

# Experimental Study of the Pyrolysis of Cyclohexane at Shock Tube Relevant Conditions

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## Abstract

As previous investigations on the thermal decomposition of cyclohexane give no consistent picture about the rate of the initial reaction steps, the aim of the present work was to get more insight into cyclohexane pyrolysis. The experiments have been carried out using two different shock tube techniques which allow studying both elementary reaction steps and dominant reaction routes by complete product analysis after a well defined dwell time. In contrast to previous investigations, a branching ratio of about 1:1 has been deduced for the two initiation channels of cyclohexane decomposition leading by C-C bond fission to molecular products (R1a) and by H-elimination to the cyclohexenyl radical (R1b), respectively. The present study indicates clearly that the molecular channel is much slower than considered up to now, whereas the H-atom elimination path proceeds much faster, by about factors 5 - 10. The residual gas analysis, carried out in the single pulse shock tube reveals a strong temperature dependency of the acetylene/ethylene-product ratios.

## Introduction

The chemical kinetics of combustion processes of fuels have been the subject of many investigations over the past years. The attention was lately focused on fuel molecules other than normal chain hydrocarbons, e.g. naphthenes. Cyclohexane is one of the prominent representatives of this group of chemical compounds found in fuels like gasoline, diesel and kerosene. Investigations on the thermal decomposition of cyclohexane show not a consistent picture of the initiation steps [1-6]. From a single-pulse shock tube study [2] it was deduced that the main initiation 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 [3]. From a flow reactor study at relatively low temperatures, Gulati and Walker [4] assumed that benzene was formed in a reaction sequence like cyclohexane  $\rightarrow$  cyclohexene  $\rightarrow$  1,3-cyclohexadiene  $\rightarrow$  benzene. Recently, from high pressure JSR experiments on cyclohexane oxidation [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 large reaction scheme for calculating species profiles measured in a flow reactor study [1] for temperatures between 900 K and 1200 K at pressures up to 10 atm over a wide range of equivalence ratio ( $0.5 \leq \Phi \leq 2$ ). 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 1 atm than at higher pressures was included in the reaction scheme to improve the prediction of 1-hexene. Ethene was found as the main product to be produced by 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  $T = 298$  K [7].

Therefore, the aim of the present work is to give more insight into the initial decomposition steps during the pyrolysis of cyclohexane, in particular to find out whether H atoms which are most important with respect to ignition may be formed directly in the thermal decomposition.

## Special Objectives

The experiments were performed in two different heatable stainless steel shock tube devices; for details of the two shock tube methods see ref. [8]. One set of experiments was carried out behind reflected shock waves under highly diluted conditions applying a very sensitive detection method, the ARAS-technique, to monitor time dependent H-atom concentrations. Thus it was possible to study the reaction system under highly isolated conditions ( $X_o = \leq 11$  ppm) with only minor influence of subsequent reactions. The other set of

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experiments has been carried out in a single pulse shock tube. The mixtures are shock heated instantaneously, then undergo reaction within a short and well defined dwell time period of approximately 1.5 milliseconds; finally, the reaction process is frozen suddenly by an expansion wave with a cooling rate of about  $10^5 - 10^6 \text{ K s}^{-1}$ . The residual gas mixture is sampled and analyzed by applying a well elaborated procedure to enrich PAHs in the samples. This study is aimed to expose the most effective reaction routes of the chemical system.

## Experimental

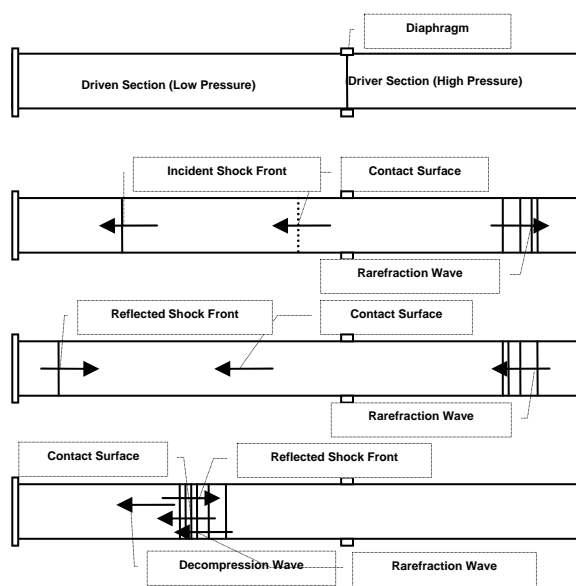
### High Purity Shock Tube with ARAS-technique

The experiments were performed behind reflected shock waves under highly diluted conditions applying a very sensitive detection method. Atomic resonance absorption spectroscopy (ARAS) at  $\lambda = 121.6 \text{ nm}$  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 chromatographic analysis of samples taken from the shock tube immediately before the experiment. The uncertainty is found to be about  $\pm 20\%$  due to the applied internal standard technique. Thus it was possible to study the reaction system under very isolated conditions, with only minor influence of subsequent reactions. The experiments covered 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 ca. 5 mm away from the end flange. An oxygen spectral filter and an interference-filter (10 nm FWHM) were used for H-atom detection. The concentration profiles reported are based on calibration experiments, using the reaction of O-atoms – stemming from the decomposition of  $\text{N}_2\text{O}$  – with  $\text{H}_2$  to produce H-atoms.

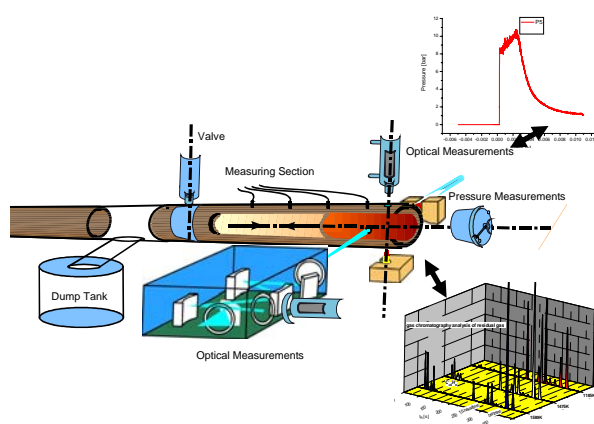
### Single Pulse Shock Tube

A second set of experiments has been performed in the single pulse shock tube. Initial mole fractions of 651 ppm cyclohexane at pressures around 5 bar were shock heated to temperatures ranging from 1400 K to 1900 K. Figure 1 shows the operation scheme of the shock tube, whereas Fig. 2 displays the experimental setup, emphasizing the test section regime. The experiments are conducted behind reflected shock waves. After the high temperature reaction period, the mixture is cooled down by the decompression wave. The residual gas mixture is then analyzed with the aid of gas- and high pressure liquid- chromatography (GC and HPLC) and by quadrupole mass-spectrometry. Figure 3 shows a typical gas chromatography of products obtained from cyclohexane pyrolysis. For example, large amounts of ethene and acetylene are found. By applying a single

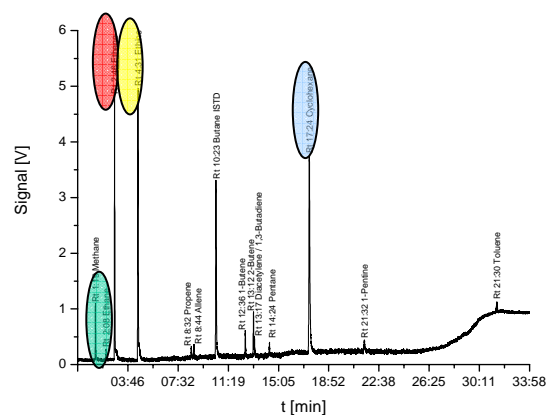
pulse study, the most effective routes for cyclohexane decomposition can be investigated.



**Figure 1.** Principle operation scheme of a single pulse shock tube



**Figure 2.** Experimental setup of the single pulse shock tube (only the high pressure part is shown)

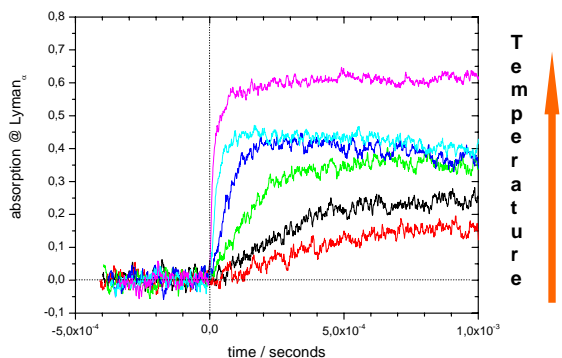
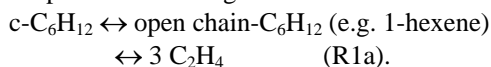


**Figure 3.** Typical GC residual gas analysis: 651 ppm cyclohexane;  $T_5 = 1564 \text{ K}$ ;  $p_5 = 5.05 \text{ bar}$

## Results and Discussions

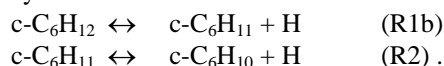
### ARAS technique

From the previous investigations, one expects that the dominant decomposition reaction leads to ethene as the main product occurring via C-C bond fission:



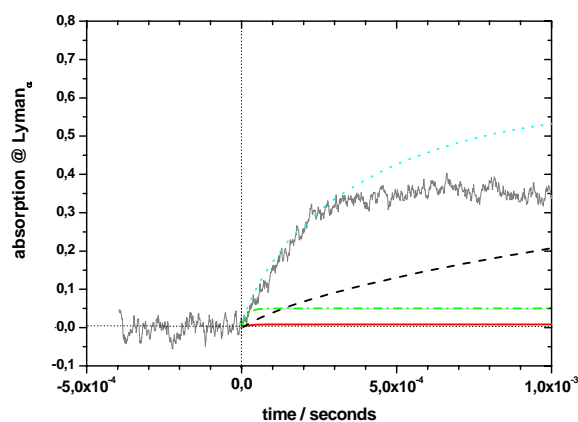
**Figure 4.** H-atom absorption measured behind reflected shock front. 1.05 ppm cyclohexane diluted with argon for  $T_5 = 1335 - 1895$  K and  $p_5 = 1.77 - 1.93$  bar.

Therefore, hydrogen atoms can be produced only by subsequent reaction steps which should exhibit a pronounced delay time under the highly diluted conditions of the present investigation. However, time resolved H-absorption profiles measured at relatively small initial cyclohexane concentrations of about 1 ppm in the temperature range 1335 – 1895 K (Fig. 4), clearly show that hydrogen atoms are produced instantaneously. Therefore it was assumed that H-atoms are produced directly by an additional C-H bond fission reaction pathway according to channel R1b, which is followed by a fast H elimination reaction leading to cyclohexene:



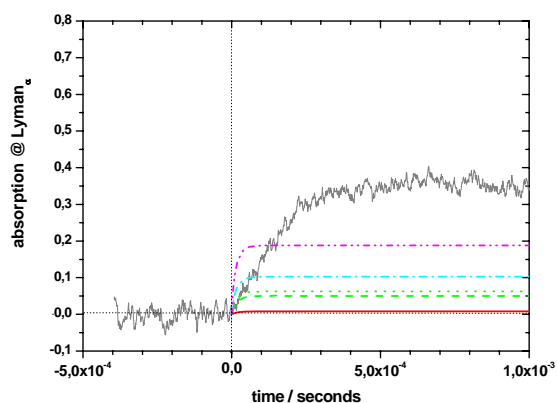
As a base set for modeling the measured H-atom absorption profiles, the rate coefficient expressions of Voisin et al. [5] have been used. For the conditions of very low initial concentration used in the present study, a reaction scheme was used which consisted essentially of the initiation reactions R1a / R1b, R2 and bimolecular reactions like  $c\text{-C}_6\text{H}_{12} / c\text{-C}_6\text{H}_{11} + \text{H} / c\text{-C}_6\text{H}_{10} + 2\text{H}$ ; the bimolecular reactions are only of minor influence due to the low initial concentration. Figure 5 shows the influence of the rate coefficient values and of the branching ratio of reactions R1a and R1b, for a typical experimental profile obtained at about 1450 K. With the original values for  $k_{1a}$  and  $k_{1b}$  from ref. [5], nearly no H-atoms are calculated (full line). Neglecting channel R1a, the calculation results in H-atom concentrations which are still too small (dashed line). Only if the value of  $k_{1b}$  is increased considerably by a factor of 7.5 with respect to the value in ref. [5], the initial slope of the measured profile is met; however, 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 (dashed-dotted curve) is much too low, compared with the observed one.



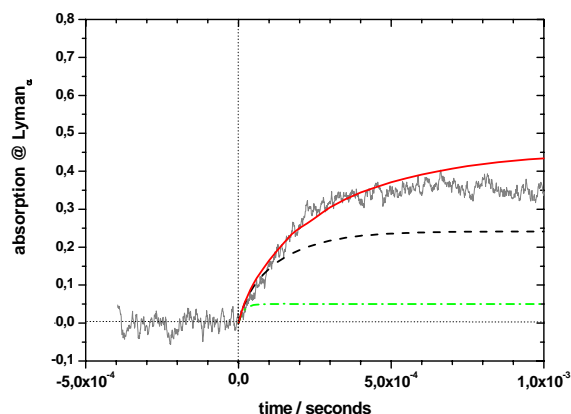
**Figure 5.** H-atom absorption profile measured behind reflected shock front. 1.05 ppm cyclohexane diluted in argon.  $T_5 = 1447$  K;  $p_5 = 1.92$  bar. Influence of molecular channel. Full line:  $k_{1a}$  &  $k_{1b}$  from ref. [5]; dashed line:  $k_{1a}=0$ ,  $k_{1b}$  from [5]; dotted line:  $k_{1a}=0$ ,  $k_{1b}*7.5$ ; dashed dotted line:  $k_{1a}$  from [5] &  $k_{1b}*7.5$ .

The influence of the H-atom producing channel R1a is depicted in Fig. 6. For the rate of the molecular channel R1a, the value given by Voisin et al. [5] was used, whereas the rate coefficient of the H-atom producing channel was increased within a factor of 7.5 and 50. It can be clearly seen from Fig. 6 that the predicted absorption is much too high at the onset of the reaction time interval if  $k_{1b}$  proceeds faster and faster. Thus we concluded that it is not possible to match the observed H-atom absorption without reducing the rate coefficient of the molecular channel.



**Figure 6.** 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 H-atom producing channel. Full line:  $k_{1a}$  &  $k_{1b}$  from ref. [5]; dashed line:  $k_{1a}$  from [5], but  $k_{1b}*7.5$ ; dotted line:  $k_{1a}$  from [5], but  $k_{1b}*10$ ; dashed dotted line:  $k_{1a}$  from [5], but  $k_{1b}*20$ ; dashed-dotted-dotted-line:  $k_{1a}$  from [5], but  $k_{1b}*50$ .

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 Fig. 7, the measured absorption profile is reproduced sufficiently good 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 7.** 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. Dashed dotted line:  $k_{1a}$  from [5],  $k_{1b} \cdot 7.5$ ; dashed line:  $k_{1a} \cdot 0.1$ ,  $k_{1b} \cdot 7.5$ ; full line:  $k_{1a} \cdot 0.02$ ,  $k_{1b} \cdot 7.5$

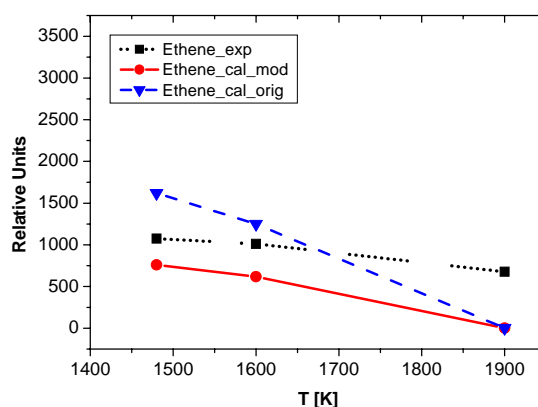
**Table 1.** Important reactions used for the modelling of experiments of decomposition of cyclohexane. Values for the rate coefficient  $k$  are given in:  $k = A T^n \exp(-E_{act}/RT)$ ;  $T$  in K;  $A$  in  $s^{-1}$  or  $cm^3 mol^{-1} s^{-1}$ , respectively.

No.	Reaction	A	n	$E_{act}/R$ (K)	Ref.
1a	$c-C_6H_{12} \rightarrow 3C_2H_4$	$1.6 \cdot 10^{16}$	-	43893	this work
1b	$c-C_6H_{12} \rightarrow c-C_6H_{11} + H$	$2.3 \cdot 10^{17}$	-	47806	this work
2	$c-C_6H_{11} \rightarrow c-C_6H_{10} + H$	$2.5 \cdot 10^{13}$	-	17921	[5]
3	$c-C_6H_{10} \rightarrow C_2H_4 + C_4H_6$	$2.5 \cdot 10^{14}$	-	31688	[5]
4	$c-C_6H_{10} \rightarrow C_6H_9 + H$	$5.0 \cdot 10^{15}$	-	41113	[5]
5	$C_6H_9 \rightarrow C_6H_8 + H$	$1.2 \cdot 10^{14}$	-	24809	[5]
-6	$2 C_2H_3 \rightarrow C_4H_6$	$5.0 \cdot 10^{13}$	-	0	[1]
-7	$C_2H_2 + H \rightarrow C_2H_3$	$4.53 \cdot 10^{14}$	-0.7	1353	[1]
8	$C_4H_6 \rightarrow C_2H_4 + C_2H_2$	$1.0 \cdot 10^{14}$		37741	[9]

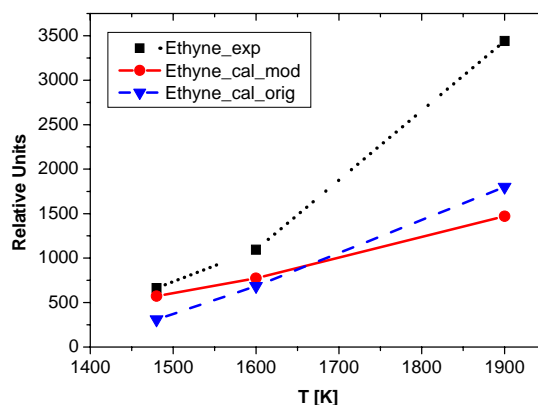
The most important reactions and their rate coefficient expressions used for the model calculations in the present work are given in Table I.

### Single Pulse Shock Tube

A second set of experiments has been performed in the single pulse shock tube. Under these conditions, much higher initial mole fractions (about 650 ppm) have been used in order to receive product species concentrations large enough for chromatographic and mass-specific detection. As an example, the relative concentrations for ethene and ethyne, respectively, are shown in Figs. 8a-b. It is clearly to be seen that with increasing temperature ethene concentration decreases whereas ethyne increases, in accordance with the model's predictions.



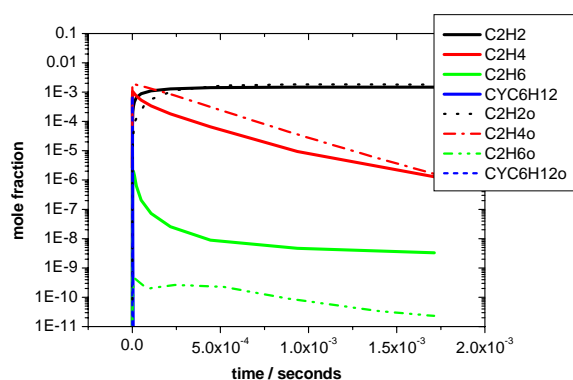
**Figure 8a.** Comparison between measured (symbols) and calculated profiles (modified model: full line, base model: dashed line) for ethene.



**Figure 8b.** Comparison between measured (symbols) and calculated profiles (modified model: full line, base model: dashed line) for ethyne.

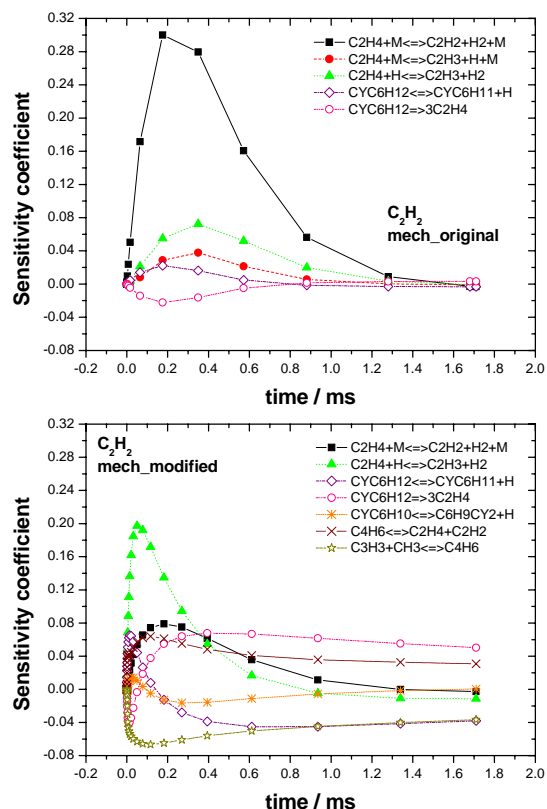
The comparison of model simulations using the base model from Voisin et al. [5] and the modified model derived from our ARAS investigation (Table 1) shows the same trend with respect to the temperature dependence for ethene and ethyne. For ethyne, only a slight difference in the residual concentrations is observed (Fig. 8b, full line and dashed line curves). But, there is a different trend for ethene at low temperatures (Fig. 8a, full line and dashed line curves) by both model calculations.

The temporal behavior of the reaction system at a temperature value close to the upper end of the investigated temperature regime is shown in Fig. 9. Ethyne is produced very quickly by both models.

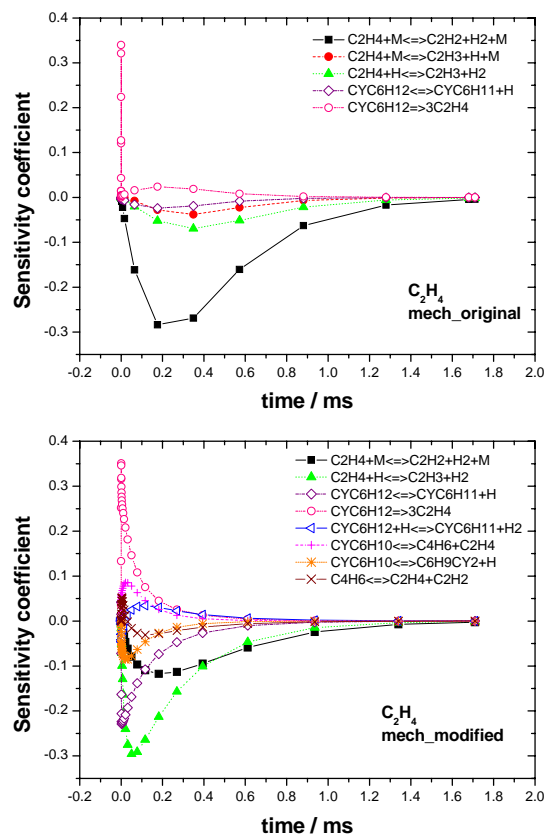


**Figure 9.** Calculation of species profiles with base and modified model: 651 ppm cyclohexane diluted in argon;  $T_5 = 1871$  K;  $p_5 = 3.0$  bar

The sensitivity analysis carried out for the same conditions (Figs. 10 and 11) reveals that in the base mechanism ethyne is mainly produced by the unimolecular decomposition of ethene which is formed rapidly by the initial reaction R1a, as a consequence of the much too high rate coefficient for R1a. In case of the modified mechanism (see Table 1), the dominant reaction responsible for ethyne formation is the H-abstraction to ethene because due to the increased reaction rate of R1b much more H-atoms are produced during the cyclohexane decomposition, compared to the base model. In the later stages of reaction time, the decay of cyclohexene (R4) and of butadiene  $C_4H_6 \rightarrow C_2H_4 + C_2H_2$  (R8, Table 1) turned to be of importance – besides the contribution of the direct initiation channel R1a – due to the relatively high initial concentration of cyclohexane compared to the ARAS-experiments. The decay of butadiene is the rate limiting step in the reaction sequence  $c-C_6H_{12} \rightarrow c-C_6H_{11} \rightarrow c-C_6H_{10} \rightarrow C_2H_4 + C_4H_6$ . Thus, a similar study of the initial decomposition steps of cyclohexene and of the main products should be carried out in order to derive an even more precise reaction model for describing the high temperature behaviour of these naphthenic species.



**Figure 10.** Sensitivity plot of the most important reactions for ethyne. Calculation with base and modified model. Same condition as in Fig. 9.



**Figure 11.** Sensitivity plot of the most important reactions for ethene. Calculation with base and modified model. Same condition as in Fig. 9.

## Conclusions

The results of the present investigations on cyclohexane decomposition give rise to a branching ratio of about 1:1 for the channels leading to molecular products like ethyne, ethene and butadiene, and by H-elimination to the cyclohexenyl radical, respectively. Hence, the molecular channel is much slower than considered up to now, whereas the H-atom elimination path proceeds much faster, by about a factor of 5 – 10. The residual gas analysis, carried out in the single pulse shock tube apparatus reveals a strong temperature dependency in particular of the ethene / ethyne product ratio. Thus, a much better understanding of the initial reaction steps of the decomposition of cyclohexane has been now enabled.

## Acknowledgements

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