

The Growth of Polycyclic Aromatic Hydrocarbons in Benzene Pyrolysis and Benzene/Oxygen Mixtures at High Pressures and Temperatures

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Abstract

This study presents results on soot formation and polycyclic aromatic hydrocarbon formation in pure C_6H_6 pyrolysis and on various C_6H_6/O_2 mixtures. In the experiments by the shock wave method, it was found that the induction time for soot formation in the temperature range $1600\text{ K} < T < 2200\text{ K}$ was rather independent on the oxygen content of the mixture. For the soot mass growth rates, there was a distinction between two temperature regions: i) $T > 2000\text{ K}$, and ii) $2000\text{ K} < T < 2300\text{ K}$, in dependence on the oxygen content of the mixtures. The measurements were related to calculations on the contribution of different reaction pathways on the formation of the actual soot precursors, the polycyclic aromatic hydrocarbons. These results indicate a promoting impact of small quantities of oxygen on the formation of radicals important for the production of soot precursors.

Introduction

Polycyclic aromatic hydrocarbons, PAH, are discussed to be direct precursors of soot particles. For this reason, the study of the formation and the growth of the PAH is essential in understanding the details of soot formation. Soot formation which is based on a pure pyrolytic process takes also place in an oxidative environment, such as in flame systems. In this context the question arises, whether - and if so - in which way and at what stage of the whole process, the formation of soot and its precursors is influenced by an oxidative environment. Due to limiting temporal resolution of the oxidation zone and the particle formation zone, these questions on the precursor formation, and also on the first steps of soot growth cannot be answered by measuring premixed flames at elevated pressures. However, these difficulties can be partly overcome by applying the shock wave method. By this method, it is possible to investigate the induction time for soot formation, and the growth of soot particles in dependence on time. Since this measured induction time of soot formation is a composed quantity of complex chemical processes, the growth of only PAH cannot be studied by the shock wave method. Therefore, the formation and also the growth of the PAH were modeled, and related to the induction time of soot and its growth rates.

Experimental and Modeling

The hydrocarbon used for the present investigations was C_6H_6 , a compound with aromatic structures already available at the beginning of the chemical reactions. For benzene, the influence of oxygen on the PAH and on the soot formation process was studied by varying the oxygen content of the mixtures. The ratio of the C_6H_6/O_2 mixtures was (1:0), (1:0.3), (1:1), and (1:3). The temperatures in the studied systems were 1600 K - 2300 K, the pressure was 5.5 MPa, and the total carbon content was maintained at a constant value of 4 mole/m³.

The experiments were carried out behind reflected shock waves in a 70 mm i.d. steel shock tube consisting of a 4.5 m long driven section and a 3.5 m long driver section. The shock speed and the pressure time profile were measured by piezo-electric conductors. Shock parameters were calculated based on the standard procedure [1, 2] using the measured incident shock speed. The conversion of hydrocarbon to soot was determined by the attenuation of the light beam from a 15 mW He-Ne-laser at $\lambda = 632,8\text{ nm}$. The extinction profiles $I(t)$ were converted into soot yield profiles $SY(t)$ using Beer's

law [3], a refractive index of $m = 1.57 - 0.56 i$, a soot density of 1.86 g/cm^3 , and the molar mass of carbon. The test gas mixtures were prepared manometrically and mixed by convection. The gases O_2 ($> 99.8 \%$), and Ar ($> 99.9 \%$) were used without further purification. Benzene ($> 99.9 \%$) was purified by distillation.

Simulations of the benzene/oxygen mixtures were performed with the HOMRUN program [4]. Whenever possible, thermochemical data for the species were taken from readily available sources [5 - 9]. Otherwise, thermodynamic estimates of the species were made using group additivity technics and others [10 - 12]. The core of the reaction model for the C_1 to C_6 chemistry was gathered from the work of Warnatz and coworkers [13 - 15], Frenklach and coworkers [16, 17], Homann and coworkers [18, 19]. Further benzene reactions as proposed e.g. by Miller et al. [20], Zhang et al. [21], and Lindstedt et al. [22] were also included. For the formation of high molecular weight PAH of roughly 700 amu, several reaction pathways were incorporated into the mechanism taking the different structures of the PAH into account. The developed mechanism includes the alternating H abstraction C_2H_2 (HACA) route [16], combinative reaction sequences [23], and also the cyclopentadienyl pathway [24]. For further details of the mechanism see [25].

Results and Discussion

In the temperature range of 1600 K - 2200 K, the investigated induction times for soot formation show no dependence on the oxygen content of the studied mixtures. The activation energy of the induction time for the pure C_6H_6 pyrolysis and for the $\text{C}_6\text{H}_6/\text{O}_2$ mixtures is about 229 kJ/mole, a value which is similar to the obtained data for C_2H_2 pyrolysis. From these results, it can be concluded that the rate of the pyrolysis leading to soot particles is rather independent of its chemical environment.

For the experimental data about soot mass growth rates, two temperature ranges can be distinguished: i) $T < 2000 \text{ K}$, and ii) $2000 \text{ K} < T < 2300 \text{ K}$. At $T < 2000 \text{ K}$, the soot growth rate $k_f/[C]$ increases linearly with $1/T$. These result holds for pure C_6H_6 , as well as for $\text{C}_6\text{H}_6/\text{O}_2$ mixtures. An activation energy of about 200 kJ/mole is found for the C_6H_6 pyrolysis, and the $\text{C}_6\text{H}_6/\text{O}_2$ mixtures. At $C/O = 10$ and $C/O = 3$, the soot growth rates of the mixtures are only slightly below those of pure C_6H_6 . With increasing oxygen content, the $k_f/[C]$ values are shifting to those values found in premixed flame systems. For temperatures between 2000 - 2300 K, the soot growth rates of the $\text{C}_6\text{H}_6/\text{O}_2$ mixtures decrease with rising temperature. For $C/O = 10$, and $C/O = 3$, the resulting activation energy is also about 200 kJ/mole, in the limit of error. For mixtures with a very high oxygen content ($C/O = 1$), the activation energy becomes much smaller than in the case of pure C_6H_6 pyrolysis. With increasing oxygen content of the mixtures, the changing point of these two temperature ranges is shifted to lower temperatures.

The obtained data from the measurements were related to calculations for these reaction systems. The experimentally determined results are in line with the computed induction times of high molecular weight PAH. These results indicate that a small additive of oxygen favoured the formation of radicals important for the production of soot precursors reacting to soot particles. In contrast, at a very high oxygen content the formation of PAH and soot precursors is decreased. In the calculations it is also found that the cyclopentadienyl pathway becomes more prominent in producing high molecular weight PAH when the oxygen content of the mixtures is increased.

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