A study on the initial product channels of cyclohexane pyrolysis behind reflected shock waves

M. Braun-Unkhoff, C. Naumann, P. Frank

German Aerospace Center, Institute of Combustion Technology
Stuttgart, Germany

Introduction

The chemical kinetics of combustion processes of fuels has been the subject of many investigations over the past years. In the last decade, the chemistry of naphthenes – which belong to the main components of practical fuels such as gasoline, diesel, and kerosene – has attracted much attention as their contribution to the formation of aromates can be significant. For example, due to the complexity of kerosene composition – kerosene Jet A1 is a complex mixture of long-chained alkanes as dominant components, of mono- and poly-aromatics and of cycloalkanes or naphthenes (mono- and polycyclic) –, usually a model fuel is designed for simulating its oxidation. In this context, cyclohexane is discussed as a representative for naphthenic species, see e.g. ElBakali et al. /1/. Therefore, a detailed reaction mechanism is needed to describe oxidation of cyclohexane and its way to aromatic species in order to model the formation of aromatics in the oxidation of practical fuels.

Presently, investigations on the thermal decomposition of cyclohexane do not show a consistent picture regarding the initiation steps. From a single-pulse shock tube study (Tsang, 1978 /2/) it was deduced that the main initial process involves isomerisation to 1-hexene, followed by subsequent decomposition of the primary products. The same dominant end products have been also found in VLPP experiments (Brown et al., 1986 /3/). From a flow reactor study at relatively low temperatures, Gulati and Walker (1989) /4/ assumed that benzene was formed in a reaction sequence starting from cyclohexane → cyclohexene → 1,3-cyclohexadiene → benzene. Recently, from high pressure JSR experiments on cyclohexane oxidation (Voisin et al., 1998, /5/) at different mixture conditions, it was concluded that the main initiation step on cyclohexane decomposition occurs via C-C bond fission and results in ethene as the main product. In the same study, a much slower rate coefficient was attributed to the H-elimination reaction step. Furthermore, this scheme was used as part of a big reaction scheme for calculating species profiles measured in a flow reactor study (ElBakali et al., 2000, /1/) for temperatures between 900 K and 1200 K at pressures up to 10 atm over a wide range of equivalence ratio (0.5 to 2). It was found that 1-hexene which is produced via cyclohexane isomerization was formed at 1 atm, but not at 10 atm. A submechanism of 1-butene which was formed in higher concentration at 1atm than at higher pressures was included in the reaction scheme to improve the prediction of 1-hexene. As the main product, ethene was found stemming from a direct C-C fission of cyclohexane. The molecular decomposition channel was found to be mainly responsible for the decay of cyclohexane besides H-atom abstraction via OH– and H-radicals. The model was also able to model laminar burning velocities of atmospheric cyclohexane / air flames at T_0 = 298 K /6/. Therefore, the aim of the present work is to give more insight into the initial decomposition steps during the pyrolysis of cyclohexane, especially to find out whether H atoms, which are most important with respect to ignition, may be formed directly in the thermal decomposition.

Experimental

The experiments were performed behind reflected shock waves under highly diluted conditions applying a very sensitive detection method. Atomic resonance absorption spectroscopy at a wavelength λ = 121.6 nm was applied to monitor time dependent H-atom concentrations. Very small initial concentrations of cyclohexane were used, ranging from 1 to 11 ppm diluted in highly purified argon. Cyclohexane exhibited a relatively strong propensity for wall adsorption. Therefore, in most experiments, its initial concentration was examined by the use of gas chromatography analysis of samples taken from the shock tube immediately before the experiment. The uncertainty was found to be about ± 20% due as an internal standard technique has been applied. Thus it was possible to study the reaction system under very isolated conditions, with only minor influence of subsequent reactions. The experiments cover a temperature range of 1180 to 1900 K at pressures between 1.5 and 2 bar. All experiments of the present study were conducted in a stainless steel shock tube of 7.5 cm internal diameter which was heated to 363 K. Measurements were performed 5 mm away from the end flange. An oxygen spectral filter combined with a L_α-interference-filter (10 nm FWHM) was used. Calculated absorption profiles reported are based on calibration experiments, using the reaction of O-atoms – stemming from the decomposition of N_2O – with H_2 to produce H-atoms.

Results and Discussion

From previous investigations, one might expect that the dominant decomposition reaction occurs via C-C bond fission leading to ethene as the main product:

c-C_6H_{12} → open chain-C_6H_{12} (e.g. 1-hexene) → 3 C_2H_4 (R1a).

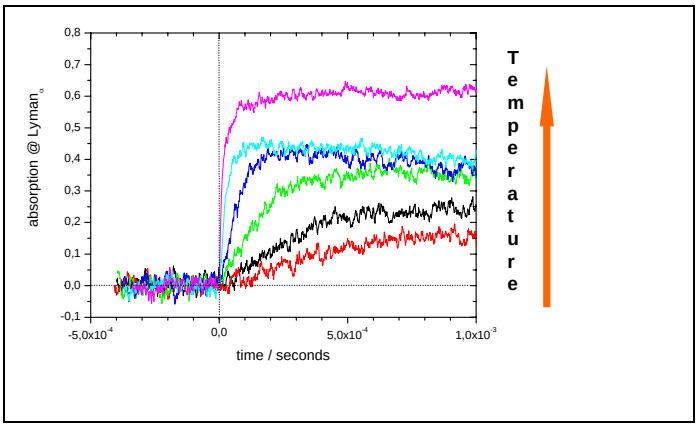

Figure 1: H-atom absorption measured behind reflected shock front. 1.05ppm cyclohexane diluted with argon for T_5 = 1335-1895K & p_5 = 1.77–1.93bar.

Therefore, hydrogen atoms can only be produced by subsequent reaction steps which should reveal a pronounced delay time under the highly diluted conditions of the present investigation. However, time resolved H-absorption profiles measured at the lowest initial cyclohexane concentrations of about 1 ppm (Figure 1) in the temperature range 1335 – 1895 K, clearly show that hydrogen atoms are produced immediately at the onset of the reaction. Therefore it was assumed that H-atoms are produced directly by an additional C-H bond fission according to reaction path R1b, which is followed by a fast H elimination reaction leading (R2) to cyclohexene:

c-C_6H_{12} → c-C_6H_{11} + H (R1b)

c-C_6H_{11} → c-C_6H_{10} + H (R2) .

As a base set for modeling the measured H-atom absorption profiles, the rate coefficient expressions of Voisin et al. (1998) have been used. For the conditions of very low initial concentration used in the present study, a reaction scheme was set up which essentially consisted of the initiation reactions R1a / R1b, R2 and bimolecular reactions like $c\text{-}C_6H_{12}$ / $c\text{-}C_6H_{11} + H \rightarrow c\text{-}C_6H_{11}$ / $c\text{-}C_6H_{10} + H_2$ which are only of minor influence. Figure 2 shows for a typical experimental profile at about 1450 K the influence of the rate values and of the branching ratio of reactions R1a and R1b. With the original values for k_{1a} and k_{1b}, nearly no H-atoms are calculated (full line). Neglecting channel R1a, gives absorption profiles which are still too small (dashed line). Only if the value of k_{1b} is increased considerably by a factor of 7.5, the initial slope of the measured profile is met, but in the later stage, too much H-atoms are predicted (dotted line). With the latter value for k_{1b} and the original value for k_{1a}, the predicted profile is much too low, compared with the observed one (dashed-dotted curve).

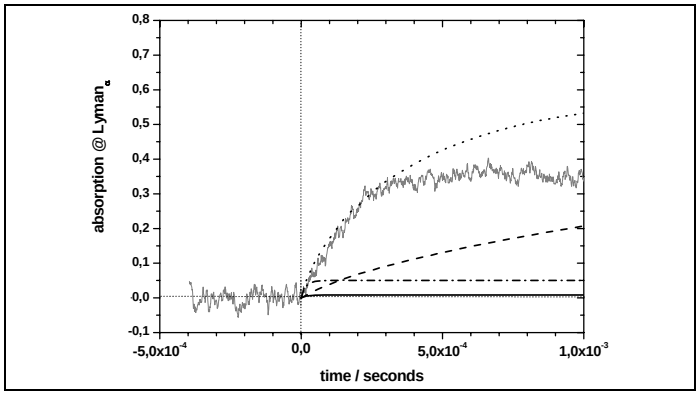

Figure 2. H-atom absorption profile measured behind reflected shock front. 1.05 ppm cyclohexane diluted in argon. T_5 = 1447 K; p_5 = 1.92 bar. Influence of molecular channel. Full line: k1a & k1b from /5/; dashed line: k1a*0, k1b from /5/; dotted line: k1a*0, k1b*7.5; dashed dotted line: k1a from /5/ & k1b*7.5.

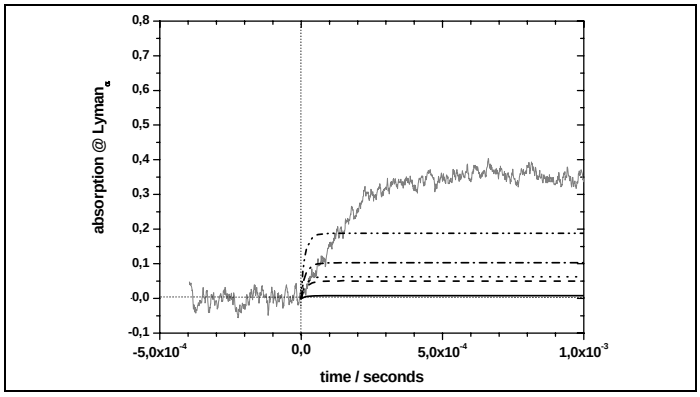

Figure 3. H-atom absorption profile measured behind reflected shock front. Same experimental condition as in Figure 2. Influence of H-atom producing channel. Full line: k1a & k1b from /5/; dashed line: k1a from 5/, but k1b*7.5; dotted line: k1a from /5/, but k1b*10; dashed dotted line: k1a from /5/, but k1b*20; dashed-dotted-dotted-line: k1a from /5/, but k1b*50.

The influence of the H-atom producing channel R1a is depicted in Figure 3. The molecular channel R1a was sticked to the value given by Voisin et al. whereas the rate coefficient of the H-atom producing channel was increased within factors of 7.5 and 50. It can clearly be seen from Figure 3 that the predicted absorption is much too high at the onset of the reaction time interval if R1b proceeds faster and faster. This leads to the conclusion that it is not possible to match the observed H-atom absorption without reducing the rate coefficient of the molecular channel.

Consequently, both values for the rate of the two initial decomposition steps of cyclohexane were modified, with respect to the data given in /5/. As can be seen in Figure 4, the measured absorption profile is reproduced over the entire observation time interval, if the rate coefficient of the molecular channel is reduced considerably by about a factor of 50 and if simultaneously, the H-atom producing channel R1b is increased by a factor of 7.5 (full line).

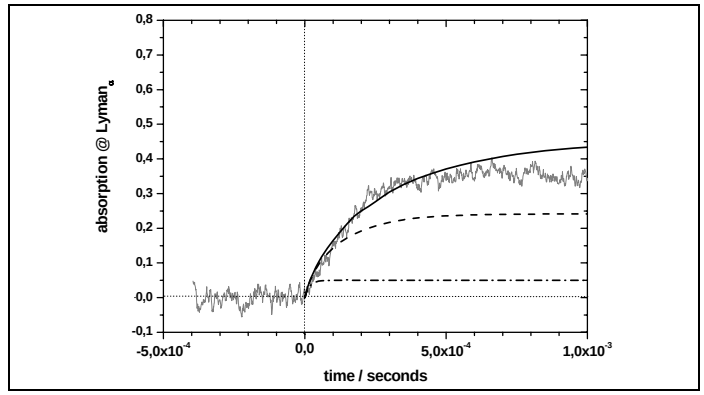

Figure 4. H-atom absorption profile measured behind reflected shock front. Same experimental condition as in Figure 2. Dash dotted line: k1a from /5/, k1b*7.5; dashed line: k1a*0.1, k1b*7.5; full line: k1a*0.02, k1b*7.5

Conclusions

The results of the present study lead to a branching ratio of about 0.5 for k_{1a} / (k_{1a} + k_{1b}). Hence, the molecular channel R1a is much slower than considered up to now, whereas the hydrogen elimination path R1b proceeds much faster, by about a factor of 5 - 10. Further measurements such as non-resonant absorption either of the educt itself and/or some of the product species are needed to determine the rate of the molecular channel R1a. Thus, a much better understanding of the initial reaction steps of the decomposition of cyclohexane would be enabled.

Acknowledgement. The authors are grateful to N. Ackermann for technical assistance. The financial support of the Deutsche Forschungsgemeinschaft DFG, SFB 606 *Instationäre Verbrennung, Transportphänomene, Chemische Reaktionen, Technische Systeme* is gratefully acknowledged.

References

(1) ElBakali, A., Braun-Unkhoff, M., Dagaut, P., Frank, P, Cathonnet, M., Proc. Comb. Inst. 28, 2000, pp. 1631-1638
(2) Tsang, W., 1978, Int.J.Chem.Kinet., **10**, pp. 1119
(3) Brown, T.C., King, K.D,. Nguyen,T.T., J.Phys.Chem. **90**, 1986, pp. 419
(4) Gulati, K.S. and Walker, R.W,. 1989, J.Chem.Soc.Faraday Trans. **2**, 85, pp. 17
(5) Voisin, D., Marchal. A., Reuillon, M., Boettner, J.-C. and Cathonnet, M., 1998, Combust. Sci .and Tech., **138**, pp. 137
(6) Davis, S.G. and Law, C.K., 1998, Combust. Sci. Tech. 140, pp. 427-449