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MODELING OF THE TERT.-BUTYLBENZENE PYROLYSIS IN SUPERCRITICAL WATER

ABSTRACT

Supercritical water ($T > 374^{\circ}\text{C}$, $p > 22.1$ MPa) is an effective medium for disintegration reactions of organic substances. It becomes more interesting also for synthesis of new products. Reasons are the continuously variable density and the high solubility of organic compounds in this reaction medium.

Modeling of reactions in supercritical water should - as usually - be carried out on the basis of elementary reactions resulting in a system of ordinary differential equations. The main problem is that most of the reaction rate parameters are known only for low pressures. Few approaches were made to calculate the pressure dependence of elementary reactions, as it is a difficult task to incorporate the solvent effects in a quantitative way.

In this work the kinetic parameters of the elementary reactions for the tert.-butylbenzene pyrolysis are optimized using experimental data as well as results of the model calculations. The chemical mechanism, the kinetic parameters, the initial concentrations and the experimental parameters, like reaction time and reaction temperature are fed in an input file for calculation of the formation of the chemical products. These calculations were executed by the LARKIN code for homogeneous, isothermal and isobaric conditions. The extent of agreement between calculated and experimental data was quantified by an objective function $f(p_1, p_2, p_3, \dots, p_{342})$, where p_{2i-1} and p_{2i} are the kinetic parameter of the i 'th elementary reaction. In principle f is the weighed sum of squares of differences between the experimental and the calculated data. The aim is to minimize the objective function f obeying certain non-linear restrictions, i.e. fixed domains of the concentrations of the chemical species. In order to incorporate these restrictions 'punishment functions' are added to f . For optimization, the downhill simplex method was used. This method is not very efficient, however it requires only objective function evaluations and no derivatives. Therefore it is suitable for the implantation of imposed constraints. Also, it is a robust method and allows to start the optimization routine far away from the optimum.

The basis of the calculations are the results of app. 50 experiments of the pyrolysis of tert.-butylbenzene in supercritical water and for comparison also in nitrogen, nitrogen-water mixtures and heavy water. The reaction conditions were: 500-540 $^{\circ}\text{C}$, 5-25 MPa, reaction time 10-60 sec., and 0.004-0.02 initial molar fraction tert.-butylbenzene. 29 reaction products were measured.

The reaction model consists of 171 elementary reactions. Optimized simulations show good agreement with the experimental results for conversion as well as for product formation. The pyrolysis is a chain reaction mechanism with one initiation step, which is much slower than the appropriate value of the low pressure rate taken from the literature. A rather fast phenyl shift reaction leads to a variety of products. The results show that higher pressures increase the substitution reactions, which become more important for the product formations than expected from low pressure data. Recombination reactions are also faster at higher pressure, which is in agreement with the LE-CHATELIER-principle.

The concept of optimizing kinetic parameters on the basis of experimental results leads to a realistic description of the chemical reaction. In spite of the lack in elementary reaction rates at high pressure, this procedure contributes to the understanding of the pyrolysis reaction in supercritical water.

DIE MODELLIERUNG DER TERT.-BUTYLBENZOL-PYROLYSE IM ÜBERKRITISCHEN WASSER

ZUSAMMENFASSUNG

Überkritisches Wasser ($T > 374^\circ\text{C}$, $p > 22.1 \text{ MPa}$) ist ein effektives Reaktionsmedium für den Abbau von organischen Substanzen. Es wird auch für die Synthese von neuen Produkten interessant. Die Gründe hierfür sind die variable Dichte und die hohe Löslichkeit von organischen Komponenten in diesem Reaktionsmedium.

Die Modellierung von Reaktionen in überkritischem Wasser sollte - wie allgemein üblich - auf der Basis von Elementarreaktionen erfolgen, die zu einem System von gewöhnlichen Differentialgleichungen führen. Das Hauptproblem ist, daß die meisten Reaktionsgeschwindigkeits-Parameter nur für niedrige Drücke bekannt sind. Es sind einige wenige Ansätze gemacht worden, um die Druckabhängigkeit von Elementarreaktionen zu berechnen, aber es ist schwierig, die Lösungsmittelleffekte quantitativ zu berücksichtigen.

In der vorliegenden Arbeit wurden die kinetischen Parameter der Elementarreaktionen mit Hilfe von experimentellen Ergebnissen und Modellberechnungen optimiert. Der chemische Mechanismus, die kinetischen Parameter, die Anfangskonzentrationen und die experimentellen Parameter, wie Reaktionszeit und Reaktionstemperatur, bilden die Ausgangsdatei für die Berechnung der Produktbildung. Die Berechnungen wurden durch das LARKIN-Programmpaket für homogene, isotherme und isobare Bedingungen durchgeführt. Der Grad der Übereinstimmung zwischen experimentellen und berechneten Daten wird durch eine Zielfunktion $f(p_1, p_2, p_3, \dots, p_{342})$ quantifiziert, wobei p_{2i-1} und p_{2i} die kinetischen Parameter der i 'ten Elementarreaktion sind. Im Prinzip handelt es sich um die Summe der gewichteten mittleren Abweichungen zwischen experimentellen und berechneten Werten. Aufgabe ist es, die Zielfunktion f zu minimieren, wobei sie einigen nicht-linearen Beschränkungen gehorchen muß, z.B. festen Konzentrationsbereichen der chemischen Spezies. Diese Beschränkungen werden über die „Bestrafungsfunktion“ eingeführt, die zu f addiert wird. Für die Optimierung wurde die „DOWNHILL SIMPLEX-Methode“ benutzt. Diese Methode ist nicht sehr effizient, aber sie benötigt nur die Berechnung der Zielfunktion und keine Ableitungen. Sie ist deshalb für die Implantation von auferlegten, oben genannten Beschränkungen geeignet. Außerdem ist sie eine robuste Methode, die den Start der Optimierungsroutine weit weg vom Optimum erlaubt.

Die Basis der Berechnungen bilden etwa 50 Experimente zur Pyrolyse von tert.-Butylbenzol im überkritischen Wasser und zum Vergleich auch in Stickstoff, Stickstoff-Wasser-Mischungen und in schwerem Wasser. Die Versuchsbedingungen waren: $500\text{-}540^\circ\text{C}$, $5\text{-}25 \text{ MPa}$, $10\text{-}60 \text{ s}$ Reaktionszeit und $0,004\text{-}0,02$ Anfangsmolenbruch tert.-Butylbenzol. 29 Reaktionsprodukte wurden gemessen.

Das Reaktionsmodell besteht aus 171 Elementarreaktionen. Die optimierte Simulation zeigt gute Übereinstimmung mit den experimentellen Ergebnissen für Umsatz und Produktbildung. Die Pyrolyse ist ein Kettenmechanismus mit einer Startreaktion, die viel langsamer ist, als dem Nieder-Druck-Wert in der Literatur entspräche. Eine recht schnelle Phenyl-Wanderung führt zu einer Vielzahl von Produkten. Die Ergebnisse zeigen, daß höherer Druck ein Ansteigen von Substitutionsreaktionen bewirkt, die damit wichtiger für die Produktbildung werden, als aufgrund der Nieder-Druck-Literaturwerte zu erwarten war. Rekombinationsreaktionen sind bei höherem Druck ebenfalls schneller als bei niedrigerem, was in Übereinstimmung mit dem LE-CHATELIER-Prinzip steht.

Das Konzept der Optimierung von kinetischen Parametern auf der Basis experimenteller Ergebnisse führt zu einer realistischen Beschreibung von chemischen Reaktionen. Trotz des Fehlens von Elementarreaktionsgeschwindigkeiten bei hohem Druck trägt dieses Vorgehen zum Verständnis der Pyrolyse in überkritischem Wasser bei.

CONTENTS

| | |
|---|----|
| INTRODUCTION | 3 |
| EXPERIMENTAL | 3 |
| MODELING TECHNIQUE | 5 |
| CALCULATION OF REACTION PRODUCTS | |
| COMPARISON OF EXPERIMENTAL RESULTS | |
| OBJECTIVE FUNCTION | |
| OPTIMIZATION METHOD | |
| SENSITIVITIES AND FLOW ANALYSIS | |
| DEVELOPING THE REACTION MECHANISM | 8 |
| COMPARISON WITH EXPERIMENTAL DATA | 9 |
| REACTION PATHS AND FLOWS ALONG THESE PATHS | 13 |
| DISCUSSIONS | 16 |
| DISCUSSIONS OF CONVERSION | |
| DISCUSSION OF PRODUCT FORMATION | |
| DISCUSSION OF SENSITIVITIES | |
| CONCLUSIONS | 18 |
| APPENDIX | 18 |
| REFERENCES | 24 |

INTRODUCTION

Supercritical water SCW ($T > 374^{\circ}\text{C}$, $p > 22.1 \text{ MPa}$) shows extraordinary physical and chemical properties [1]. The density can be varied continuously from gas like to liquid like values, viscosity decreases significantly, and the solubility of organic compounds increases. A considerable quantity of reactions in supercritical water, believed to be free-radical or ionic are investigated [2,3].

Tert.-butylbenzene (TBB) was employed as a model compound for the pyrolysis to choose a relative simple substance containing an aromatic and an aliphatic structure.

The role of water during the pyrolysis of tert.-butylbenzene basing on comparison of experimental results is shown to be minor because the product formation is identical in SCW and nitrogen as reaction media which is a strong indication for a free radical chain mechanism. Free radicals react with water which is confirmed by investigating the pyrolysis in heavy water but this formation of the OH radical doesn't change the product distribution within the experimental error.

Pyrolysis reactions in gaseous phases are very well understood. They are free radical chain reactions usually described by systems of elementary reactions [4]. Kinetic parameters of a great variety of elementary reactions are given in the literature. Usually they are measured at very low pressures. The initiation reaction rate of the TBB reaction for example is measured at 5-60 Pa [5]. The first experiments have shown that the global reaction rate of TBB pyrolysis in supercritical water is lower than the reported initiation reaction. Consequently a simulation of TBB pyrolysis basing on literature data was not possible. The reaction model is similar to gas phase models but as a consequence of the high pressure, substitution and addition reactions are of much more importance. In this work a kinetic parameters identification procedure, using all available experimental data, is applied. The results of simulations by a reaction model of 171 elementary reactions with optimized kinetic parameters are presented.

EXPERIMENTAL

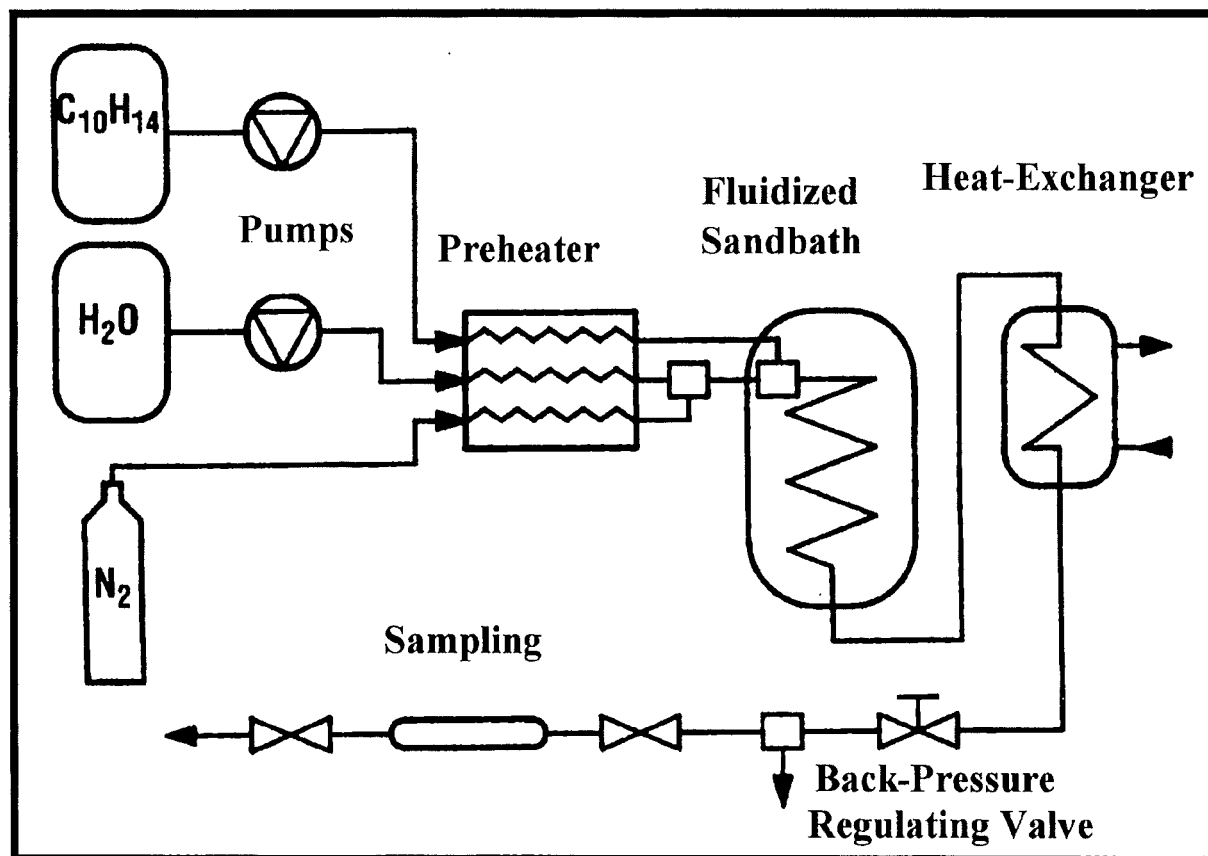


Fig. 1: Schema of the experimental set-up

The experimental apparatus consists of a feeding device, preheaters, the tube reactor thermalized by a fluidized sand-bath, a cooler and an expansion valve before sampling (Fig. 1). The pressure in the reactor was varied from 5 to 25 MPa and the temperature from 505 to 540 °C. Prior to feeding to the apparatus the water had been deionized and saturated with argon to replace dissolved oxygen. Nitrogen and tert.-butylbenzene was used without any pre-treatment. The three flows were metered and than mixed in two mixing tees, which were specially machined for efficient mixing. The reactor was a 6 m long stainless steel tube (2mm inner diameter) immersed in a fluidized sand bath to ensure isothermal reaction conditions. The temperature at the inlet, outlet and along the tube reactor was controlled by six Ni-NiCr- thermocouples. The effluent of the reactor was quenched in a water-cooled heat exchanger down to a temperature of ~ 17 °C. The pressure was reduced to atmospheric by a back pressure regulating valve and the resulting liquid and vapor phases were collected in sample tubes. Both liquid and gas flow rates were measured separately. The composition of the gas phases was determined by gas chromatography. Organic and aqueous phases were extracted by n-pentane and then also analyzed by gas chromatography. Most of the compounds were identified by mass spectrometry or by gas-chromatographic comparison with pure component samples.

Experimental set-up and a detailed description of the reaction condition are published elsewhere [6,7]. Some fifty experiments were carried out at pressures between 5 and 25 MPa, at temperatures between 505 and 540°C and residence times between 15 and 55 s. Twenty-six different reactions conditions in five different reaction media (light water, two different water-nitrogen-mixtures, nitrogen, heavy water) were studied [6,7]. The experimental conditions are summarized in Table 1. Here, experiments investigated in nitrogen, nitrogen-water-mixtures and supercritical water are summarized because no difference in product formation was found.

A severe problem in kinetic studies in supercritical water reaction is the phase separation or the product mixture after cooling and expansion to normal pressure. The separation in an organic, an aqueous and a gas phase causes difficulties in sampling, which leads to fluctuations in the compositions of the phases and to scattering of the kinetic results.

Table 1: Experimental conditions

| Number of Experiments | Reaction media | Pressure MPa | Temperature °C | Nitrogen flow g/h | Water flow g/h | tert.-Butylbenzene flow g/h |
|-----------------------|------------------|--------------|----------------|-------------------|----------------|-----------------------------|
| 28 | Water | 5-25 | 500-540 | - | 600-1200 | 30-60 |
| 7 | Mixture I | 25 | 500-540 | 28-40 | 600-900 | 30-60 |
| 7 | Mixture II | 25 | 500-540 | 320-640 | 600-700 | 30-60 |
| 7 | Nitrogen | 25 | 500-540 | 320-640 | - | 30-60 |
| 1 | D ₂ O | 25 | 535 | - | 600 | 30 |

Conversions of t-butylbenzene were measured in the range up to 7%. The variety of the products was high. Fig.2 shows a typical gas chromatogram of a liquid product mixture. All of the peaks containing more than 0.01% of the product have been identified. The gas phase contained hydrogen and the C₁ to C₄ hydrocarbons.

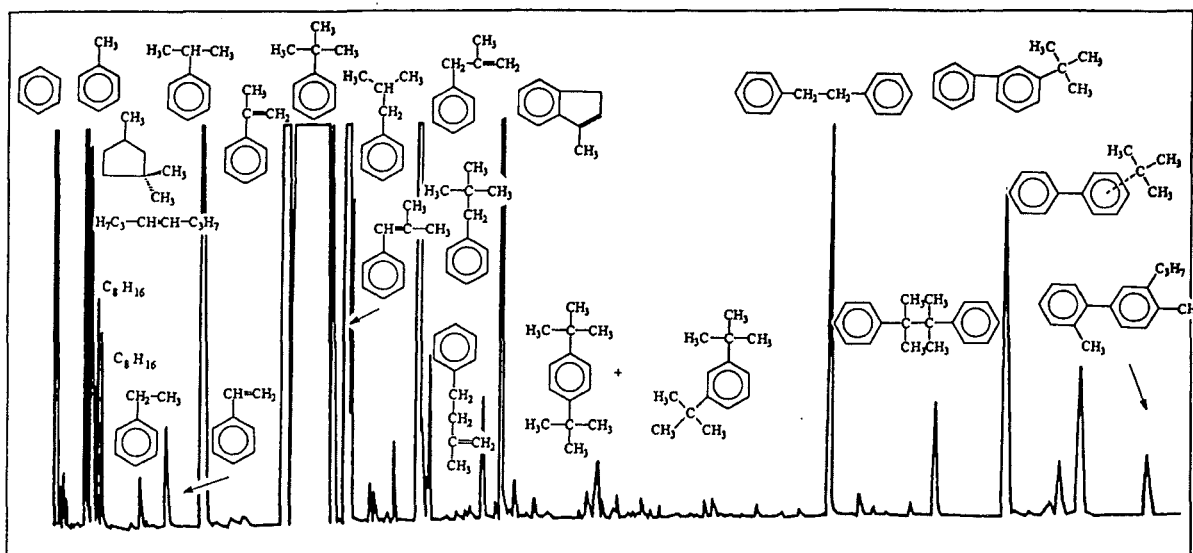


Fig. 2: A gas chromatogram of liquid products after the reaction of TBB in supercritical water at 25 MPa and 813 K at a conversion of 4%.

MODELING TECHNIQUE

In the reaction mechanisms worked out for the thermal decomposition in supercritical water, no Arrhenius parameters are known. They can only be estimated by the data available for low pressure reactions. One way is to calculate approximately the influence of pressure and the supercritical water to the kinetic parameters of the elementary reactions [4]. But this idea is mostly realized by some intuitive methods leading to arbitrary results. Therefore we tried a different way. We attempted to receive a solution for the inverse problem, which can be described as follows: Given a chemical reaction mechanism consisting of elementary reactions or lumped reactions where the reaction order is equal to the molecularity. In addition all experimental results are used, which are intended to be described by the reactions mechanism. The solution of the inverse problem leads to a set of kinetic parameter (not necessarily unique) which describe the experimental results optimally.

CALCULATION OF REACTION PRODUCTS

The problems arising in setting up a chemical reaction mechanism together with its kinetic parameters is discussed in the next section. The mechanism, its kinetic parameters, the initial concentrations and the experimental parameters, like reaction time and reaction temperature, is given as an input file for the calculation of the concentrations of the chemical products after the reaction time. The calculations were carried out by the LARKIN [8] code for homogeneous, isothermal and isobaric conditions.

COMPARISON WITH EXPERIMENTAL RESULTS

We used experiments with 25 different reaction conditions (e.g. varying temperatures, varying initial concentration of TBB) as data base for comparison. For some experimental conditions there are more than one reaction time at which the concentrations of the products have been determined. For all reaction conditions and all reaction times we calculated the concentrations for all products contained in the model. The quality of agreement between calculated and experimental data was quantified by a likelihood function $f(p_1, p_2, p_3, \dots, p_{342})$, where p_{2i-1} and p_{2i} are the kinetic parameter of the i 'th elementary reaction. We use a sort of summed weighed squared deviation as likelihood function.

$$f(p_1, p_2, \dots, p_{342}) = \sum_i \sum_j w_{i,j} \cdot (C_{i,j}^{\text{experimental}} - C_{i,j}^{\text{calculated}}(p_1, p_2, \dots, p_{342}))^2$$

We have to sum over all products i and over all experiments j . As concentrations we used sometimes absolute and sometimes relative values, depending on the accuracy of the respective experimental measurements. (For some cases we used sums of two or three concentrations because in the GC analysis of the isomers couldn't be identified unambiguously). Sometimes it may be meaningful to use ratios of concentrations, if the ratios of the experimental concentrations are more accurate than the individual concentrations. The weighting factors w_{ij} were usually set to 1; but in some cases (depending on the absolute accuracy of the experimental concentration) they were set higher or lower than 1; they were set to zero if in an experiment this special product has not been measured. The calculated concentrations (for a given fixed reaction mechanism) depend on the Arrhenius parameters $p_1 \dots p_{342}$ and on the experimental set-up conditions like temperature, time etc.. Because the experimental set-up conditions and the $c^{\text{experimental}}$ values are given and the weights w_{ij} are fixed, f is only a function of the kinetic parameters p_i . The aim is of course to minimize the likelihood function f obeying certain additional restrictions. The resulting kinetic parameter we call the optimal parameter.

OBJECTIVE FUNCTION

The inverse problem can be solved if the minimum of the likelihood function f is known. But from a chemical point of view some additional restrictions have to be considered. The kinetic parameters are not totally free. They have to be at least positive, or better we can assign individual limits for each kinetic parameter. On the other hand, the calculated concentrations of reactive species like free radicals have to be less than a certain concentration. It is easy to implant these ideas as *punishment functions* or *punishment terms* which are added to f . The punishment can be done continuously rising with the degree of violation of the limits or it may be just a punishment term which is added if a condition is offended. This sum is used as the objective function g for the optimization problem.

$$g = f + \text{punishment functions}$$

To summarize, each evaluation of the objective function requires 25 runs of the LARKIN program plus the calculation of the squares and the punishments.

OPTIMIZATION METHOD

The downhill simplex method [9] was chosen to carry out the optimization calculations. The method is not very efficient, but it requires only objective function evaluations and not derivatives and is therefore suitable for the implantation of imposed constraints. It is a robust method and you can start rather far away from the optimum. If all the 342 kinetic parameters are considered as one point or one vector in an 342-dimensional vector space, the method starts with a 343 different such vectors. The additional 342 vectors are obtained by changing each element of the starting vector by a small amount. The 343 points or vectors spans a non-degenerated simplex in the 342-dimensional vector space. For each point in the simplex the objective function is evaluated. The strategy of the downhill simplex method is to improve the 'worst' point - that means the one with the highest value of the objective function - of the simplex corner points. This is always obtained by one of the four actions: reflection of this worst point on the average of the remaining points, elongated reflection on this average point, a contraction to this average point or contraction of all points to the 'best' point. A sequence of such steps will always converge to a minimum of the objective function. The method, however, cannot claim to find the global minimum. It is therefore a good idea to run the method repeatedly using different starting values. The minimum of the objective function for this chemical problem cannot be very distinct because it is known from experience that most of the parameters of the mechanism have very low sensitivities and there is a net of cross correlation between the parameters. For our problem a usual downhill simplex run needed about some hundred thousands objective function evaluations and some days computer time on a SUN workstation. We didn't use a computerized termination criteria, but we observed the computer results and the convergence behavior, and terminated by hand.

The method is schematically shown in Fig. 3. In the schema there are three inputs: the measured experimental concentrations, the experimental set-up conditions and an initial parameter set together with a reaction mechanism. The output is the up to now best or improved set of kinetic parameters. The central simplex optimization program generates a working parameter set, which is used to produce CHEMINS for the LARKIN program. The calculated concentrations are used by the COMPARATOR program to calculate the value of the objective function for the working parameter set.

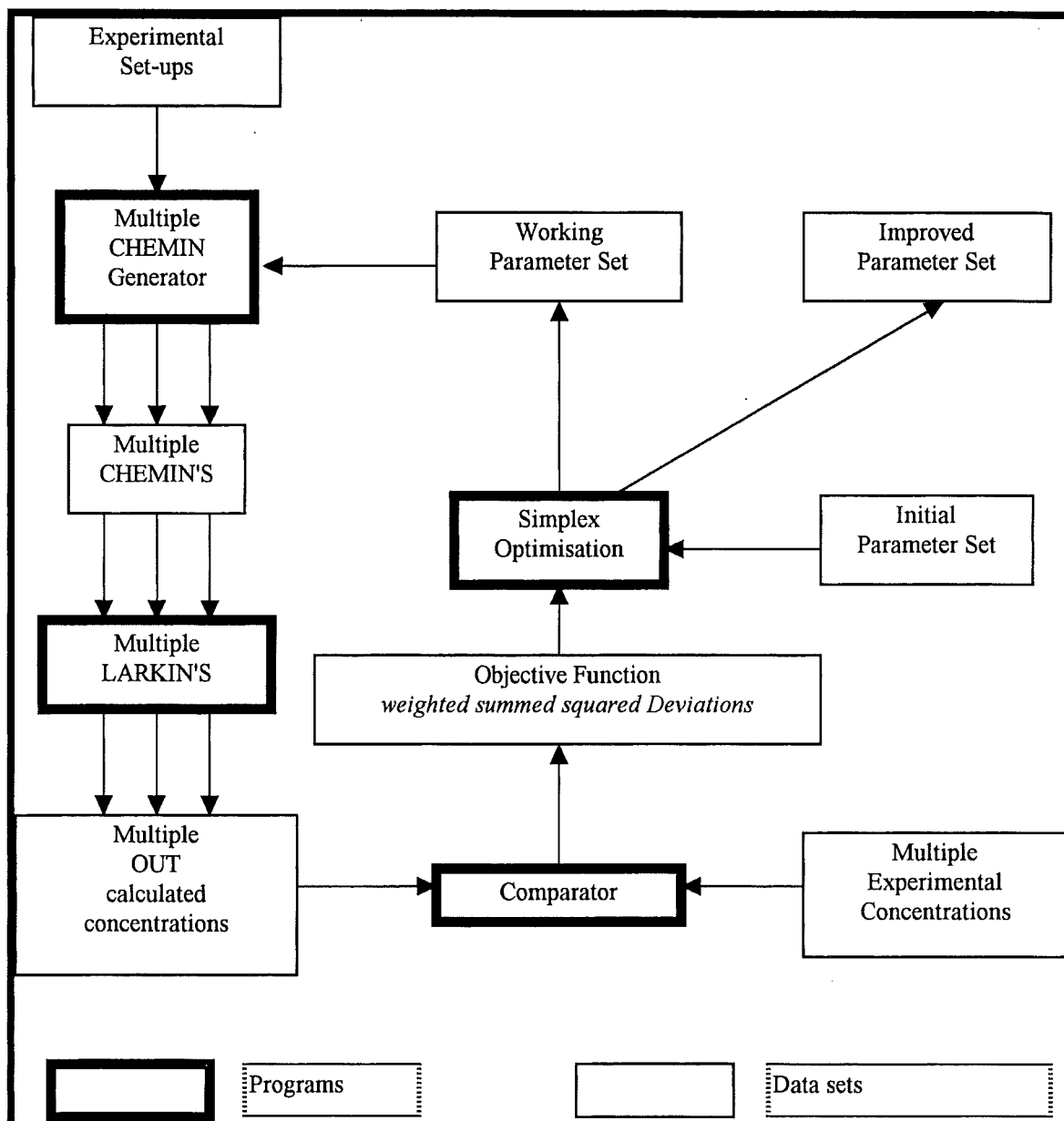


Fig. 3: The connection schema of programs and data sets for a parameter identification run.

SENSITIVITIES AND FLOW ANALYSIS

In order to understand and to know more about the chemical reaction mechanism two additional calculations for a reaction mechanism with optimized kinetic parameters are carried out. The sensitivities $S_{i,j}$ are defined as

$$S_{i,j}(t) = \frac{\partial c_i(t)}{\partial k_j}$$

where $c_i(t)$ is the concentration of substance i at reaction time t and k_j is one of the kinetic parameter of reaction $\text{int}(j/2+1)$. Each element of a sensitivity matrix $S_{i,j}$ describes the change of the concentration of one species (at a fixed reaction time) in dependence of a small change of one kinetic parameter. These sensitivities were calculated using a 'brute force' method which evaluates the whole ODE-system for each parameter changed. For comparison purposes the relative or logarithmic sensitivities $^rS_{i,j}$

$$r_{S_{i,j}}(t) = \frac{\partial c_i(t) / c_i(t)}{\partial k_j / k_j} = \frac{\partial \log(c_i(t))}{\partial \log(k_j)}$$

are often used. If there are large positive or negative numbers for a sensitivity entry the influence of this parameter on the concentrations of the respective species is high, but if the sensitivity is very small or even zero for all species, this parameter may be changed within certain limits without affecting the numerical results; however these elementary reactions associated with such a parameter may be still important for the chemistry of the reaction system and must not be deleted.

Flow analysis means the calculation of the amount which 'flows' via every chemical elementary reaction during the reaction time and they are therefore often called integrated rates (IR).

$$IR_j(t) = \int_0^t r_j(t) dt \quad , \quad \text{where } r_j(t) \text{ is the rate of the elementary reaction } j.$$

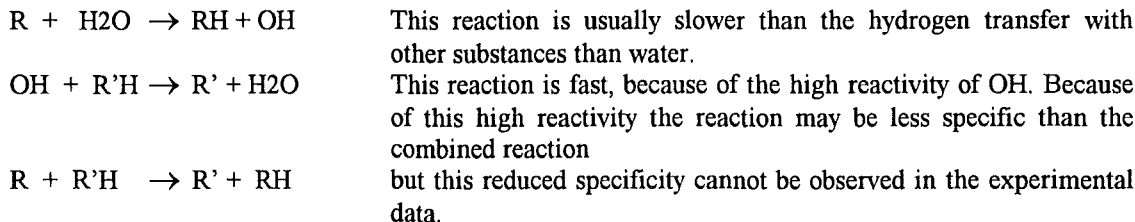
If the interest is focused to a specific species, these flows can be selected in respect to the species under consideration and sorted by the flowing quantity. This should be carried out for all species and the information on the major and minor paths for the formation and for the reaction of the substances is obtained.

DEVELOPING THE REACTION MECHANISM

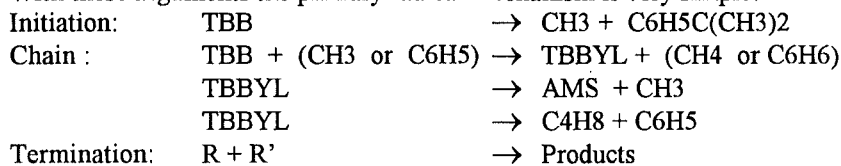
The abbreviations used for the various chemical substances are explained in the Appendix. From the experimental results there is strong evidence that the thermal decomposition of TBB in supercritical water follows a radical chain mechanism:

- the reaction products are only hydrocarbons, there are no oxygen containing substances found,
- if water is partially substituted by nitrogen the same product spectra is found with the same concentrations, within the experimental error limits,
- if deuterated water is used only 10-20% of some substances are monodeuterated.

The influence of water can be estimated by considering the reactions water may undergo in a radical mechanism. R, R' are free radicals, RH and R'H stable hydrocarbons.



With these arguments the primary radical mechanism is very simple:



Compared with the experimental results this simple mechanism cannot explain the variety of products which were detected in the experiments. On the other hand if the kinetic parameter of the initiation reaction is taken from the literature, then this initiation reaction alone is faster than the overall decomposition of TBB, evaluated from the experiments. To be able to explain all the species found in the experiments, we had to expand the reaction mechanism by radical isomerizations (e.g. TBBYL \rightarrow IBBYL₂) and by substitution reactions. In example, without such reactions it is impossible to explain the formation of considerable amounts of toluene. For the kinetical parameters we changed the values even beyond the limits given in the literature. As a first approach we used the ideas of LeChatelier: if a bond is broken, the reaction in SCW is slower than in the low pressure gas phase; if a bond is formed the reaction in SCW is faster.

With these ideas we were able to set up a reaction mechanism, which described in principle our results. To receive better agreement between calculation and experiments, we used the optimization methods outlined above. For the evaluation of the final mechanism a multistage procedure was used; after an optimiza-

tion step with an unsatisfactory agreement new elementary reaction were added and a new optimization run was started.

COMPARISON WITH EXPERIMENTAL DATA

Because we used more than 20 different experimental conditions and we analyzed more than 20 different substances, more than 500 product formation versus reaction time plots were received, which compare the experimental values with the calculations. In Fig.4 - Fig. 11 a few examples from one experimental set-up are shown, where data for more than one reaction time were obtained. The agreement is sufficient for the shown examples, it is at least reasonable for the substances and conditions not shown here.

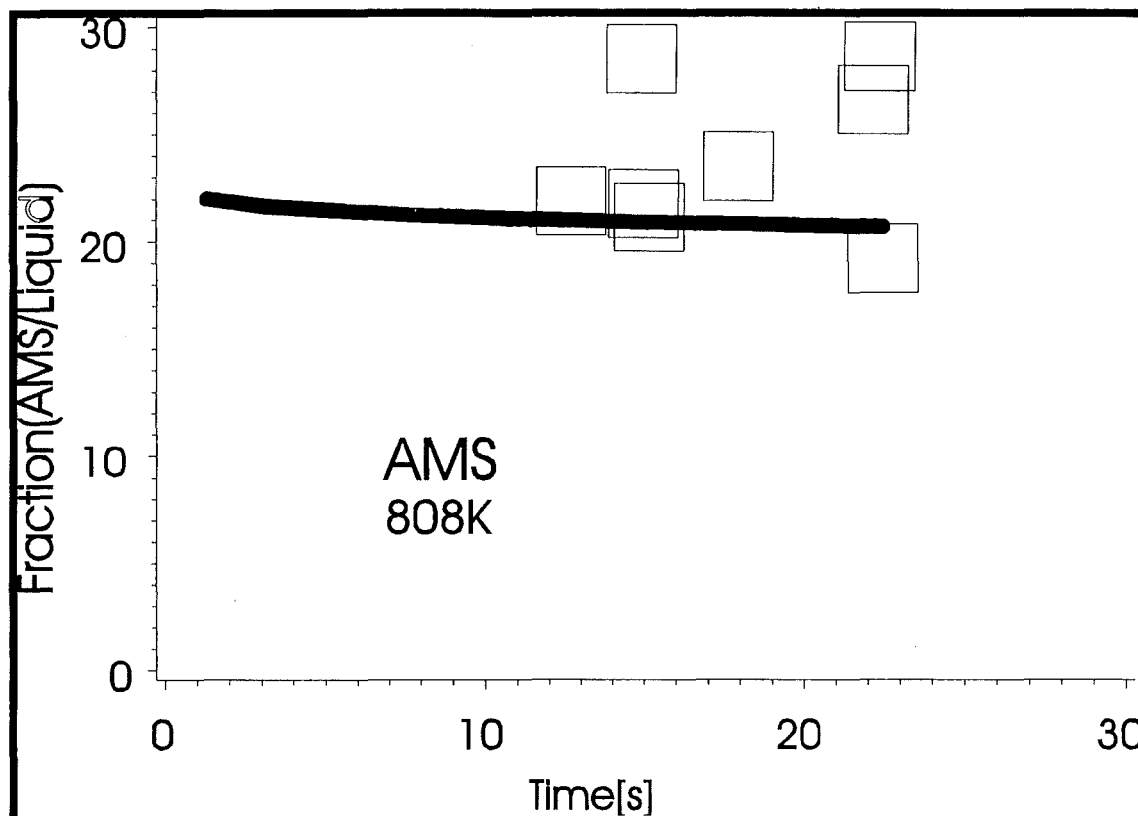


Fig. 4: Molar amount in % of α -methyl-styrene within the liquid fraction. The rectangles are experimental points and the line is the calculation.

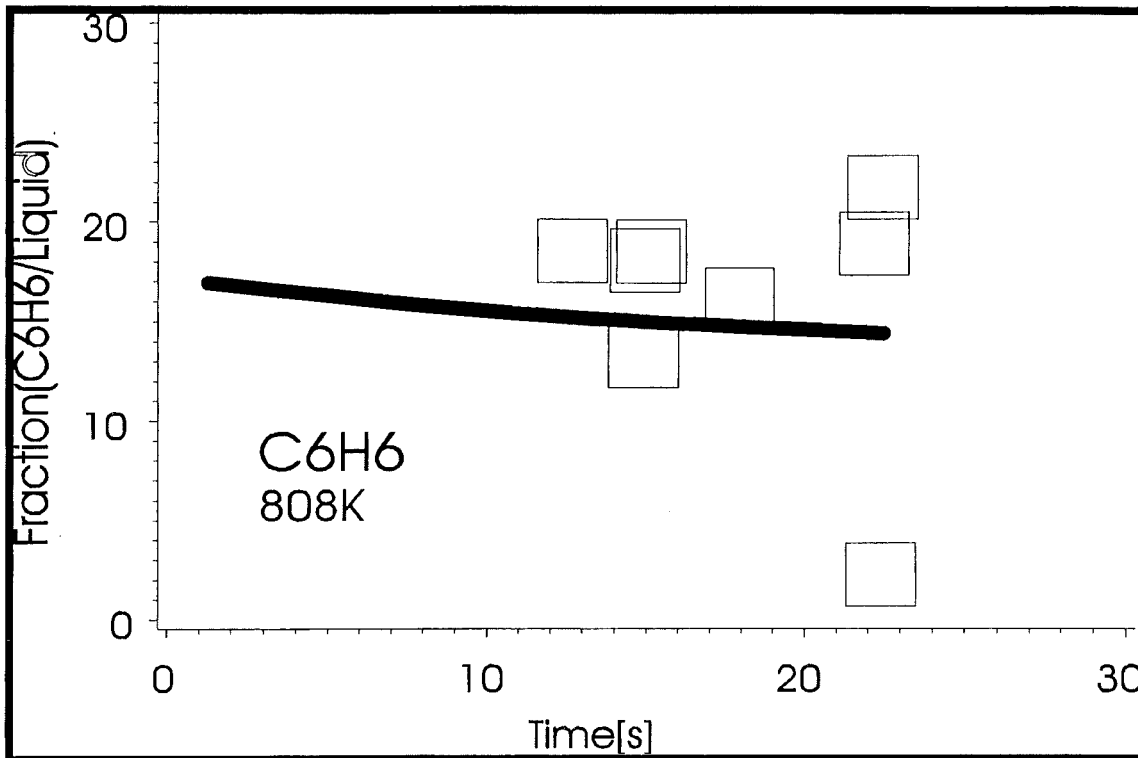


Fig. 5: Molar amount in % of benzene within the liquid fraction. The rectangles are experimental points and the line is the calculation.

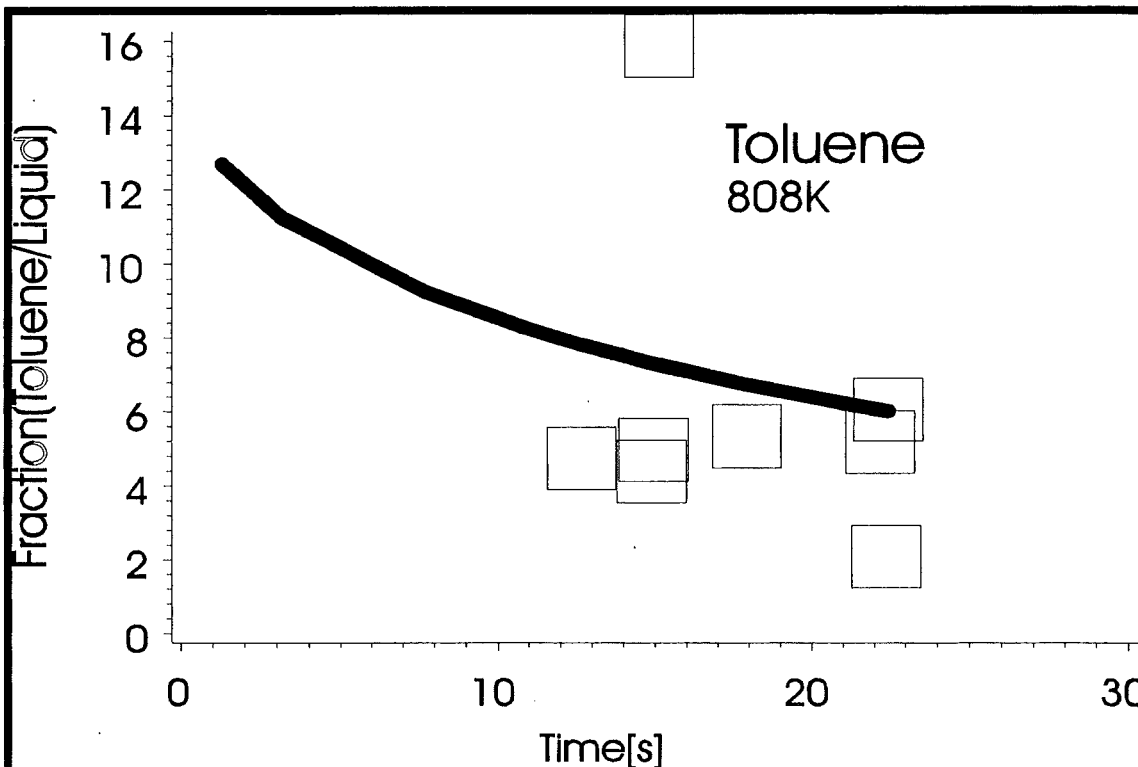


Fig. 6: Molar amount in % of toluene within the liquid fraction. The rectangles are experimental points and the line is the calculation.

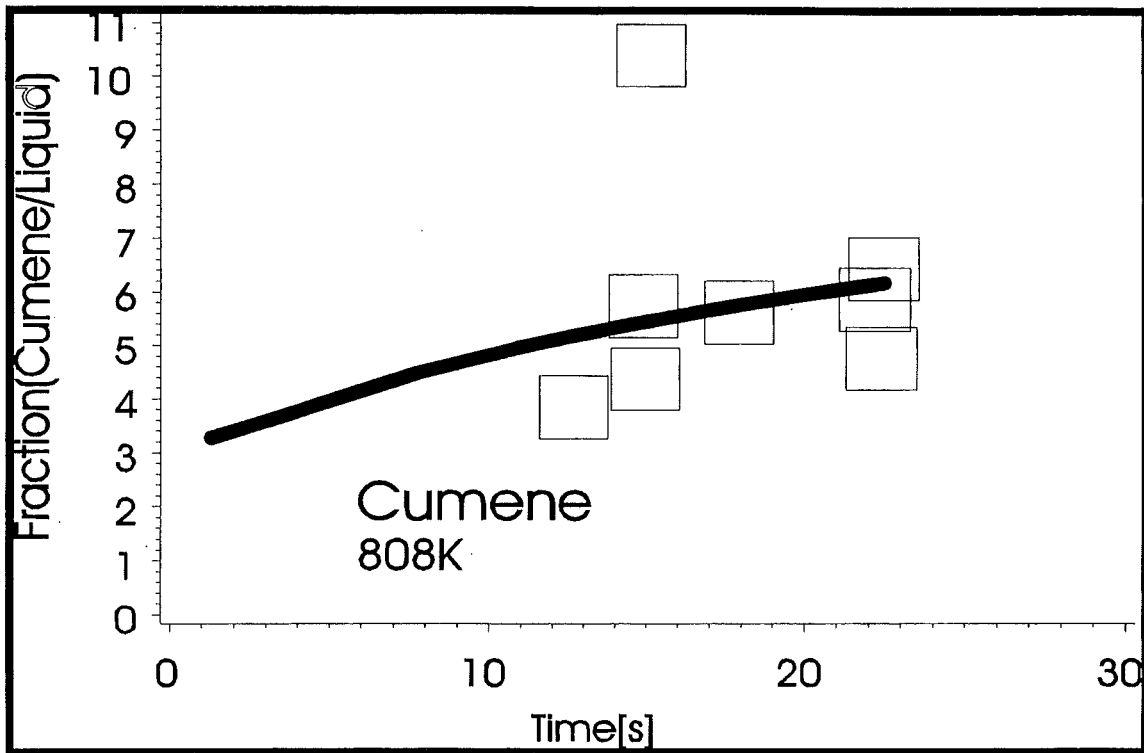


Fig. 7: Molar amount in % of cumene within the liquid fraction. The rectangles are experimental points and the line is the calculation.

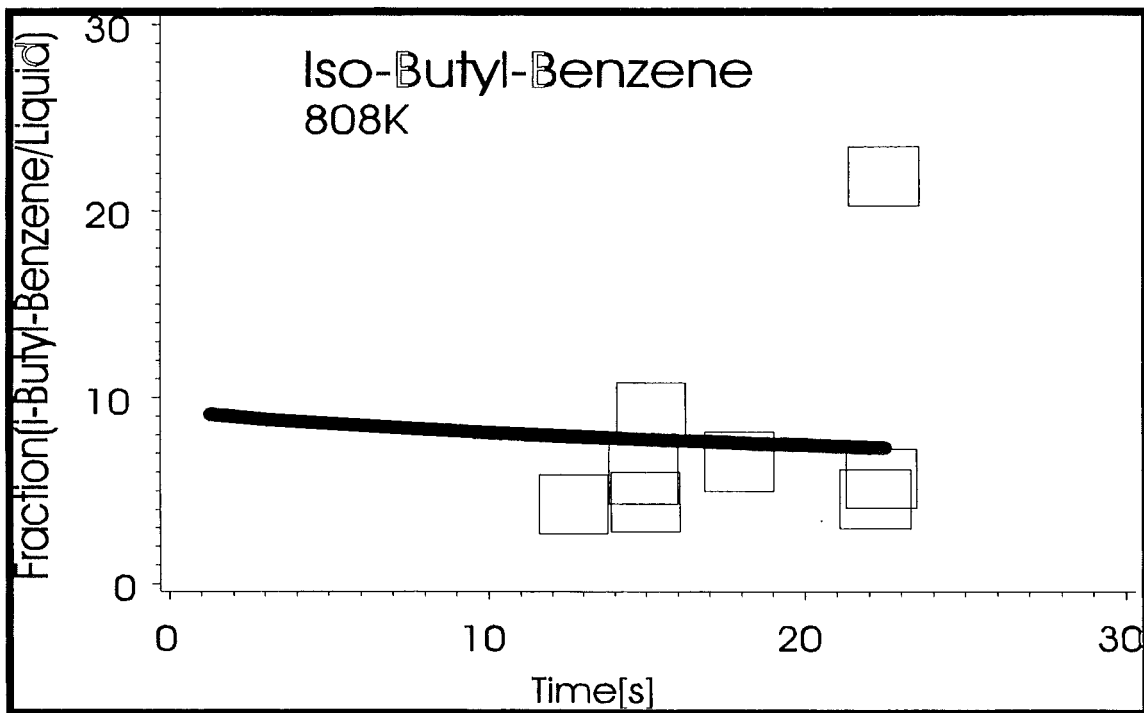


Fig. 8: Molar amount in % of iso-butyl-benzene within the liquid fraction. The rectangles are experimental points and the line is the calculation.

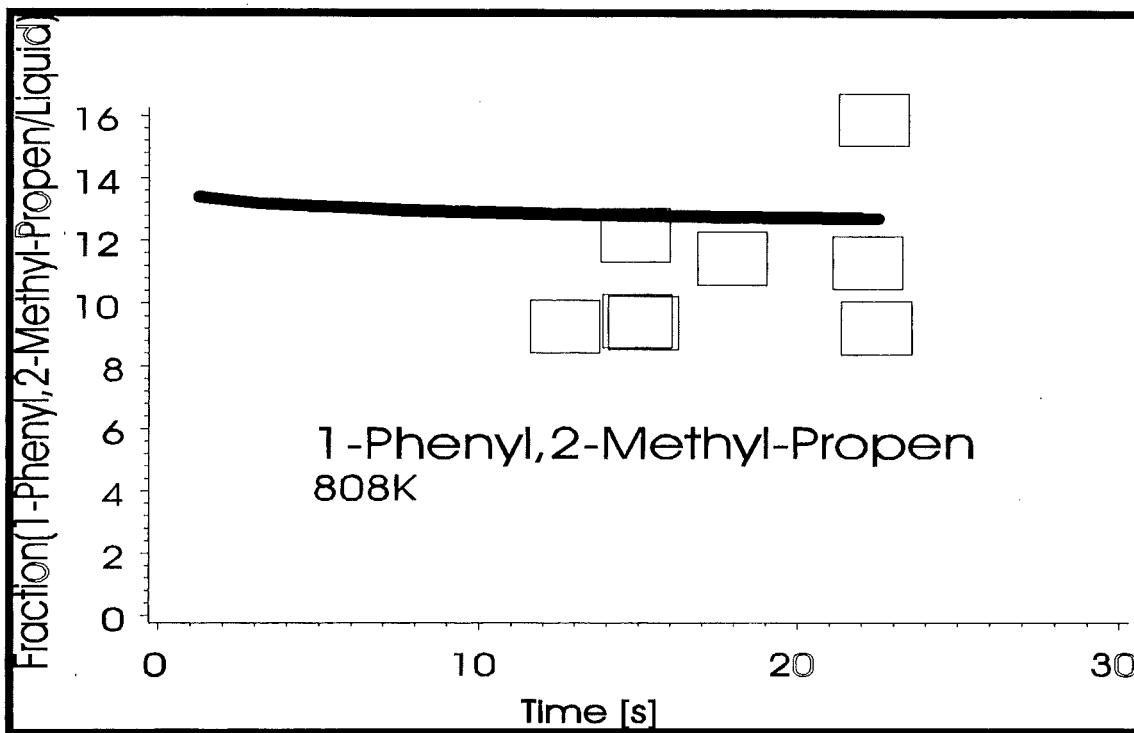


Fig. 9: Molar amount in % of 1-phenyl,2-methyl-propen within the liquid fraction. The rectangles are experimental points and the line is the calculation.

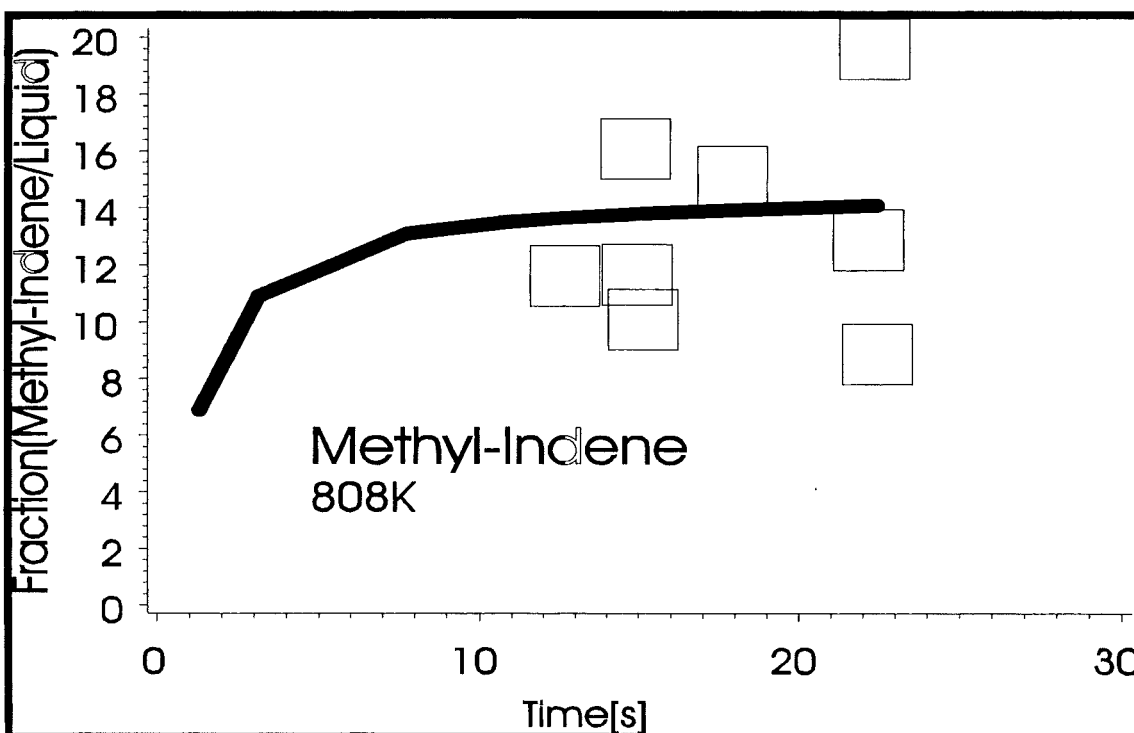


Fig. 10: Molar amount in % of methyl-indene within the liquid fraction. The rectangles are experimental points and the line is the calculation.

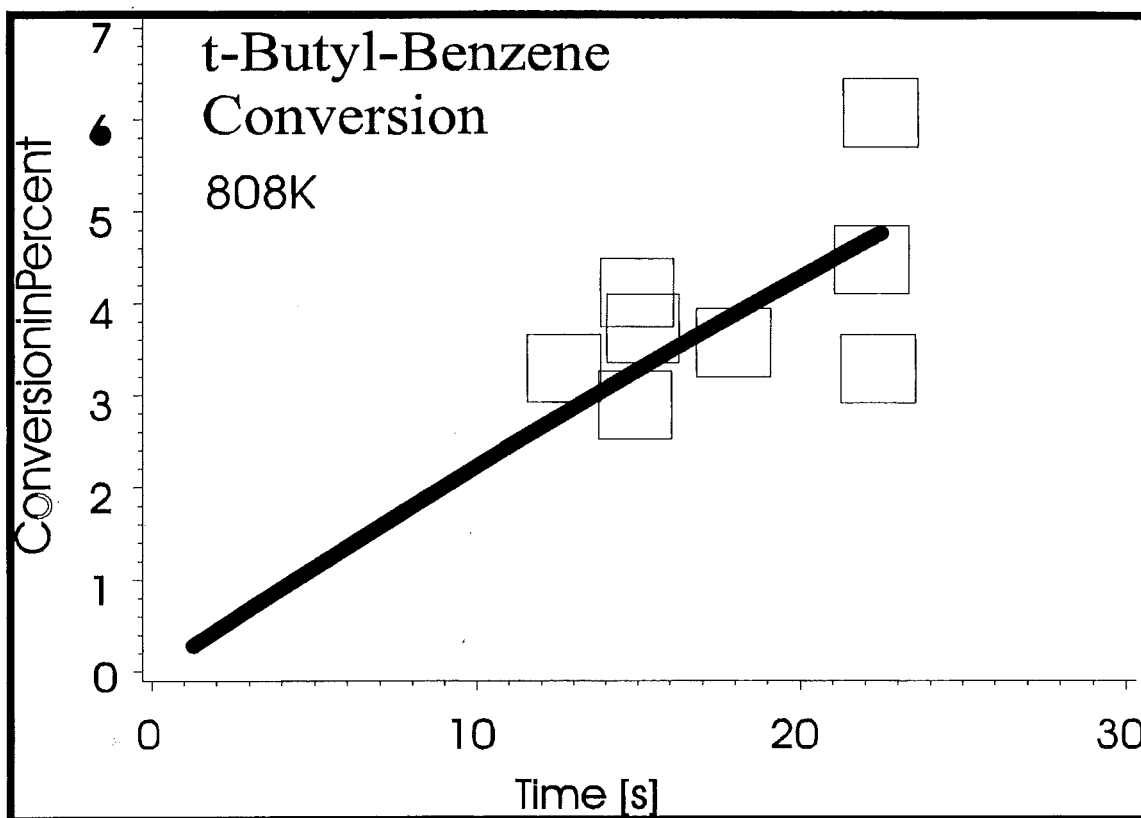


Fig. 11: Conversion of t-butyl-benzene in %. The rectangles are experimental points and the line is the calculation.

REACTION PATHS AND FLOWS ALONG THESE PATHS

The main paths of the reaction mechanism are shown as a flow schema in Fig. 12. To designate an isomerization reaction an arrow with a loop is used. A decomposition reaction is shown by using an arrow which bifurcates. For an addition reaction two arrows merge to one. The metathesis reactions are shown by two arrows - a straight one and a bent one - which touches. If different free radicals R and stable substances RH are reacting in a metathesis reaction, the necessary R and RH have been omitted. Two crossing arrows stay for substitution reaction. The numbers at the beginning of the arrow represent the percentage of the species reacting via this path. The numbers at the end of the arrows show the percentage of the respective substance formed by this reaction. The numbers within the rectangles, enclosing the substances, show the percentage of the formed substance which is reacting further. (The 0 for real stable substances and the 100 for free radicals have been dropped.) All numbers are taken for the reactions run at 808 K and 25 seconds reaction time which represents 5% conversion.

Another way looking at the reaction paths is shown in Table 2 where for 25 substances and free radicals the relative amounts of formation and of conversion is shown. The values are normalized to unity for the initiation reaction.

Table 2: Global flows values for the 25 main species. The flows are given relative to the initial elementary reaction (2). The table is arranged by the decreasing with the sum of flows. The short names of the species are explained in the reaction mechanism in the Appendix.

| <i>No.</i> | <i>Species</i> | <i>Flow to species</i> | <i>Flow from species</i> | <i>Sum of flows</i> |
|------------|----------------|------------------------|--------------------------|---------------------|
| 1 | TBBYL | 36.4594 | 36.4244 | 72.8838 |
| 2 | TBB | 9.5382 | 49.2050 | 58.7431 |
| 3 | H | 20.5697 | 20.5697 | 41.1394 |
| 4 | IBBYL2 | 13.9854 | 13.9852 | 27.9706 |
| 5 | I-C4H8 | 11.1815 | 11.0177 | 22.1993 |
| 6 | CH3 | 10.5698 | 10.5688 | 21.1386 |
| 7 | H2 | 18.4872 | 0.0000 | 18.4872 |
| 8 | T-C4H9 | 6.7811 | 6.7810 | 13.5621 |
| 9 | 3P2MPEN | 5.6270 | 5.3302 | 10.9572 |
| 10 | 2M3PALLYL | 5.4568 | 5.4568 | 10.9136 |
| 11 | MALLYL | 5.4130 | 5.3983 | 10.8113 |
| 12 | C6H5 | 5.0024 | 5.0025 | 10.0049 |
| 13 | IBUTAN | 5.5626 | 4.1156 | 9.6782 |
| 14 | A-M-S | 8.3485 | 0.2404 | 8.5890 |
| 15 | 2MPROPYL | 3.9706 | 3.9706 | 7.9412 |
| 16 | TOLUENE | 4.5181 | 2.2034 | 6.7215 |
| 17 | 3MCYPENYL | 3.1634 | 3.1632 | 6.3266 |
| 18 | C6H6 | 5.6168 | 0.0000 | 5.6168 |
| 19 | MINDEN | 5.4568 | 0.0000 | 5.4568 |
| 20 | 1P2MPEN | 5.1076 | 0.1266 | 5.2342 |
| 21 | CH4 | 5.0341 | 0.0000 | 5.0341 |
| 22 | BENZYL | 2.5528 | 1.9892 | 4.5420 |
| 23 | IBB | 3.4218 | 0.5763 | 3.9981 |
| 24 | PTBBYL | 1.9904 | 1.9883 | 3.9787 |
| 25 | C3H6 | 2.3013 | 1.3768 | 3.6781 |

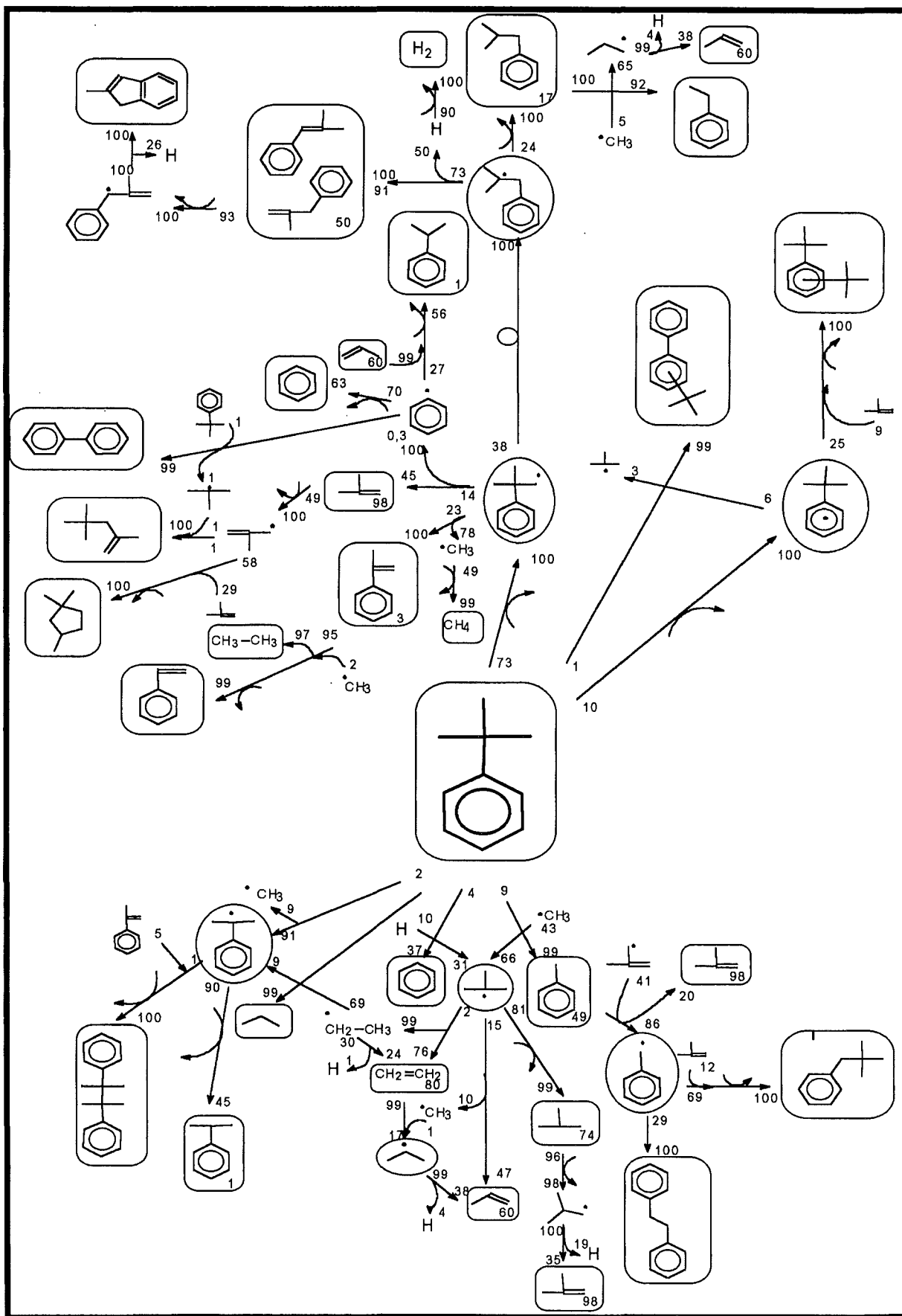


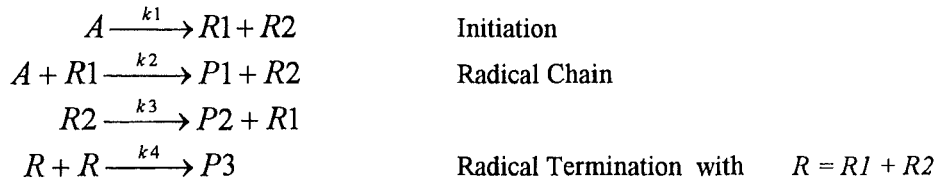
Fig. 12: Main reaction paths for the main products. Explanation see Text.

DISCUSSIONS

DISCUSSION OF CONVERSION

More than half of the experiments were carried out at temperatures at about 535 °C . The theoretical conversions describe the experiments very well in this temperature range (included are different times, different initial conditions, and different compositions of the 'inert' media) . The conversions were also calculated in accordance with the experiments at higher temperatures. Only at lower temperatures (501 °C - 510 °C) the calculated conversions are lower than the experimental ones (e.g. modeling: 0.6 %, experiment 0.9 %). There may be two reasons for this discrepancy: 1.) for this very low conversions, the experimental results are less accurate for analytical reasons, 2.) the optimization of the reaction model has been performed for all experiments and only three of 25 are at the lower temperatures.

A comparison of runs at the same temperature but for different initial conditions results in the relation: the higher the initial concentration, the lower the conversion. This is expressed by a conversion rate law for TBB, which has to have a reaction order less than 1. Graphical interpretation of all experimental data result in an overall order of approximately 0.5. In our sensitivity matrix there is an entry for the relative sensitivity of the conversion of TBB due to a change in the initial concentrations with a numerical value of about -0.4. This may be interpreted as an overall order of 0.6 for TBB conversion. This low overall reaction order may be explained assuming the following radical chain mechanism:



If the rates for the initiation reaction (k1) and the termination reaction (k4) is small compared with the radical chain reactions, then the ODE's for A, R1, R2 can be approximated by:

$$\begin{array}{ll}
 \frac{d[A]}{dt} \approx -k_2 \cdot [A] \cdot [R_1] & \text{neglecting initial reaction} \\
 \frac{d[R_1]}{dt} \approx -k_2 \cdot [A] \cdot [R_1] + k_3 \cdot [R_2] \approx 0 & \text{applying the quasi-stationary assumption} \\
 \frac{d[R_2]}{dt} \approx +k_2 \cdot [A] \cdot [R_1] - k_3 \cdot [R_2] \approx 0 & \text{applying QSSA}
 \end{array}$$

from this it follows: $k_2 \cdot [A] \cdot [R_1] \approx k_3 \cdot [R_2]$ and $[R_1] \approx \frac{k_3 \cdot [R_2]}{k_2 \cdot [A]}$

and therefore: $\frac{d[A]}{dt} \approx -k_3 \cdot [R_2]$

The concentration of all free radicals R is determined only by the initial and the termination reactions.

$$\begin{array}{ll}
 \frac{d[R]}{dt} \approx +2 \cdot k_1 \cdot [A] - k_4 \cdot [R] \cdot [R] \approx 0 & \text{applying QSSA} \\
 [R] \approx \sqrt{\frac{2 \cdot k_1 \cdot [A]}{k_4}} \approx [R_1] + [R_2] \approx \frac{k_3 \cdot [R_2]}{k_2 \cdot [A]} + [R_2] = [R_2] \cdot \left(1 + \frac{k_3}{k_2 \cdot [A]}\right)
 \end{array}$$

this results for R2 in:

$$R_2 = \sqrt{\frac{2 \cdot k_1 \cdot [A]}{k_4}} \left/ \left(1 + \frac{k_3}{k_2 \cdot [A]}\right)\right.$$

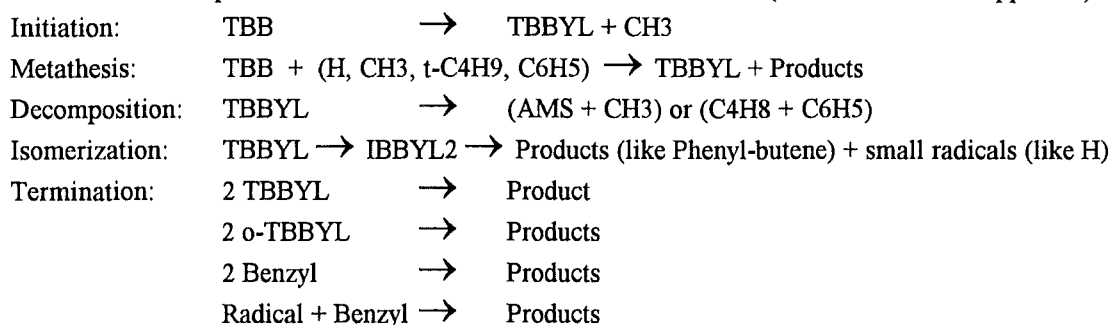
Two extremes are now considered:

$$k_3 \gg k_2 \cdot [A] \text{ then } \frac{d[A]}{dt} \approx -k_3 \cdot [R_2] \approx -k_{\text{overall}} \cdot [A]^{3/2} \quad \text{overall order is } 1.5$$

$$k_3 \ll k_2 \cdot [A] \text{ then } \frac{d[A]}{dt} \approx -k_3 \cdot [R_2] \approx -k_{\text{overall}} \cdot [A]^{1/2} \quad \text{overall order is } 0.5$$

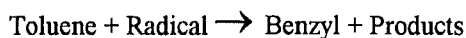
The latter expression describes our experiments best, which means that the decomposition reaction of the most important radical chain radical is slow compared with the metathesis reaction of the other radicals. This radical was identified as TBBYL for our mechanism. This result is in accordance with our assumption that the reaction rate constants for the decomposition reactions decrease at high pressures. The radicals R1 (the small ones which react in metathesis reactions, e.g. H, CH₃ ...) should have a lower concentration for higher initial concentrations. This is in agreement with our model calculation of the complex mechanism, if runs with different initial concentrations are compared.

The reactions or reaction paths which determine the conversion of TBB are: (abbreviations: see Appendix)



These reactions are extracted from the mechanism by flow and sensitivity analysis using model calculations.

There is an additional retardation of the overall TBB decomposition with time. There is a product inhibition caused by toluene:



Toluene is a radical scavenger for the small reactive radicals which lead to the rather stable benzyl radical. The mechanisms discussed for the conversion explains the influence of water which couldn't be found experimentally. The main metathesis radicals like H or CH₃ may react with water to form the same product as if they react with TBB or other hydrocarbons and the very reactive OH radical. The OH radicals undergo very fast a hydrogen transfer reactions to form water and radicals (which could have been formed directly without the detour via water). There is no influence in the overall reactivity - but there may be a minor influence on the selectivity, because OH should be less selective (it is more reactive) than for example CH₃ (which may prefer the less stable hydrogen bonding).

If the reaction model is used to calculate an overall activation energy for the conversion of t-butylbenzene a value of 320 kJ is obtained, which is in agreement with the direct evaluation of the experimental data.

DISCUSSION OF PRODUCT FORMATION

The products α-methylstyrene, i-butene, methane and benzene are formed by the reaction paths in the basis mechanism as pointed out in the section: developing the reaction mechanism. In this mechanism there is no hydrogen atom included, but as one can see from Table 2, H is the most important of the small free radicals. Only after isomerization of the TBBYL radical to the IBBYL radical, new paths which then involve H radicals are introduced. This leads to the formation of the isomers of butyl-benzenes and phenyl-butenes and products derived from those like methyl-indene. For the formation of products like toluene and propene, radical substitution reactions are the main reactions. Higher molecular weight products like phenyl-pentane or di-t-butyl-benzenes are formed by radical addition reactions.

The main paths of the model can be studied in Fig. 12 or in more detail by flow analysis using simulation runs. In order to keep the reaction mechanism small, not all chemically possible reactions were included. More than 1000 elementary reaction would have been needed for a more complete mechanism. We selected the reactions from a chemical point of view to keep the reaction mechanism small because the effort for the parameter identification increases more than linear with the number of reactions.

Some proposed reaction ways for product formation paths have been nearly cut by the optimization routine although they seem to be chemically reasonable.

DISCUSSION OF SENSITIVITIES

Only about 10% of all elementary reactions have high sensitivities for the majority of the substances in the mechanism. And only the kinetic parameter of these one must be compared with values from the literature, which are low pressure values. Only for the initial reaction and for some recombination reactions are literature data available. For all other types of reaction where TBB or other higher hydrocarbons are involved no data are available. It is only possible to compare them with analogous or similar reactions.

Initial reaction: This reaction is definitively slower at high pressure, the pre-exponential factor is more than 100 times lower, but has a similar activation energy.

Termination reaction: The most sensitive recombination reaction is the combination of two benzyl radicals. It has a reaction rate constant about a factor of 100 higher than the literature value.

Radical decomposition: They may be considered as retarded by high pressure too, but less drastically than the initiation. The activation energies are similar.

Radical addition: These reactions show a tendency of running faster at high pressure.

Metathesis reactions: Though there are some very sensitive reactions, it seems there are no significant differences to the literature data.

Isomerization and substitution reactions: For these reaction types it is nearly impossible to evaluate values from low pressure literature data, because only very few of such reactions are available. As these reactions are very important for pyrolysis in supercritical water, one cannot describe the experiments without them. This looks like one of the great differences to pyrolysis at low pressures.

CONCLUSIONS

For the pyrolysis of TBB in SCW a parameter identification program has been developed to describe the experimental data on the basis of elementary reactions. The kinetic parameter obtained don't claim to be universal, they are specific for the limited experimental conditions for this mechanism. They show a significant pressure dependency. It was not attempted to calculate these pressure dependencies for the individual elementary reactions; the experimental basis is for too small. Some experiments at 15 MPa (instead of 25 MPa) show a much higher conversion but a similar product distribution as calculated by our model. This can be explained by the assumption that the reaction rate of some elementary reactions is changing with pressure.

APPENDIX

Reaction system for the thermal decomposition of t-Butyl-Benzene (TBB) as it is used for input in the LARKIN code. The two numbers at the end of each reaction are the \log_{10} of the pre-exponential factor and the activation energy. The dimension used are: second, mole, m^3 and Joule.

Heading the reaction system is a list of the substances used within the mechanism, arranged by the molecular weight. The first column is the abbreviation used within LARKIN, the second column are the molecular formulas and the last one is its chemical name.

----- t - Butyl-Benzene -----

*SPECIES

| | | |
|-------|------|---------------|
| H | H1 | Hydrogen-Atom |
| H2 | H2 | Hydrogen |
| CH3 | C1H3 | Methyl |
| CH4 | C1H4 | Methane |
| VINYL | C2H3 | CH2=CH |
| C2H4 | C2H4 | Ethene |
| C2H5 | C2H5 | Ethyl |
| C2H6 | C2H6 | Ethane |

| | | |
|------------|--------|--|
| ALLYL | C3H5 | CH ₂ =CH-CH ₂ |
| C3H6 | C3H6 | Propene |
| 2PROPYL | C3H7 | 1-Methyl-Ethyl CH ₃ -CH-CH ₃ |
| PROPAN | C3H8 | Propane CH ₃ -CH ₂ -CH ₃ |
| MALLYL | C4H7 | Methyl-Allyl CH ₂ -C(CH ₃)-CH ₂ |
| I-C4H8 | C4H8 | i-Butene |
| 2BUTEN | C4H8 | 2-Butene CH ₃ -CH=CH-CH ₃ (E and Z) |
| 1BUTEN | C4H8 | 1-Butene CH ₃ -CH ₂ -CH=CH ₂ |
| 2MPROPYL | C4H9 | 2-Methyl-Propyl CH ₃ -CH(CH ₃)-CH ₂ |
| T-C4H9 | C4H9 | t-Butyl-Radical |
| 2BUTYL | C4H9 | 1-Methyl-Propyl C ₂ H ₅ -CH-CH ₃ |
| IBUTAN | C4H10 | i-Butane |
| NBUTAN | C4H10 | n-Butane CH ₃ -CH ₂ -CH ₂ -CH ₃ |
| C6H5 | C6H5 | Phenyl-Radical |
| C6H6 | C6H6 | Benzene |
| BENZYL | C7H7 | Benzyl-Radical |
| TOLUENE | C7H8 | Toluene |
| STYYL | C8H7 | Phenylvinyl C ₆ H ₅ -C=CH ₂ |
| STY | C8H8 | Styrene C ₆ H ₅ -CH=CH ₂ |
| EBYL | C8H9 | 1-Phenyl-Ethyl C ₆ H ₅ -CH-CH ₃ |
| EB | C8H10 | Ethyl-Benzene |
| 3MCYPENYL | C8H15 | 1,3,3-Trimethyl-Cyclo-Pentyl CH ₃ -C ₅ H ₆ (CH ₃)-CH ₃ |
| 3MCYPEN | C8H16 | 1,3,3-Trimethyl-Cyclo-Pentane CH ₃ -C ₅ H ₇ (CH ₃)-CH ₃ |
| 244TMPEN | C8H16 | 2,4,4-Trimethyl-Pentene-1 CH ₂ =C(CH ₃)-CH ₂ -C(CH ₃)(CH ₃)-CH ₃ |
| A-M-S | C9H10 | Alpha-Methyl-Styrene |
| 2-P-2-C3H6 | C9H11 | 2-Phenyl-2-Propyl-Radical C ₆ H ₅ -C(CH ₃)-CH ₃ |
| 2-P-PRYL | C9H 11 | 2-Phenyl-Propyl-Radical C ₆ H ₅ -CH(CH ₃)-CH ₂ |
| CUMOL | C9H12 | Cumene |
| MINDEN | C10H10 | 2-Methyl-Indene C ₆ H ₄ -CH=C(CH ₃)-CH ₂ !-----! |
| 2M3PALLYL | C10H11 | 2-Methyl-3-Phenyl-Allyl C ₆ H ₅ -CH=C(CH ₃)-CH ₂ |
| 1P2MPEN | C10H12 | 1-Phenyl-2-Methyl-Propene-1 CH ₃ -C(CH ₃)=CH-C ₆ H ₅ |
| 3P2MPEN | C10H12 | 3-Phenyl-2-Methyl-Propene-1 CH ₂ =C(CH ₃)-CH ₂ -C ₆ H ₅ |
| 2PBUTEN1 | C10H12 | 2-Phenyl-Butene-1 CH ₂ =C(C ₆ H ₅)-CH ₂ -CH ₃ |
| 2PBUTEN2 | C10H12 | 2-Phenyl-Butene-2 CH ₃ -C(C ₆ H ₅)=CH-CH ₃ |

| | | |
|------------|--------|---|
| TBBYL | C10H13 | 2-Phenyl, 2, 2-Di-Methyl-Ethyl C6H5-C(CH3)(CH3)(CH2) |
| OTBBYL | C10H13 | 2-t-Butyl-Phenyl o-C6H4-C(CH3)(CH3)(CH3) |
| MTBBYL | C10H13 | 3-t-Butyl-Phenyl m-C6H4-C(CH3)(CH3)(CH3) |
| PTBBYL | C10H13 | 4-t-Butyl-Phenyl p-C6H4-C(CH3)(CH3)(CH3) |
| 1P1MPROPYL | C10H13 | 1-Phenyl-1-Methyl-Propyl CH3-C(C6H5)-CH2-CH3 |
| IBBYL2 | C10H13 | 1, 1-Dimethyl-2-Phenyl-Ethyl CH3-C(CH3)-CH2-C6H5 |
| 2PBUTAN | C10H14 | 2-Phenyl-Butane CH3-CH(C6H5)-CH2-CH3 |
| IBB | C10H14 | i-Butyl-Benzene CH3-CH(CH3)-CH2-C6H5 |
| TBB | C10H14 | t-Butyl-Benzene |
| NPEPHYL | C11H15 | 2, 2-Dimethyl-3-Phenyl-Propyl C6H5-CH2-C(CH3)(CH3)-CH2 |
| NPEB | C11H16 | 2, 2-Dimethyl-3-Phenyl-Propane C6H5-CH2-C(CH3)(CH3)-CH3 |
| BIPHENYL | C12H10 | Bi-Phenyl |
| DIBENZYL | C14H14 | Di-Benzyl C6H5-CH2-CH2-C6H5 |
| ODITBBYL | C14H21 | 2, 2-Dimethyl-2(o-t-Butylphenyl)-Ethyl CH3-C(CH3)(CH3)-o-C6H4-C(CH3)(CH3)CH2 |
| MDITBBYL | C14H21 | 2, 2-Dimethyl-2(m-t-Butylphenyl)-Ethyl CH3-C(CH3)(CH3)-m-C6H4-C(CH3)(CH3)CH2 |
| PDITBBYL | C14H21 | 2, 2-Dimethyl-2(p-t-Butylphenyl)-Ethyl CH3-C(CH3)(CH3)-p-C6H4-C(CH3)(CH3)CH2 |
| ODITBB | C14H22 | o-di-t-Butyl-Benzene CH3-C(CH3)(CH3)-p-C6H4-C(CH3)(CH3)CH3 |
| MDITBB | C14H22 | m-di-t-Butyl-Benzene CH3-C(CH3)(CH3)-m-C6H4-C(CH3)(CH3)CH3 |
| PDITBB | C14H22 | p-di-t-Butyl-Benzene CH3-C(CH3)(CH3)-p-C6H4-C(CH3)(CH3)CH3 |
| PHETBB | C16H18 | Phenyl-t-Butyl-Benzene C6H5-C6H4-C(CH3)(CH3)CH3 |
| TMDIBYL | C18H21 | 2, 3-Dimethyl-2, 3-Diphenyl-Butyl C6H5-C(CH3)(CH3)-C(CH3)(CH2)-C6H5 |
| TMDIBEN | C18H22 | 2, 3-Dimethyl-2, 3-Diphenyl-Butane C6H5-C(CH3)(CH3)-C(CH3)(CH3)-C6H5 |

*** Reaction System TBB in Supercritical Water ***

*C

*C Initiation Reactions

*C

| | | | | | | |
|---|--------|----|------------|---|---------|--------------------------|
| 1 | TBB | => | T-C4H9 | + | C6H5 | (0.4913E+13, 0.5915E+06) |
| 2 | TBB | => | 2-P-2-C3H6 | + | CH3 | (0.6940E+14, 0.2796E+06) |
| 3 | IBUTAN | => | 2PROPYL | + | CH3 | (0.2743E+17, 0.2894E+06) |
| 4 | PROPAN | => | C2H5 | + | CH3 | (0.4770E+14, 0.3958E+06) |
| 5 | I-C4H8 | => | CH3 | + | ALLYL | (0.8156E+14, 0.3380E+06) |
| 6 | A-M-S | => | CH3 | + | STYYL | (0.1222E+15, 0.3232E+06) |
| 7 | IBUTAN | => | CH3 | + | 2PROPYL | (0.1063E+15, 0.3411E+06) |

```

8 C3H6 => CH3 + VINYL (0.9671E+14, 0.4984E+06)
*C
*C Inverse Reactions of Recombination
*C
9 DIBENZYL => BENZYL + BENZYL (0.6675E+14, 0.2879E+06)
10 TMDIBEN => 2-P-2-C3H6 + 2-P-2-C3H6 (0.3882E+14, 0.4454E+06)
*C
*C Metathesis Reactions
*C
11 TBB + 2BUTYL => TBBYL + NBUTAN (0.1043E+07, 0.3922E+05)
12 TBB + STYYL => TBBYL + STY (0.1321E+07, 0.4158E+05)
13 TBB + ALLYL => TBBYL + C3H6 (0.8985E+06, 0.5563E+05)
14 TBB + EBYL => TBBYL + EB (0.1095E+07, 0.4858E+05)
15 TBB + VINYL => TBBYL + C2H4 (0.8804E+06, 0.4404E+05)
16 TBB + TMDIBYL => TBBYL + TMDIBEN (0.1079E+07, 0.2280E+05)
17 TBB + CH3 => TBBYL + CH4 (0.2378E+07, 0.5619E+05)
18 TBB + CH3 => OTBBYL + CH4 (0.6334E+05, 0.9083E+05)
19 TBB + CH3 => MTBBYL + CH4 (0.1172E+06, 0.5515E+05)
20 TBB + CH3 => PTBBYL + CH4 (0.9478E+05, 0.5490E+05)
21 TBB + H => TBBYL + H2 (0.1035E+08, 0.4074E+05)
22 TBB + H => OTBBYL + H2 (0.7292E+06, 0.8263E+05)
23 TBB + H => MTBBYL + H2 (0.1907E+07, 0.4805E+05)
24 TBB + H => PTBBYL + H2 (0.2618E+07, 0.4650E+05)
25 TBB + C6H5 => TBBYL + C6H6 (0.5288E+06, 0.2733E+05)
26 TBB + C6H5 => OTBBYL + C6H6 (0.6668E+05, 0.6853E+05)
27 TBB + C6H5 => MTBBYL + C6H6 (0.4363E+05, 0.6549E+05)
28 TBB + C6H5 => PTBBYL + C6H6 (0.4494E+04, 0.8023E+05)
29 TBB + 2-P-2-C3H6 => TBBYL + CUMOL (0.2918E+06, 0.1237E+05)
30 TBB + 2-P-2-C3H6 => OTBBYL + CUMOL (0.1027E+05, 0.5429E+04)
31 TBB + 2-P-2-C3H6 => MTBBYL + CUMOL (0.1018E+05, 0.3072E+05)
32 TBB + 2-P-2-C3H6 => PTBBYL + CUMOL (0.6030E+04, 0.5625E+05)
33 TBB + 2-P-PRYL => TBBYL + CUMOL (0.9625E+05, 0.1043E+05)
34 TBB + 2-P-PRYL => OTBBYL + CUMOL (0.1313E+05, 0.8176E+05)
35 TBB + 2-P-PRYL => MTBBYL + CUMOL (0.1289E+05, 0.5143E+05)
36 TBB + 2-P-PRYL => PTBBYL + CUMOL (0.1077E+05, 0.2161E+06)
37 TBB + T-C4H9 => TBBYL + IBUTAN (0.1137E+07, 0.2326E+05)
38 TBB + T-C4H9 => OTBBYL + IBUTAN (0.1976E+06, 0.9221E+05)
39 TBB + T-C4H9 => MTBBYL + IBUTAN (0.2795E+06, 0.6186E+05)
40 TBB + T-C4H9 => PTBBYL + IBUTAN (0.3478E+06, 0.5733E+05)
41 TBB + 1P1MPROPYL => TBBYL + 2PBUTAN (0.9129E+05, 0.2943E+05)
42 TBB + 1P1MPROPYL => OTBBYL + 2PBUTAN (0.1309E+05, 0.4697E+05)
43 TBB + 1P1MPROPYL => MTBBYL + 2PBUTAN (0.5753E+04, 0.4219E+05)
44 TBB + 1P1MPROPYL => PTBBYL + 2PBUTAN (0.4894E+04, 0.4360E+05)
45 TBB + IBBYL2 => TBBYL + IBB (0.4034E+04, 0.3296E+05)
46 TBB + IBBYL2 => OTBBYL + IBB (0.6312E+03, 0.1767E+05)
47 TBB + IBBYL2 => MTBBYL + IBB (0.3146E+04, 0.3723E+05)
48 TBB + IBBYL2 => PTBBYL + IBB (0.3702E+04, 0.3608E+05)
49 TBB + OTBBYL => TBBYL + TBB (0.3648E+04, 0.1242E+06)
50 TBB + MTBBYL => TBBYL + TBB (0.9372E+04, 0.2516E+05)
51 TBB + PTBBYL => TBBYL + TBB (0.4431E+04, 0.3868E+05)
52 TBB + ODITBBYL => TBBYL + ODITBB (0.8715E+04, 0.4350E+05)
53 TBB + MDITBBYL => TBBYL + MDITBB (0.8185E+04, 0.9435E+05)
54 TBB + PDITBBYL => TBBYL + PDITBB (0.5770E+04, 0.4246E+05)
55 TBB + BENZYL => TBBYL + TOLUENE (0.1330E+03, 0.6767E+05)
56 TBB + NPEPHYL => TBBYL + NPEB (0.9537E+04, 0.1657E+05)
57 TBB + 3MCYPENYL => TBBYL + 3MCYPEN (0.5357E+04, 0.2993E+05)
58 TBB + 2PROPYL => TBBYL + PROPAN (0.7693E+06, 0.2565E+05)

```

| | | | | | | | | |
|----|---------|---|--------|----|-----------|---|--------|--------------------------|
| 59 | TBB | + | C2H5 | => | TBBYL | + | C2H6 | (0.3087E+06, 0.8449E+05) |
| 60 | IBUTAN | + | CH3 | => | 2MPROPYL | + | CH4 | (0.1551E+05, 0.2081E+05) |
| 61 | IBUTAN | + | H | => | 2MPROPYL | + | H2 | (0.1108E+09, 0.2179E+05) |
| 62 | IBUTAN | + | C6H5 | => | 2MPROPYL | + | C6H6 | (0.3034E+06, 0.1644E+05) |
| 63 | IBUTAN | + | TBBYL | => | 2MPROPYL | + | TBB | (0.2973E+05, 0.2368E+05) |
| 64 | I-C4H8 | + | CH3 | => | MALLYL | + | CH4 | (0.3611E+08, 0.3287E+05) |
| 65 | I-C4H8 | + | H | => | MALLYL | + | H2 | (0.2953E+05, 0.1782E+05) |
| 66 | I-C4H8 | + | C6H5 | => | MALLYL | + | C6H6 | (0.6651E+05, 0.1690E+05) |
| 67 | I-C4H8 | + | TBBYL | => | MALLYL | + | TBB | (0.2071E+06, 0.6889E+04) |
| 68 | 1P2MPEN | + | CH3 | => | 2M3PALLYL | + | CH4 | (0.3814E+06, 0.2885E+05) |
| 69 | 1P2MPEN | + | H | => | 2M3PALLYL | + | H2 | (0.2267E+08, 0.9540E+05) |
| 70 | 1P2MPEN | + | C6H5 | => | 2M3PALLYL | + | C6H6 | (0.5698E+05, 0.4956E+05) |
| 71 | 1P2MPEN | + | TBBYL | => | 2M3PALLYL | + | TBB | (0.2447E+05, 0.1158E+06) |
| 72 | 3P2MPEN | + | CH3 | => | 2M3PALLYL | + | CH4 | (0.8690E+06, 0.1477E+05) |
| 73 | 3P2MPEN | + | H | => | 2M3PALLYL | + | H2 | (0.4867E+08, 0.8970E+04) |
| 74 | 3P2MPEN | + | C6H5 | => | 2M3PALLYL | + | C6H6 | (0.1352E+06, 0.1795E+05) |
| 75 | 3P2MPEN | + | TBBYL | => | 2M3PALLYL | + | TBB | (0.2729E+05, 0.8992E+02) |
| 76 | TOLUENE | + | MALLYL | => | I-C4H8 | + | BENZYL | (0.1143E+05, 0.2845E+05) |

*C

*C Radical Decomposition Reactions

*C

| | | | | | | |
|----|------------|----|----------|---|--------|--------------------------|
| 77 | 2BUTYL | => | 2BUTEN | + | H | (0.8439E+13, 0.9711E+05) |
| 78 | 2BUTYL | => | 1BUTEN | + | H | (0.1076E+14, 0.1702E+06) |
| 79 | C2H5 | => | C2H4 | + | H | (0.1863E+14, 0.1376E+06) |
| 80 | 2PROPYL | => | C3H6 | + | H | (0.2250E+13, 0.1839E+05) |
| 81 | 2MPROPYL | => | I-C4H8 | + | H | (0.1006E+14, 0.7174E+05) |
| 82 | 2MPROPYL | => | C3H6 | + | CH3 | (0.3385E+12, 0.1412E+06) |
| 83 | T-C4H9 | => | I-C4H8 | + | H | (0.6908E+13, 0.2433E+06) |
| 84 | T-C4H9 | => | C3H6 | + | CH3 | (0.4631E+15, 0.1446E+06) |
| 85 | T-C4H9 | => | C2H4 | + | C2H5 | (0.4312E+20, 0.2350E+06) |
| 86 | 2-P-2-C3H6 | => | A-M-S | + | H | (0.9860E+13, 0.3053E+06) |
| 87 | TBBYL | => | A-M-S | + | CH3 | (0.1861E+16, 0.1934E+06) |
| 88 | TBBYL | => | C6H5 | + | I-C4H8 | (0.5253E+13, 0.1574E+06) |
| 89 | 1P1MPROPYL | => | 2PBUTEN2 | + | H | (0.7369E+13, 0.2481E+06) |
| 90 | 1P1MPROPYL | => | 2PBUTEN1 | + | H | (0.6605E+03, 0.1860E+06) |
| 91 | 1P1MPROPYL | => | A-M-S | + | CH3 | (0.1400E+14, 0.1869E+06) |
| 92 | IBBYL2 | => | 1P2MPEN | + | H | (0.4566E+13, 0.1390E+06) |
| 93 | IBBYL2 | => | 3P2MPEN | + | H | (0.8037E+13, 0.1428E+06) |
| 94 | IBBYL2 | => | C3H6 | + | BENZYL | (0.1852E+12, 0.1355E+06) |

*C

*C Radical Isomerization and Shift Reactions

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|----|-------|----|------------|--------------------------|
| 95 | TBBYL | => | 1P1MPROPYL | (0.7871E+09, 0.2295E+06) |
| 96 | TBBYL | => | IBBYL2 | (0.3831E+12, 0.1329E+06) |

*C

*C Radical Addition Reactions

*C

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|-----|------|---|--------|----|----------|--------------------------|
| 97 | H | + | I-C4H8 | => | T-C4H9 | (0.1027E+07, 0.4625E+05) |
| 98 | H | + | I-C4H8 | => | 2MPROPYL | (0.9560E+06, 0.7922E+05) |
| 99 | H | + | C3H6 | => | 2PROPYL | (0.9251E+06, 0.6096E+05) |
| 100 | H | + | C2H4 | => | C2H5 | (0.1378E+07, 0.7239E+05) |
| 101 | H | + | 2BUTEN | => | 2BUTYL | (0.1090E+07, 0.6170E+05) |
| 102 | H | + | 1BUTEN | => | 2BUTYL | (0.8635E+06, 0.5447E+05) |
| 103 | CH3 | + | C3H6 | => | 2BUTYL | (0.8330E+06, 0.4536E+05) |
| 104 | CH3 | + | C3H6 | => | 2MPROPYL | (0.9858E+06, 0.4331E+05) |
| 105 | CH3 | + | C2H4 | => | 2PROPYL | (0.1616E+07, 0.7296E+04) |
| 106 | C6H5 | + | I-C4H8 | => | TBBYL | (0.1322E+07, 0.2121E+04) |

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|-----|--------|---|------------|----|------------|--------------------------|
| 107 | A-M-S | + | H | => | 2-P-2-C3H6 | (0.8585E+06, 0.7823E+05) |
| 108 | A-M-S | + | 2-P-2-C3H6 | => | TMDIBYL | (0.2794E+09, 0.5414E+05) |
| 109 | OTBBYL | + | I-C4H8 | => | ODITBBYL | (0.2312E+07, 0.4695E+05) |
| 110 | MTBBYL | + | I-C4H8 | => | MDITBBYL | (0.5353E+06, 0.1133E+06) |
| 111 | PTBBYL | + | I-C4H8 | => | PDITBBYL | (0.2244E+07, 0.2890E+05) |
| 112 | BENZYL | + | I-C4H8 | => | NPEPHYL | (0.1725E+08, 0.3243E+05) |
| 113 | C6H5 | + | C3H6 | => | 2-P-PRYL | (0.6371E+09, 0.3220E+05) |
| 114 | MALLYL | + | I-C4H8 | => | 3MCPENYL | (0.8734E+07, 0.5375E+05) |

*C

*C Radical Substitution Reactions

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|-----|-----------|---|--------|----|----------|---|------------|--------------------------|
| 115 | CH3 | + | IBUTAN | => | C2H6 | + | 2PROPYL | (0.2536E+05, 0.2669E+05) |
| 116 | CH3 | + | C3H6 | => | C2H4 | + | C2H5 | (0.7761E+05, 0.5563E+05) |
| 117 | CH3 | + | CUMOL | => | C2H6 | + | EBYL | (0.9170E+05, 0.8919E+05) |
| 118 | CH3 | + | A-M-S | => | C2H6 | + | STYYL | (0.7361E+07, 0.4804E+05) |
| 119 | CH3 | + | I-C4H8 | => | C2H6 | + | ALLYL | (0.1026E+06, 0.8164E+05) |
| 120 | CH3 | + | C3H6 | => | C2H6 | + | VINYL | (0.1123E+06, 0.7548E+05) |
| 121 | CH3 | + | IBB | => | 2PROPYL | + | EB | (0.1119E+08, 0.3802E+05) |
| 122 | H | + | C2H5 | => | CH3 | + | CH3 | (0.9707E+05, 0.9058E+05) |
| 123 | H | + | IBB | => | PROPAN | + | BENZYL | (0.7903E+07, 0.6491E+05) |
| 124 | TBB | + | C2H5 | => | PROPAN | + | 2-P-2-C3H6 | (0.1060E+08, 0.5842E+05) |
| 125 | 2M3PALLYL | | | => | MINDEN | + | H | (0.7644E+06, 0.3031E+05) |
| 126 | TBB | + | CH3 | => | TOLUENE | + | T-C4H9 | (0.4155E+07, 0.5908E+05) |
| 127 | TBB | + | CH3 | => | C2H6 | + | 2-P-2-C3H6 | (0.7866E+07, 0.1806E+06) |
| 128 | TBB | + | C6H5 | => | BIPHENYL | + | T-C4H9 | (0.2176E+06, 0.5799E+05) |
| 129 | TBB | + | C6H5 | => | TOLUENE | + | 2-P-2-C3H6 | (0.5944E+05, 0.1453E+06) |
| 130 | TBB | + | C6H5 | => | PHETBB | + | H | (0.3373E+05, 0.1305E+06) |
| 131 | TBB | + | T-C4H9 | => | ODITBB | + | H | (0.5270E+04, 0.8851E+05) |
| 132 | TBB | + | T-C4H9 | => | MDITBB | + | H | (0.1041E+05, 0.7749E+05) |
| 133 | TBB | + | T-C4H9 | => | PDITBB | + | H | (0.9709E+04, 0.1271E+06) |
| 134 | TBB | + | H | => | C6H6 | + | T-C4H9 | (0.1193E+07, 0.3768E+05) |
| 135 | TBB | + | H | => | CH4 | + | 2-P-2-C3H6 | (0.4508E+05, 0.1045E+06) |
| 136 | TBB | + | OTBBYL | => | PHETBB | + | T-C4H9 | (0.5600E+04, 0.7227E+05) |
| 137 | TBB | + | MTBBYL | => | PHETBB | + | T-C4H9 | (0.5662E+04, 0.8768E+05) |
| 138 | TBB | + | PTBBYL | => | PHETBB | + | T-C4H9 | (0.8190E+04, 0.1310E+06) |
| 139 | CUMOL | + | CH3 | => | TOLUENE | + | 2PROPYL | (0.9392E+04, 0.2127E+06) |
| 140 | CUMOL | + | C6H5 | => | BIPHENYL | + | 2PROPYL | (0.1620E+05, 0.1353E+06) |
| 141 | CUMOL | + | T-C4H9 | => | TBB | + | 2PROPYL | (0.1419E+05, 0.9152E+05) |
| 142 | CUMOL | + | H | => | C6H6 | + | 2PROPYL | (0.4644E+04, 0.5079E+05) |

*C

*C Radical Recombination Reactions

*C

| | | | | | | |
|-----|------|---|---------|----|----------|--------------------------|
| 143 | CH3 | + | 2PROPYL | => | IBUTAN | (0.1114E+08, 0.1160E+04) |
| 144 | CH3 | + | CH3 | => | C2H6 | (0.1196E+08, 0.1441E+04) |
| 145 | CH3 | + | H | => | CH4 | (0.3006E+09, 0.1662E+04) |
| 146 | CH3 | + | C6H5 | => | TOLUENE | (0.3837E+07, 0.8336E+03) |
| 147 | CH3 | + | BENZYL | => | EB | (0.6025E+08, 0.3381E+03) |
| 148 | CH3 | + | C2H5 | => | PROPAN | (0.6995E+07, 0.8585E+03) |
| 149 | H | + | T-C4H9 | => | IBUTAN | (0.7721E+07, 0.7707E+03) |
| 150 | H | + | 2PROPYL | => | PROPAN | (0.1449E+08, 0.5079E+03) |
| 151 | H | + | C2H5 | => | C2H6 | (0.9647E+07, 0.3274E+03) |
| 152 | H | + | H | => | H2 | (0.1434E+09, 0.7496E+03) |
| 153 | H | + | C6H5 | => | C6H6 | (0.1355E+08, 0.8406E+03) |
| 154 | H | + | BENZYL | => | TOLUENE | (0.1012E+09, 0.2090E+04) |
| 155 | H | + | C2H5 | => | C2H6 | (0.3584E+08, 0.6746E+03) |
| 156 | C6H5 | + | C6H5 | => | BIPHENYL | (0.8979E+07, 0.1230E+04) |
| 157 | C6H5 | + | C2H5 | => | EB | (0.9348E+07, 0.1028E+04) |

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|---------------------------------|------------|---|------------|----|------------------|--------------------------|
| 158 | BENZYL | + | BENZYL | => | DIBENZYL | (0.1290E+09, 0.3134E+04) |
| 159 | BENZYL | + | T-C4H9 | => | NPEB | (0.9727E+07, 0.1458E+04) |
| 160 | MALLYL | + | T-C4H9 | => | 244TMPEN | (0.6617E+06, 0.1011E+04) |
| 161 | MALLYL | + | C6H5 | => | 3P2MPEN | (0.7688E+07, 0.3338E+04) |
| 162 | 2-P-2-C3H6 | + | 2-P-2-C3H6 | => | TMDIBEN | (0.4087E+07, 0.3695E+03) |
| 163 | MALLYL | + | TBBYL | => | 3P2MPEN + I-C4H8 | (0.9435E+03, 0.5168E+03) |
| 164 | IBBYL2 | + | IBBYL2 | => | IBB + 3P2MPEN | (0.1059E+06, 0.3723E+03) |
| 165 | TBBYL | + | TBBYL | => | TBB + 3P2MPEN | (0.1027E+06, 0.5045E+03) |
| 166 | OTBBYL | + | OTBBYL | => | TBB + 3P2MPEN | (0.1100E+06, 0.2071E+03) |
| 167 | MTBBYL | + | MTBBYL | => | TBB + 3P2MPEN | (0.1012E+06, 0.4128E+03) |
| 168 | PTBBYL | + | PTBBYL | => | TBB + 3P2MPEN | (0.9977E+05, 0.9602E+03) |
| *C | | | | | | |
| *C Disproportionation Reactions | | | | | | |
| *C | | | | | | |
| 169 | T-C4H9 | + | T-C4H9 | => | I-C4H8 + IBUTAN | (0.7068E+09, 0.1161E+04) |
| 170 | C6H5 | + | C2H5 | => | C6H6 + C2H4 | (0.7898E+09, 0.7028E+03) |
| 171 | 2-P-2-C3H6 | + | 2-P-2-C3H6 | => | CUMOL + A-M-S | (0.6909E+09, 0.6342E+03) |

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