradation of small aromatic hydrocarbons are schematically represented in Fig. 2.1. The elementary steps investigated in the present work are highlighted with black arrows (see Fig. 2.1).