

Zusammenfassung

In der vorliegenden Arbeit wurden Reaktionen von kleinen, ungesättigten Kohlenwasserstoffen (C_3H_x mit $x = 2 - 5$) bei hohen Temperaturen mit Hilfe der Stoßwellentechnik untersucht. Dabei wurde die Atom-Resonanz-Absorptions-Spektroskopie (H-ARAS) verwendet, um die Bildung von H-Atomen zeitaufgelöst zu verfolgen. Weiterhin wurde die Selbstrekombination von Propargylradikalen bei Temperaturen oberhalb von 1000 K mit Hilfe der zeitaufgelösten UV-Absorptionsspektroskopie studiert.

Der thermische Zerfall von Allylradikalen ($C_3H_5 \rightarrow C_3H_4 + H$) wurde bei Temperaturen zwischen 1123 und 1567 K und im Druckbereich zwischen 0,3 und 4,5 bar untersucht. Dabei wurden Allylradikale durch den thermischen Zerfall von Allyliodid erzeugt. Es wurde eine signifikante Druckabhängigkeit der Geschwindigkeitskonstanten des C_3H_5 -zerfalls beobachtet. Die experimentell bestimmten Werte sind in guter Übereinstimmung mit theoretischen Vorhersagen.

Analog zu den Untersuchungen zum C_3H_5 wurde der unimolekulare Zerfall von Propin ($C_3H_4 \rightarrow C_3H_3 + H$) untersucht. Temperatur und Druck wurden dabei zwischen 1446 und 2056 K bzw. 0,9 und 2,7 bar variiert. Auch für diesen Zerfall wurde eine Druckabhängigkeit der Geschwindigkeitskonstanten beobachtet. Die experimentell bestimmten Geschwindigkeitskonstanten sind in guter Übereinstimmung mit Resultaten die durch Lösen der Mastergleichung erhalten wurden.

Geschwindigkeitskonstanten für den Zerfall von Propargyl ($C_3H_3 \rightarrow C_3H_2 + H$) wurden unter Verwendung von Propargyliodid als Radikalvorläufer bestimmt. Die Experimente wurden bei Temperaturen zwischen 1396 und 1994 K und Drücken zwischen 0,8 und 4,2 bar durchgeführt. Es wurde keine Druckabhängigkeit im untersuchten Druckbereich beobachtet.

Um den Zerfall von C_3H_2 ($C_3H_2 \rightarrow C_3 + 2H$) zu untersuchen, wurden Experimente bei sehr hohen Temperaturen (1750 K-2100 K) und Drücken zwischen 1 und 2,6 bar durchgeführt. Die beobachteten H-Atom-Konzentrations-Zeit-Profile konnten unter Berücksichtigung der auftretenden Folgereaktionen modelliert werden.

Darüber hinaus wurde die Selbstrekombination von Propargylradikalen hinter reflektierten Stoßwellen untersucht. Temperaturabhängige Absorptionskoeffizienten wurden aus den experimentell beobachteten Absorbanz-Zeit-Profilen bestimmt. Absorptionskoeffizienten in der Größenordnung von 10^{-18} cm^2 wurden erhalten; eine

schwache, negative Temperaturabhängigkeit wurde beobachtet. Die temperaturabhängigen Geschwindigkeitskonstanten wurden aus den Absorbanz-Zeit-Profilen bestimmt. Die Experimente wurden unter Verwendung von Propargyliodid oder Dipropargyloxalat als Radikalvorläufer bei Temperaturen zwischen 1000 und 1400 K durchgeführt. Geschwindigkeitskonstanten in der Größenordnung von $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ mit einer geringen, negativen Temperaturabhängigkeit wurden erhalten. Es wurde ferner versucht, relative H-Atom-Ausbeuten für die Reaktion $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ zu bestimmen, dabei konnte im Temperaturbereich von 1000 bis 1400 K und bei Drücken zwischen 0,08 und 1 bar eine obere Grenze von 10 % festgelegt werden.

1. Summary

In the present work, high-temperature reactions of small unsaturated hydrocarbons of the type C_3H_x ($x = 2-5$) were investigated using the shock tube technique. In these studies Atom Resonance Absorption Spectroscopy(H-ARAS) was used to monitor the production of H-atoms. Additionally, the self recombination of propargyl radicals was directly studied for the first time under high-temperature conditions using time resolved UV-Absorption to follow the reaction progress.

The thermal decomposition of allyl radicals ($C_3H_5 \rightarrow C_3H_4 + H$) was investigated at temperatures between 1123 K and 1567 K and pressures from 0.3 bar to 4.5 bar. Allyl radicals were generated by the thermal decomposition of allyl iodide. Significant pressure dependence of the rate coefficients for allyl radical decomposition was observed. The experimentally obtained values showed good agreement with theoretical calculations (RRKM and master equation).

Analogous to the studies of C_3H_5 , the unimolecular decomposition of propyne ($C_3H_4 \rightarrow C_3H_3 + H$) was investigated. The temperatures and pressures ranged from 1446-2056 K and 0.9-2.7, bar respectively. The decomposition was also found to be pressure dependent in the investigated pressure range. The rate coefficients showed good agreement with the theoretical calculations employing SACM and master equation model.

Propargyl radical unimolecular decomposition ($C_3H_3 \rightarrow C_3H_2 + H$) rates were determined using propargyl iodide as a precursor. The experiments were carried out at temperatures between 1396 - 1994 K and pressures of 0.8 bar up to 4.2 bar. No pressure dependence was observed in the investigated pressure range.

To study the further decomposition of C_3H_2 species ($C_3H_2 \rightarrow C_3 + 2H$), experiments were conducted at very high temperatures (1750 K-2100 K) and at pressures between 1 bar and 2.6 bar. The H concentration-time profiles were successfully modelled taking into account secondary reactions of the species involved

Furthermore, the self recombination of propargyl radicals was investigated behind reflected shock waves. Temperature dependent absorption coefficients were determined from the experimental profiles. Values in the order of $10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ were obtained with slight negative temperature dependence. The temperature-dependent rate coefficients were directly determined from the absorbance-time

profiles by following second order kinetics. The experiments were performed using either propargyl iodide or di-propargyl oxalate as precursors at temperatures between 1000 and 1400 K and pressures of about 1 bar. Rate coefficients in the order of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with slight negative temperature dependence were observed which is in agreement with a recent theoretical study. The determination of H-atom yields was also attempted for the propargyl + propargyl reaction to yield phenyl +H, and an upper limit of 10% for the contribution of this channel to the total recombination rate at temperatures between 1000-1400 K and pressures of 0.08 bar-1 bar was extracted.

2. Introduction

In the present days there has been a lot of concern over health problems which are associated with air pollution. The extensive use of combustion processes may it be in industrial manufacturing, motor transportation etc. are discussed to be a major source of air borne species which pose a lot of risk to human health [1,2,3,6]. Some of the air borne species are found to be associated with polycyclic aromatic hydrocarbons (PAH). The polycyclic aromatic hydrocarbons are discussed to be precursors of soot and very small soot particles are easily breathed into the lungs which can be of great danger to human health [6]. Polycyclic aromatic hydrocarbons are also found to be responsible for lung cancer. Recently it has been evident that cigarette smoke carcinogen one of which is a PAH-benzo[a]pyrene is associated with the cause of lung cancer [4].

Apart from the hazards on human health due to PAHs, the formation of soot on the other side has attracted interest in industries due to its wide applications. The property of soot intermediates to enhance heat transfer through radiation is of enormous use in furnaces and heat generators in industries [8]. However, it is important that the soot is oxidized before it is vented out in the environment. Soot finds various applications when its properties are altered according to its needs. The present day applications of soot in industries are in toners for copiers, or in printing colors, also soot is used as fillers in tires etc. [8].

On the other hand there is a need to develop cleaner and better combustion methods in order to control both the emission of pollutants and to promote an efficient utilization of fossil energy resources. In order to develop such combustion models, it is essential to have a better understanding of combustion processes. Chemical kinetics investigations have in the past few decades flourished with the hope to understand the mechanisms for soot generation, ultimately to permit control of the types and magnitudes of soot emissions [5,6,7,8]. Detailed kinetic modeling provides more information about these processes. The regulation and minimization of the formation of soot in combustion in turn requires the control of chemical processes responsible for the growth of larger PAH and their oxidation. The molecular precursors of soot particles are thought to be heavy PAHs and the growth process from small molecules such as benzene to PAH appear to involve series of reactions of C_2 , C_3 or other small unsaturated hydrocarbon species e.g. vinyl, propargyl, allyl

etc. In order to model soot formation processes it is desirable to have as much information as possible about the rate coefficients of the elementary steps involved in the formation of PAH. These rate coefficients are then used to develop a detailed kinetic model which includes the reactions of all the species involved under combustion conditions at varying temperatures and pressures. From a fundamental point of view, one of the unsolved problems is how the first aromatic ring is formed in a flame burning with an aliphatic fuel.

The C_3H_x unsaturated radicals such as the allyl and propargyl radical are resonantly stabilized free radicals. The unpaired electron in such radicals is delocalized over two or more sites in the molecule, yielding at least two resonant electronic structures of equivalent importance. As a result of the delocalization of the unpaired electron, resonantly stabilized free radicals normally form weaker bonds with stable molecules which are a cause of increased stability towards pyrolysis and comparatively slow reaction with molecular species like oxygen. Due to their relatively low reactivity, they can build up to high concentrations in flames. Thus the reactions of resonance stabilized free radicals make an important mechanism for building higher hydrocarbons in flames. One such simple and important resonance stabilized free radical is the propargyl radical which has two resonance structures as depicted in *Fig.2.1*. It is found that the first structure is dominant.

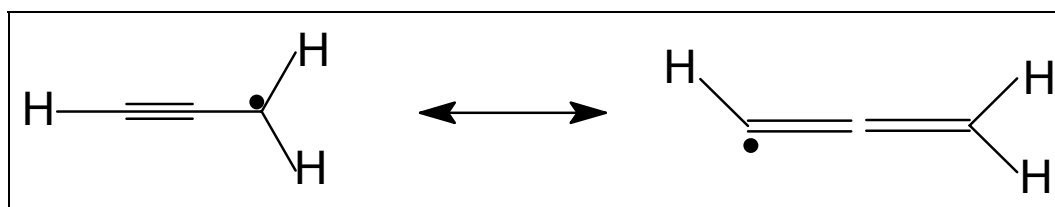
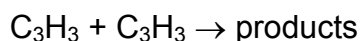


Fig.2.1: Representation of the propargyl resonance structures

Propargyl radical has been reported to reach very high concentrations in the oxidation zone of premixed acetylene [9] and benzene flames [10]. This is most probably a combined result of its relative ease of formation and its intrinsic stability. It may be readily formed by the reaction of methylene with acetylene [11]. It was Miller and Melius [12] who evaluated different pathways, leading to the first aromatic ring formation in the studies of $C_2H_2-O_2-Ar$ flame by Bastin et al [13]. The comparison of model predictions for C_3H_3 with experimental data shows very good agreement. Therefore, based on these studies, they conclude that the recombination of two C_3H_3 radicals represents an important pathway towards formation of the first benzene ring.

Although other reactions may make important contributions under certain conditions, the reaction between two propargyl radicals,



is generally believed to be an important cyclization step in flames of aliphatic fuels [6,14-23]. Also the very high exothermicity on such radical-radical reaction pathway makes it far less subject to reversibility [24].

The C_3H_x species can also be interconverted by certain hydrogen abstraction reactions, $\text{C}_3\text{H}_x + \text{H}_2 \leftrightarrow \text{C}_3\text{H}_{x+1} + \text{H}$, or recombination reactions with atomic hydrogen, $\text{C}_3\text{H}_x + \text{H} \leftrightarrow \text{C}_3\text{H}_{x+1}$. Both H_2 and H are found to be present abundantly in fuel rich hydrocarbon flames [25].

Kinetics of the C_3H_x unsaturated hydrocarbons is therefore of increased interest under combustion conditions due to its role played in the formation of PAH. Since the propargyl radical is an important species in soot formation, the rate coefficients of the reactions responsible in its formation and its destruction are to be accurately determined. Although these reactions are very critical under combustion conditions, little is known and there are few experimental data at high temperatures available.

In this present work, the rate coefficients for the reactions producing and consuming propargyl either through its unimolecular decomposition at high temperatures or its recombination is determined. A brief reaction scheme is depicted in *Fig.2.2*.

The H- Atom Resonance Absorption Spectroscopy (ARAS) was employed to monitor the H-atoms and to determine absolute H-atom concentrations. Due to the high sensitivity of this technique in detecting H-atom, unimolecular reaction steps yielding H-atoms can be well isolated and rate coefficients can be accurately determined. The C_3H_x system investigated involves the unimolecular decomposition of allyl radical (C_3H_5), propyne (C_3H_4), propargyl radical (C_3H_3), and also the further decomposition of propargyl radical to yield carbon trimer. Since H-atom is the product of these reaction steps, ARAS is a well suited technique to determine the rate coefficients. The influence of pressure dependence on some reactions was also investigated. This study also involves the comparison of experimental data with the results from statistical theories. There has been very good agreement between theory and experiments.