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Comprehensive Kinetic and Mechanistic Considerations for the Gas-Phase Behaviour of Pinane-Type Compounds[‡]

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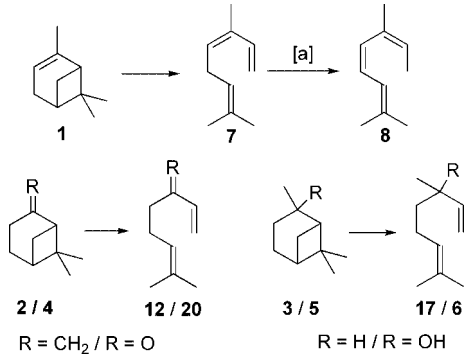
The thermal behaviour of selected pinane-type compounds, α-pinene (**1**), β-pinene (**2**), pinane (**3**) and nopinone (**4**), has been investigated. The conversion of the bicyclic starting materials to their acyclic and monocyclic isomers as well as the consecutive reactions of the acyclic main isomerisation products are discussed. The conversion of **1**–**4** in a reaction network is presented and the experimental evidence for the formation of pyrolysis products by a biradical pathway is discussed. In addition to these results a kinetic model describing the isomerisation of the bicyclic compounds to their acyclic and monocyclic isomers is presented. A good correlation between kinetic simulations and experimental data is revealed.

Introduction

Pinane-type monoterpenes and their oxygen-containing derivatives play an important role in the synthesis of flavours and fragrances as well as in the production of food additives (convenience and functional food). Two different resources can be used in their synthesis: natural-oil-based compounds (e.g., 2-methyl-2-hepten-6-one) or essential oils derived directly from plants.[2–5] The compounds extracted from natural sources have a great advantage over the natural-oil-based ones as most of them are available in enantiomeric pure form. No complex enantioselective synthetic strategies or expensive separation of enantiomers is necessary.

α-Pinene (**1**) and β-pinene (**2**) can be conveniently isolated from renewable resources by distillation from crude sulfate turpentine (CST)[6] and by the extraction of spruce or pine resins.[4,5] Pinenes **1** and **2** are important starting materials in the synthesis of linalool (**6**), which is an important intermediate in the synthesis of vitamin E and flavour compounds. In general the acyclic isomers of pinane-type monoterpenes are more important in chemical synthesis than their bicyclic precursors and they are generated from these compounds by thermal isomerisation. Scheme 1 shows that β-citronellene (**17**) can be derived from pinane (**3**).[7–9] Thermal isomerisation of **2** yields myrcene (**12**) and the transformation of **1** leads to alloocimene (**8**).[1,7,8,10–12] Alcohol **6** can be generated from 2-pinanol (**5**).[13,14] Because of the functionalisation of the acyclic compounds **6**, **7**, **12** and **17**, they are the starting materials of choice in the synthesis of fine chemicals.



Scheme 1. Thermal decyclisation of pinane-type compounds to their acyclic isomers. [a] Ocimene (**7**) isomerises rapidly to the acyclic alloocimene (**8**) (cf. the following text).

Thermal isomerisation can proceed via two different reaction mechanisms. Depending on the substitution of the pinane skeleton the rearrangement can take place either through a reaction involving biradicals (e.g., with **1** and **2**) or through a cycloreversion (e.g., with **5**).[1,7,10,15] Kinetic data for transformations of the bicyclic compounds **1**, **2** and **5** to the corresponding acyclic isomers **6**, **7** and **12** have been reported in the literature.[10–14] Table 1 lists the activation parameters and also data for the experimental settings used in these reactions.

In general, the thermal isomerisation of the discussed compounds (cf. Table 1) follows first-order kinetics, supporting the proposed reaction mechanisms. However, because of the different experimental set ups and residence

[‡] For a report on the first part of this work, see ref.[1]

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Table 1. Experimental set ups used to determine the kinetic parameters for the isomerisation of pinane-type compounds.

Compound	α-Pinene (**1**)	β-Pinene (**2**)	2-Pinanol (**5**)
Acyclic main product	ocimene (**7**)[a]	myrcene (**12**)	linalool (**6**)
Reaction mechanism	biradical	biradical	cycloreversion
Reference	[10,16]	[11,12]	[13–15]
Temperature [°C]	227–257	350–410	480–600
Pressure [mbar]	$<1.3\times10^{-3}$	27–114	3.3–56
Residence time [s]	2400–27000[b]	0.04–0.48	0.06–0.56
$E_{A(transf.)}$ [kJ mol^{-1}][c]	179	204	215/190[d]

[a] Ocimene (**7**) isomerises rapidly to the acyclic alloocimene (**8**) (see later). [b] Reaction time in a 2 L batch reactor. [c] Activation parameters for the conversion of the bicyclic compounds to isomeric compounds. [d] *cis*-**5**/*trans*-**5**.

times, the reported findings, especially with respect to reactivity, cannot be compared with each other.

Herein we report our investigations of the thermal behaviour of bicyclic pinane-type compounds α-pinene (**1**), β-pinene (**2**), pinane (**3**) and nopinone (**4**) under identical experimental conditions. Based on the composition of the liquid pyrolysis products, conclusions concerning the reaction mechanism will be drawn. The kinetics of the degradation reaction and of the formation of primary pyrolysis products have been investigated to compare the reactivity and substituent effects of the compounds studied.

Results and Discussion

In order to study the thermal behaviour of **4** and of the selected monoterpenes **1**, **2** and **3** we chose the dilution gas pyrolysis technique with oxygen-free nitrogen as the carrier gas, as reported in ref.[1] The advantages of this method are the short overall reaction time and the high reproducibility of the results, which are necessary for kinetic investigations. Furthermore, low consumption of the starting material and an uncomplicated analysis of the product mixtures generated are advantageous.

Thermal Behaviour and Reaction Mechanism of α-Pinene, β-Pinene, Pinane and Nopinone

The thermal behaviour of monoterpenes **1**–**4** were studied. Gas chromatograms of the liquid product mixtures obtained from the thermal isomerisation of **1** (400 °C, trichloromethane as solvent), **2** (450 °C, trichloromethane), **3** (500 °C, trichloromethane) and **4** (500 °C, ethyl acetate) are depicted in Figure 1. Each investigated compound leads to one acyclic structural isomer, as determined by FID-GC and GC-MS (cf. Figure 1 and Scheme 1). The dependency of the conversion on the reaction temperature is depicted in Figure 2. The conversion of the bicyclic starting materials increases with temperature and depends on the substituents. Figure 2 clearly reveals the differences in the thermal behaviour of **1** and **2** compared with **3** and **4**. The conversion of **3** and **4** was effected in the temperature range of 450 to 550 °C, whereas the conversion of **2** occurs at a temperature 100 °C lower. The isomerisation of **1** starts at about 300 °C. Relative to **3** and **4**, **1** and **2** seem to be more reactive.

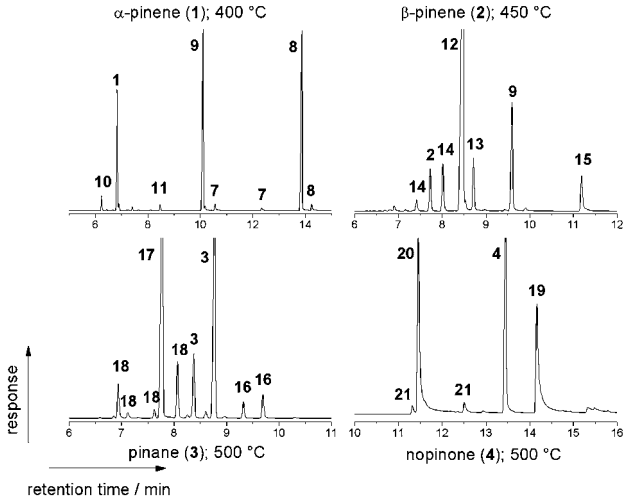


Figure 1. Gas chromatograms (GC-FID) of the liquid pyrolysis products of α-pinene (**1**), β-pinene (**2**), pinane (**3**) and nopinone (**4**) (carrier gas: N_2; flow rate: 1.0 L/min; 50 μL starting material; solvent for dissolution of products: trichloromethane for **1**, **2** and **3**, ethyl acetate for **4**; assigned compounds **7**–**21** are described in the text and a complete list of products can be found in the Supporting Information).

The relationship between the yields of the acyclic isomerisation products and the reaction temperature is depicted in Figure 3. The yield of each of the acyclic isomers reaches a maximum at a temperature that is dependent on the substituents. At temperatures higher then the maximum yield the fraction of consecutive reaction products (cp) formed from the acyclic isomers increases, which leads to an apparent decline in the yield of the acyclic isomer. By adding the yield of the cp to that of the corresponding isomer yield it is shown that after reaching a maximum, the changes in yield are minimal (Figure 3). The decrease in yield at temperatures higher than 550 °C is due to the decomposition of the thermal isomerisation products. Above this temperature, besides the liquid products, gaseous products are also formed, but these have not been investigated in this work. Compared to the acyclic isomers yielded from **1**–**3**, 7-methyl-1,6-octadien-3-one (**20**) generated from **4** is thermally more stable. Raising the temperature even higher than 550 °C led to an increase in the concentration of **20**. Side-reactions were less important in this reaction than in the reactions of **7**, **12** and **17**. Beside the main acyclic products, monocyclic isomers are also formed during the thermal isomerisation of the monoterpenes investigated: limonene (**9**) from **1** and **2**, *cis*-/*trans*-Δ8(9)-*p*-menthene (**16**) from **3**, 4-isopropenylcyclohexanone (**19**) from **4** and ψ-limonene (**13**) can be generated from **2**.

As shown in Figure 3, the acyclic products generated from **1**–**4** underwent consecutive reactions. Three of the four acyclic isomers **12**, **17** and **20** underwent a cyclisation reaction to form substituted cyclopentanes.[1,8,17] As shown

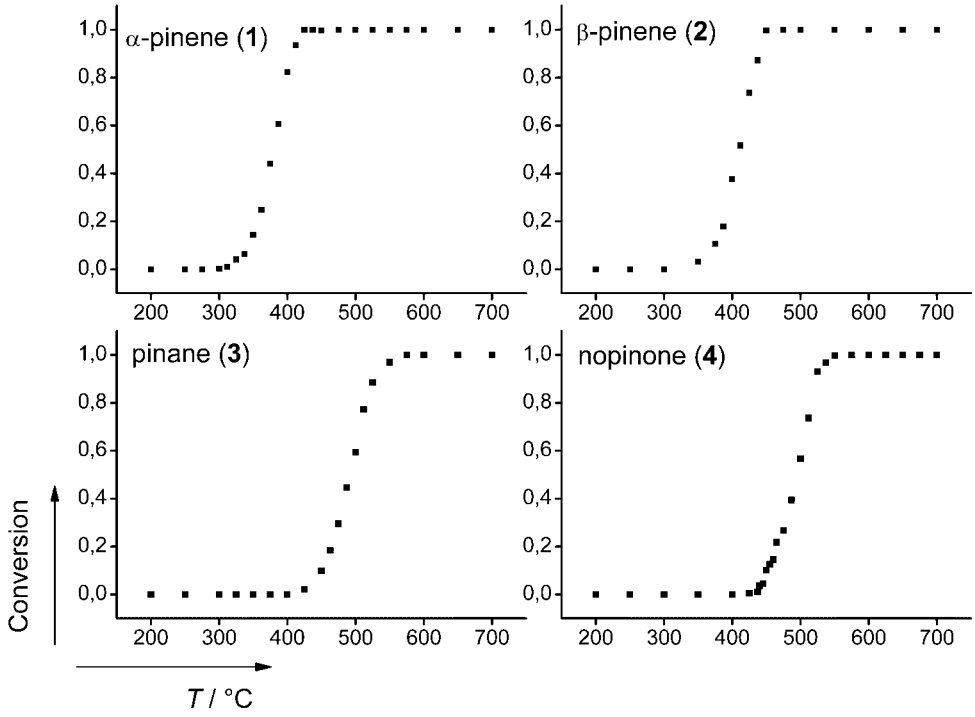


Figure 2. Conversion of compounds **1**–**4** in the thermal isomerisation reaction as a function of reactor temperature (carrier gas: N_2; flow rate: 1.0 L/min).

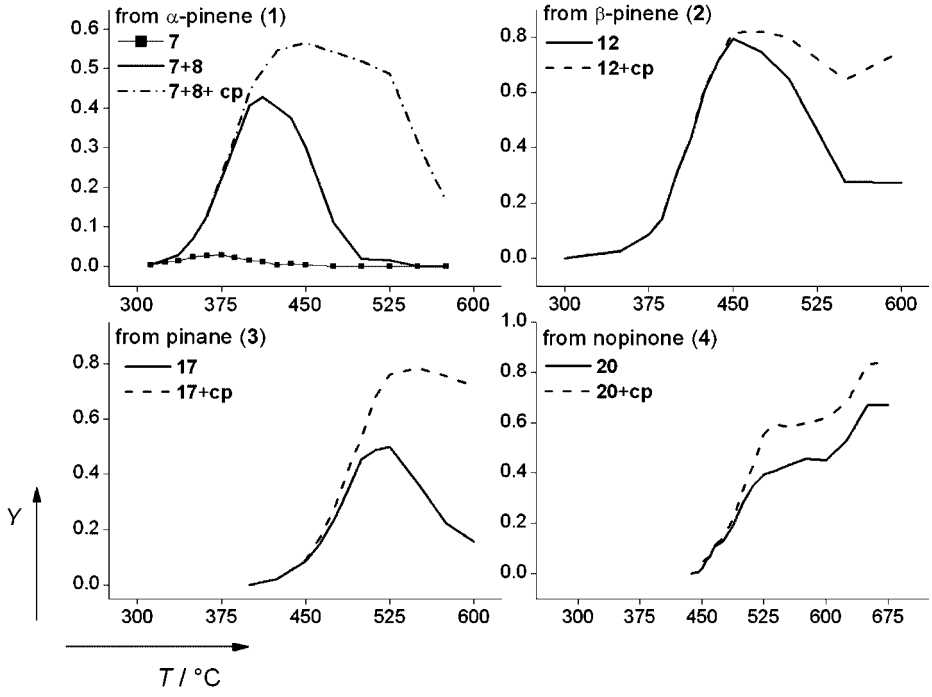
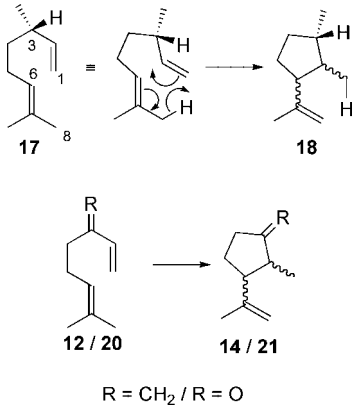


Figure 3. Yields of the acyclic and consecutive products otained from the pyrolysis of compounds **1**–**4** (Figure 2) as a function of reactor temperature (carrier gas: N_2; flow rate: 1.0 L/min; monocyclic products are not depicted; cp = consecutive reaction products of acyclic compounds).

in Scheme 2, for this type of cyclisation process two double bonds in the 1- and 6-positions (**17** as skeleton) and a hydrogen atom at C-8 are important Through hydrogen migration and a concerted cyclisation the cyclopentanes are formed in an ene-type reaction.[8,17] The number of cyclopentanes formed depends on the hybridisation of C-3 (Scheme 2). In the case of sp^2 hybridisation (**12**, **20**) four enantiomers are formed. The two diastereomeric forms **14**,

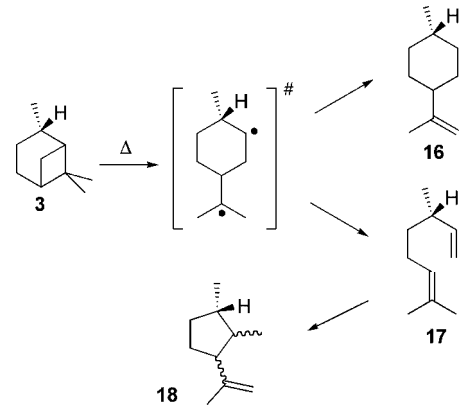
21 were separated and identified by FID-GC (Figure 1) and GC-MS. Four diastereomers of type **18** were identified by analysing the reaction mixture produced from the thermal isomerisation of **3**. The sp^3 hybridisation in the case of the acyclic isomerisation product **17** formed from **3** gave eight enantiomers (Figure 1, Scheme 2).



Scheme 2. Cyclisation of β-citronellene (**17**) analogues to the related cyclopentane derivatives by an ene-type reaction.

The thermal isomerisations of **1**–**4** proceed via biradical intermediates. In all cases, beside the acyclic isomerisation products and their consecutive products, at least one monocyclic isomer was identified in the respective reaction mixtures. The pyrolysis of pinane (**3**) led to **16**, **17** and to iridan-8-enes (**18**), as shown in Scheme 3. The formation of **16** and **17** can be explained by the reactions of the generated biradical (Scheme 3).[7,8] Compound **16** can be formed from the biradical through a [1,5] hydrogen shift, whereas **17** is formed by homolytic bond cleavage followed by intramolecular radical recombination. The consecutive reaction of **17** leading to **18** is described in Scheme 2.

Like the transformation of **3**, the isomerisation of α-pinene (**1**) proceeds via biradical intermediates. Because of the existing double bond in the reactive part of the molecule a biradical is formed with one of the radical positions being a resonance-stabilised allyl-type radical (Scheme 4). Racemic **9** is generated from these by a [1,5] hydrogen shift and the acyclic hydrocarbon **7** is formed in the same way as

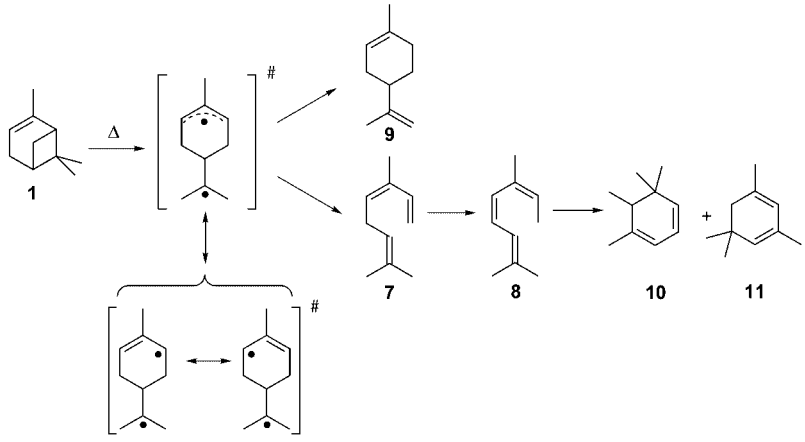


Scheme 3. Products formed by the thermal isomerisation of pinane (**3**) (carrier gas: N_2; flow rate: 1.0 L/min).

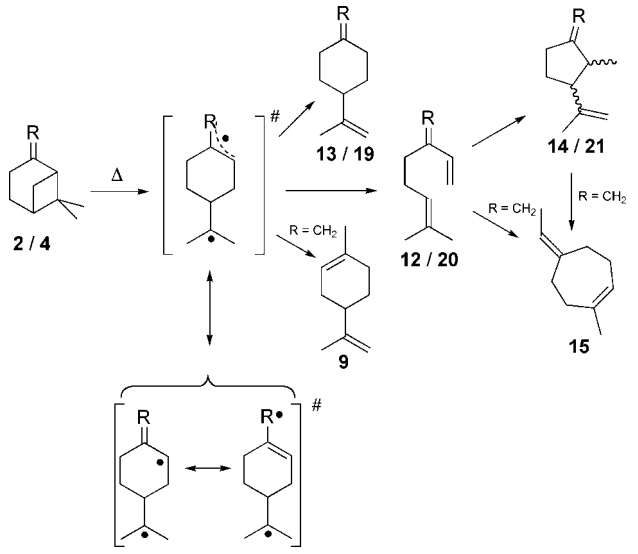
17 (Scheme 4).[7,10] Figure 1 and Figure 3 reveal that **7** was formed in only very low amounts. Through double bond migration the thermally more stable **8** with a conjugated double bond system was rapidly formed. Compound **7** as well as **8** were formed in either *cis* or *trans* isomeric forms. At elevated temperatures **8** isomerised to α-pyronene (**10**) and similarly substituted hydrocarbon **11** (Scheme 4).[10]

If β-pinene (**2**) was thermally converted primary pyrolysis products **9**, **12** and **13** would be formed from the biradical intermediates (Scheme 5).[1,7] As in the transformation of **1** the biradical generated from **2** contains one radical position stabilised as an allyl-type radical (Scheme 5). The acyclic main product **12** isomerised at temperatures higher than 450 °C to form iridane-1(6),8-dienes (**14**) and 5-ethylidene-1-methylcycloheptene (**15**), as shown in Scheme 5.[1,17,18] The key intermediates in the network of $C_{10}H_{16}$ hydrocarbons formed from **2** are the biradicals primarily formed and the acyclic unsaturated monoterpene hydrocarbon **12**. The reaction mechanism that describes both the formation of **12** and the other products has been reported in ref.[1]

To study the influence of heteroatoms on the reactivity and the reaction mechanism for the isomerisation of pinane-type compounds, nopinone (**4**) was chosen as an oxygen-containing β-pinene derivative. By formal replacement of the methylene group by oxygen, **4** can be generated from



Scheme 4. Products formed by the thermal isomerisation of α-pinene (**1**) (carrier gas: N_2; flow rate: 1.0 L/min).



Scheme 5. Thermal isomerisation of β-pinene (**2**) and nopinone (**4**) (carrier gas: N_2; flow rate: 1.0 L/min; β-pinene, R = CH_2; nopinone, R = O).

2 (ozonolysis, oxidation with $KMnO_4$).[1,19–22] The thermal behaviour of **4** is very similar to that of **2**. Formally, the C=C double bond is replaced by a carbonyl group.[23,24] By analysing the liquid product mixture obtained from the thermal isomerisation of **4**, almost all the analogous products of **2** were found (Scheme 5), except for those analogous to **9** and **15**. Owing to the fact that besides **20**, **19** is also found in the reaction mixture, the isomerisation of **4** has to proceed via biradical intermediates. The acyclic main product **20** is thermally more stable than **12**. Thus, replacement of the methylene group by oxygen leads to molecules with a lower reactivity.

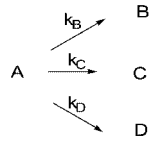
In summary, the thermal isomerisation of the investigated pinane-type compounds leads to at least one acyclic product (cf. Scheme 3, Scheme 4 and Scheme 5). The number of consecutive products formed depends on the reaction mechanism and the substituents on the pinane skeleton. The substituents have been shown to have a big influence on the reactivity of the bicyclic compounds and also on the tendency for the acyclic isomers to undergo consecutive reactions (e.g., **7**). In the case of a biradical reaction mechanism, at least one monocyclic product, which cannot be generated from the acyclic isomer, is formed during thermal isomerisation of the bicyclic compounds (e.g., **16** from **3**). The acyclic products **12**, **17** and **20** underwent ene-type cyclisation reactions leading to substituted cyclopentanes.

Kinetic and Activation Parameters

Variation of the gas velocity in the pyrolysis apparatus allowed us to set up various average residence times.[25] Thus it was possible to estimate rate constants for the degradation of the investigated monoterpenes. To calculate the residence times and the rate constants, it had to be ensured that no gaseous products were formed and that the liquid pyrolysis products were completely condensed. Despite these facts, the kinetic investigations had to be carried out in a temperature range in which the conversion of the bicyclic starting materials increases linearly with rising temperature (cf. Figure 2). The reaction products did not undergo further degradation and the liquid products were trapped completely within these temperature ranges. First-order kinetics were chosen for the kinetic model of the isomerisation reaction, viz. the formation of biradical intermediates was disregarded in the first approximation. Consecutive reactions of the products were neglected and the corresponding parts in the reaction mixture were added to the respective primary formed product. The parallel first-order reaction model was chosen to describe the thermal behaviour of the compounds investigated. General equations for the kinetic model used are given in Equation (1), where $k = k_B + k_C + \ldots$ and P = B, C, … (Figure 4).

$$\frac{d[A]}{dt} = -k[A] \Rightarrow [A] = [A_0] \cdot e^{-kt}$$

$$\frac{d[P]}{dt} = k_P[A] \Rightarrow [P] = [P_0] + \frac{k_P[A_0]}{k} \cdot \left(1 - e^{-kt}\right) \quad (1)$$



A	B	C	D
α-pinene (**1**)	**7**	**9**	
β-pinene (**2**)	**9**	**12**	**13**
pinane (**3**)	**16**	**17**	
nopinone (**4**)	**19**	**20**	

Figure 4. General reaction scheme for the kinetic investigations.

Various rate constants were determined by performing kinetic pyrolysis experiments at various temperatures. These data were fitted to calculate the Arrhenius parameters for the degradation of the investigated compounds and the products generated from them [Equation (2)]. Table 2 lists the activation parameters (activation energy E_A, frequency factor A) for the reaction networks investigated.

$$k_T = A \cdot e^{-\frac{E_A}{R} \cdot \frac{1}{T}} \quad (2)$$

With these data the thermal behaviour of each investigated compound under given experimental parameters (reactor volume, temperature, residence time, flow rate) was simulated and compared with the experimental data. On the basis of differences between simulation and experiment it is possible to benchmark the performance of the kinetic model. Figure 5 compares simulations of the reaction mixture composition with changing temperature with the experimental data for the investigated compounds **1**–**4**.

Table 2. Activation energies E_A and frequency factors A for the compounds investigated [Equation (2)].

Compound	E_A [kJ mol^{-1}]	A [s^{-1}]
α-Pinene (**1**)[a]	170 ± 2	5.0×10^{13}
Ocimene (**7**)	178 ± 2	1.3×10^{14}
Limonene (**9**)	161 ± 3	4.1×10^{12}
β-Pinene (**2**)[b]	186 ± 3	2.3×10^{14}
Myrcene (**12**)	188 ± 3	2.9×10^{14}
ψ-Limonene (**13**)	176 ± 4	1.8×10^{12}
Limonene (**9**)	177 ± 4	5.5×10^{12}
Pinane (**3**)[c]	168 ± 9	4.4×10^{11}
β-Citronellene (**17**)	165 ± 10	2.4×10^{11}
Δ8(9)-*p*-Menthene (**16**)	207 ± 18	1.8×10^{13}
Nopinone (**4**)[d]	166 ± 7	3.5×10^{11}
7-Methyl-1,6-octadien-3-one (**20**)	170 ± 16	3.4×10^{11}
4-Isopropenylcyclohexanone (**19**)	161 ± 10	6.3×10^{10}

[a] Temperature range (T) for the determination of the Arrhenius parameters: 337–412 °C. [b] T = 375–425 °C. [c] T = 450–512 °C. [d] T = 475–512 °C.

Correlation between simulation and experiment depends on the substituents and on the temperature (Figure 5). In general, experimental data and calculated values correlate very well until the temperature reaches the point of the curve corresponding to total conversion.[26] Visible discrepancies are within the error margins of the activation parameters E_A and A (Table 2). Notwithstanding, it seems to clear that the thermal behaviour of **2**, **3** and **4** is described much better by the calculated model than that of **1**. The differences between model and experiment in the case of **2**, **3** and **4** are marginal, which indicates that the thermal behaviour of theses compounds can be described by competing parallel reactions very well. It seems that the biradical intermediates the reactions proceed through have a minimal effect on the kinetic model. Hence the biradicals formed from **2**, **3** and **4** have very short half-lives: because of this they are not reaction intermediates but rather transition states.[27,28] In the case of **1**, the discrepancies between simulation and experiment are larger. However, they are within the calculated margin of error. Because of the thermal instability of **7**, which isomerises rapidly to **8**, the model of competing parallel reactions appears to be extended by the isomerisation of ocimene (**7**).

A comparison of the activation energies calculated for the isomerisation of **1** and **2** with the data reported in the literature (cf. Table 1 and Table 2) revealed that our values are smaller than those reported in the literature.[10,11] Nevertheless, the smaller activation energy for the thermal isomerisation of **1** compared with that of **2** was approved and is in agreement with the higher reactivity of **1**.

Conclusions

The thermal behaviour of the pinane-type monoterpenes α-pinene (**1**), β-pinene (**2**), pinane (**3**) and nopinone (**4**) has been investigated under similar experimental conditions. The bicyclic compounds clearly differ in their reactivity. Their thermal behaviour is directly influenced by the substitution of the bicyclic compounds, affecting the reactivity as well as the products found. α-Pinene **1** was the most reactive

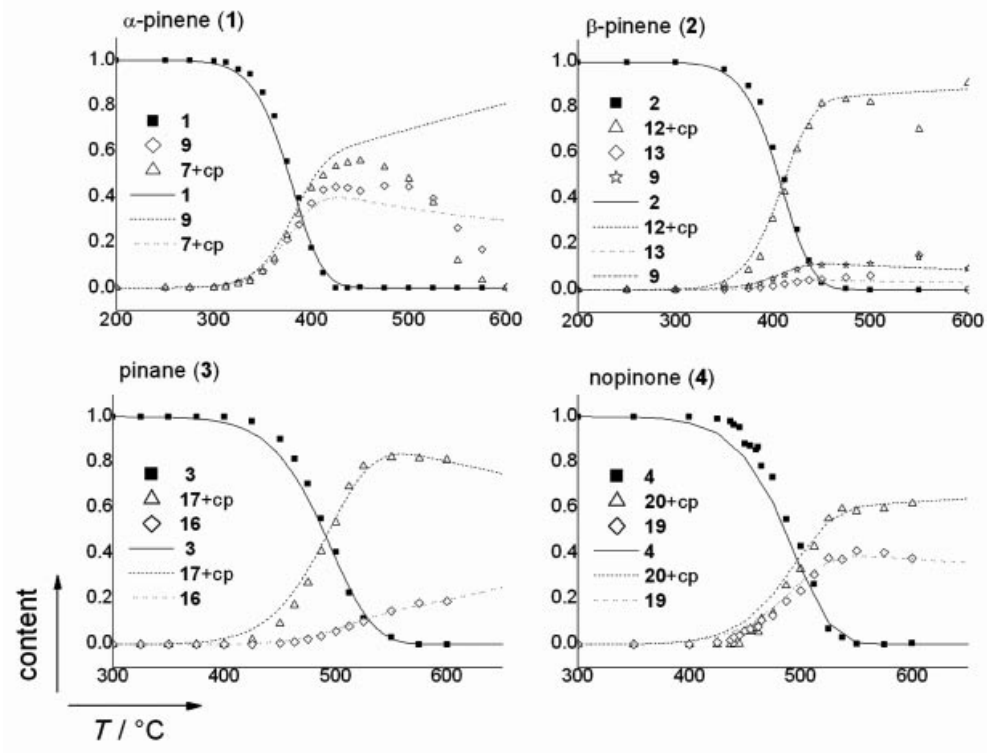


Figure 5. Simulated (lines) with experimental (symbols) data for α-pinene (**1**), β-pinene (**2**), pinane (**3**) and nopinone (**4**) product distributions at various temperatures (V_R: 23 mL; carrier gas: N_2; flow rate: 1.0 L/min; filled square: bicyclic starting material; open triangle: acyclic product and cp; open diamond/asterisk: monocyclic product).

compound, followed by **2**. The hydrogenated (**3**) and (oxygen-) modified molecules (**4**) have similar reactivities, but are less reactive than **1** and **2**.

The thermal isomerisations of the compounds investigated proceed via biradical transition states as acyclic as well as monocyclic products were identified.[1,7,11,12] Compounds that isomerise via transition states that are resonance-stabilised through the formation of an allyl-type radical are especially reactive in this type of isomerisation (**1** and **2**). It is shown in this work that the acyclic main products **12**, **17** and **20** undergo ene-type cyclisation reactions leading to cyclopentane derivatives **14**, **18** and **21**.

For the first time kinetic models for the thermal isomerisation of **3** and **4** are presented. Owing to the fact that all reactions were performed in the same apparatus and similar kinetic models were used, the activation parameters gained could be compared directly with each other. Comparison of the kinetic models and experimental data reveals that they match very well. Because of their short life-times, the biradicals formed during the thermal isomerisation reactions are considered transition states rather than reaction intermediates.

Based on the work presented herein the thermal behaviour of the acyclic compounds will be investigated. The ene-type cyclisation to the observed cyclopentanes will be analysed kinetically. The kinetic model presented will be improved with additional data. The palladium- or platinum-catalysed isomerisation of **7** to **8** is a topic of ongoing research.

Experimental Section

General Remarks: α-Pinene (**1**, ca. 98%), β-pinene (**2**, ca. 99%) and pinane (**3**, ca. 98%; *trans*/*cis*: 0.103) were purchased from Fluka and used without further purification. Purity was determined by capillary gas chromatography. Analyses were carried out with a 6890 Series GC and a 5890 Series II/5972 Series MSD GC from Agilent Technologies. Products were identified by comparison with either retention times and/or mass spectra of pure reference compounds. FID-GC: HP 5, 30 m × 0.32 mm × 0.25 μm, 5 psi H_2; program: 35 °C (hold 1 min), 4 K/min up to 80 °C, 4.5 K/min up to 90 °C, 35 K/min up to 280 °C (hold 3 min); injector temperature: 250 °C; detector temperature: 280 °C. GC-MS: HP 5, 30 m × 0.32 mm × 0.25 μm, 7 psi He; program: 55 °C (hold 1 min), 5 K/min up to 150 °C, 20 K/min up to 280 °C (hold 5 min); injector temperature: 280 °C, EI (70 eV). NMR spectra were recorded with a Bruker Avance 200 MHz system (measurement frequency was 200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR) in a 5-mm tube at room temperature. Measurements were carried out using $CDCl_3$ as solvent. IR spectra were measured with a Perkin-Elmer FT-IR spectrum 100 series device equipped with a universal ATR sampling accessory.

Pyrolysis: The investigated monoterpenes were pyrolysed in a temperature range of 250 to 700 °C. Dilution gas pyrolysis (DGP) was carried out in an electrically heated quartz tube of 50 cm length and with a pyrolysis zone of approximately 20 cm, using the apparatus reported in ref.[1]. In all experiments, oxygen-free nitrogen with a purity of 99.999% was used as the carrier gas. Residence times were varied by selecting different carrier gas flow rates (0.25, 0.4, 0.6, 0.8, 1.0 and 1.2 L/min). The starting material (50 μL) was introduced on a quartz ladle into the top part of the pyrolysis apparatus using a glass syringe (50 μL). The starting material was carried along with the nitrogen stream into the reactor. Vaporisation of the starting material was supported by heating the ladle to 200 °C with a hot blast. Pyrolysis products were collected in a cold trap (liquid nitrogen) and were dissolved in trichloromethane (1.5 mL) (for **1**, **2** and **3**) or in ethyl acetate (1.5 mL) (for **4**). The liquid products obtained were analysed by FID-GC and GC-MS.

Synthesis of 6,6-Dimethylbicyclo[3.1.1]heptan-2-one (Nopinone, 4): Nopinone was synthesised and purified as described in ref.[1] The purity after column chromatography and removal of the eluent was determined by FID-GC to be 99% pure nopinone. Yield: 3.5 g (60% based on β-pinene after purification); $n_D^{[20]}$ = 1.480. ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3 H), 1.33 (s, 3 H), 1.59 (d, 1 H), 1.96–2.06 (m, 2 H), 2.24–2.25 (m, 1 H), 2.35–2.38 (dd, 1 H), 2.51–2.58 (m 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.3, 21.9, 25.3, 25.7, 32.7, 40.2, 41.0, 57.7, 214.8 ppm. IR (ATR): $\tilde{\nu}$ = 2949, 2928, 2837 ($\nu_{aliph.\ C-H}$), 1706 ($\nu_{C=O}$), 1459 (δ_{C-H}) cm^{-1}. MS (EI, 70 eV, $C_9H_{14}O$): *m*/*z* (%) = 139 (0.9) [M + 1]$^+$, 138 (8.6) [M]$^+$, 123 (16.5), 109 (26.3), 95 (40.8), 83 (100), 81 (37.3), 67 (23.1).

Supporting Information (see also the footnote on the first page of this article): A scheme of the experimental set up used, a list of important monoterpenes with their IUPAC names, the procedures for the calculation of the average residence times and the kinetic simulations.

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[1] A. Stolle, C. Brauns, M. Nüchter, B. Ondruschka, W. Bonrath, M. Findeisen, *Eur. J. Org. Chem.* **2006**, 3317–3325.
[2] K. A. D. Swift, *Top. Catal.* **2004**, *27*, 143–155.
[3] N. Ravaiso, F. Zaccheria, M. Guidotti, R. Psaro, *Top. Catal.* **2004**, *27*, 157–168.
[4] J. L. F. Monteiro, C. O. Veloso, *Top. Catal.* **2004**, *27*, 169–180.
[5] B. Eloers, S. Hawkins (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, **1996**, vol. A27, p. 267.
[6] CST is a side-product from the pulp and paper industry containing large amounts of α- and β-pinene.
[7] L. Lemée, M. Ratier, J.-G. Duboudin, B. Delmond, *Synth. Commun.* **1995**, *25*, 1313–1318.
[8] R. Rienäcker, *Brennstoff-Chemie* **1964**, *45*, 20–23.
[9] W. D. Huntsman, V. C. Solomon, D. Eros, *J. Am. Chem. Soc.* **1958**, *80*, 5455–5458.
[10] J. J. Gajewski, I. Kuchuk, C. Hawkins, R. Stine, *Tetrahedron* **2002**, *58*, 6943–6950.
[11] H. G. Hunt, J. E. Hawkins, *J. Am. Chem. Soc.* **1950**, *72*, 5618–5620.
[12] J. E. Hawkins, J. W. Vogh, *J. Phys. Chem.* **1953**, *57*, 902–905.
[13] I. I. Ilyna, I. L. Simakova, V. A. Semikolenov, *Kinet. Catal.* **2001**, *42*, 686–692.
[14] I. I. Ilyna, I. L. Simakova, V. A. Semikolenov, *Appl. Catal., A* **2001**, *211*, 91–107.
[15] V. A. Semikolenov, I. I. Ilyna, I. L. Simakova, *J. Mol. Catal. A* **2002**, *182–183*, 383–393.
[16] J. J. Gajewski, L. P. Olson, M. R. Willcott, *J. Am. Chem. Soc.* **1996**, *118*, 299–306.
[17] J. de P. Teresa, I. S. Bellido, M. R. Alberdi Albistegui, A. San Feliciano, M. G. Benito, *Anal. Quim.* **1978**, *74*, 305–310.

[18] A. Stolle, Diploma Thesis, University of Jena, **2005**.
[19] B. R. Larsen, D. di Bella, M. Glasius, R. Winterhalter, N. R. Jensen, J. Hjorth, *J. Atmos. Chem.* **2001**, *38*, 231–276.
[20] J. Z. Yu, D. R. Cocker, R. J. Griffin, R. C. Flagan, J. H. Seinfeld, *J. Atmos. Chem.* **1999**, *34*, 207–258.
[21] P. L. Joshi, B. G. Hazra, *J. Chem. Res.* **2000**, 38–39.
[22] M. Nüchter, B. Ondruschka, R. Trotzki, *J. Prakt. Chem.* **2000**, *342*, 720–724.
[23] C. F. Mayer, J. K. Crandall, *J. Org. Chem.* **1970**, *35*, 2688–2690.
[24] J. M. Coxon, R. P. Garland, M. P. Hartshorn, *Aust. J. Chem.* **1972**, *25*, 2409–2415.
[25] The calculation procedure is described in the Supporting Information.
[26] At temperatures higher than the temperature corresponding to total conversion the difference between simulation and experiment increased because of decomposition of the products into smaller molecular fragments. These fragments cannot be condensed with the apparatus used and so the mass balance is not correct. Note that the kinetic model describes only the isomerisation of the bicyclic compounds. Decomposition products are not considered.
[27] A. F. Parsons, *An Introduction to Free Radical Chemistry*, Blackwell Science, Oxford, **2000**, chapter 5.
[28] O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., Wiley, New York, **1999**, chapter 2.

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