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SUPPORTING INFORMATION

Title: Comprehensive Kinetic and Mechanistic Considerations for the Gas-Phase Behaviour of Pinane-Type Compounds

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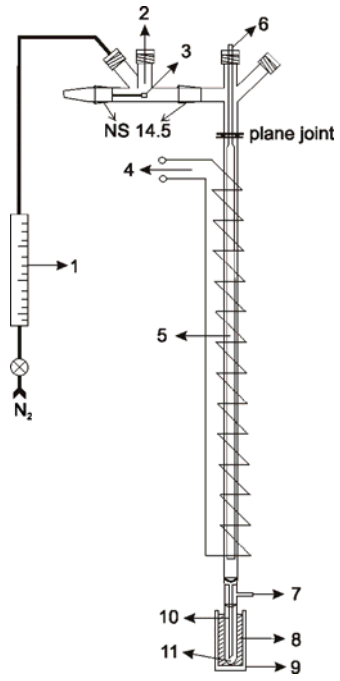
Schematic experimental setup for dilution gas pyrolysis:



Legend: 1 - rotameter for carrier gas, 2 - septum for dosing substrate, 3 - quartz ladle, 4 - electrical heating, 5 - quartz reactor, 6 - variable insert, 7 - exhaust for pyrolysis and carrier gas, 8 - coolant (liquid N_2), 9 - Dewar, 10 - cold finger, 11 - liquid product collector

Systematic IUPAC names for important compounds:

No.	Common name	IUPAC name	CAS-Reg.
1	α-pinene	2,6,6-trimethylbicyclo[3.1.1]hept-2-ene	7785-70-8
2	β-pinene	6,6-dimethyl-2-methylenbicyclo[3.1.1]heptane	18172-67-3
3	pinane	2,6,6-trimethylbicyclo[3.1.1]heptane	473-55-2
4	nopinone	6,6-dimethylbicyclo[3.1.1]heptane-2-one	38651-65-9
5	*cis*-2-pinanol	cis-2,6,6-trimethylbicyclo[3.1.1]heptane-2-ol	4948-28-1
6	linalool	3,7-dimethyl-1,6-octadiene-3-ol	22564-99-4
7	ocimene	3,7-dimethyl-1,3,6-octatriene	13877-91-3
8	alloocimene[a]	2,6-dimethyl-2,4,6-octatriene	673-84-7
9	limonene[b]	4-isopropenylmethylcyclohexene	9003-73-0
10	α-pyronene	1,5,5,6-tetramethyl-1,3-cyclohexadiene	514-94-3
11		1,3,5,5-tetramethyl-1,3-cyclohexadiene	4724-89-4
12	myrcene	7-methyl-3-methylene-1,6-octadiene	123-35-3
13	ψ-limonene	4-isopropenyl-1-methylenecyclohexane	499-97-8
14	iridane-1(6),8-diene	3-isopropenyl-2-methyl-1-methylenecyclopentane	56710-83-9
15		5-ethylidene-1-methylcycloheptene	15402-94-5
16	Δ8(9)-*p*-menthene	4-isopropenylmethylcyclohexane	6252-33-1
17	β-citronellene	3,7-dimethyl-1,6-octadiene	10281-56-8
18	iridane-8-ene	3-isopropenyl-1,2-dimethylcyclopentane	6983-03-5
19		4-isopropenylcyclohexanone	22460-53-3
20		7-methyl-1,6-octadiene-3-one	24903-94-4
21		3-isopropenyl-2-methylcyclopentanon	342614-82-8

[a] Commonly the (E,E)-form is know as alloocimene and the (E,Z)-form as neo-alloocimene.

[b] The racemic form of limonene is commonly known as dipentene.

Calculation procedure of average residence time: The average residence time τ was calculated approximately under following conditions: It was assumed that vaporisation of the educt was quantitative. Volume expansion during the reaction was neglected. Both, the carrier gas and the evaporated educt were handled like ideal gases, thus it was possible to calculate the total gas flow at room temperature $\dot{V}^*_{RT}$ with the following equation (1):

$$\dot{V}_{RT} = \frac{\rho_E \cdot V_E \cdot V_M}{M_E \cdot t_R} + \dot{V}_{N2} \qquad (1)$$

ρ_E - density of educt / g/mL

V_E - volume of educt / mL

M_E - molar mass of educt / g/mol

V_M - molar gas volume / 22.14 L/mol

t_R - reaction time / min

$\dot{V}^*_{N2}$ - carrier gas flow rate / L/min

The volume expansion due to the elevated reaction temperature was estimated with the ideal gas equation. It was shown by measurement of the temperature gradient that inside the reactor isothermal conditions were realised. It was possible to calculate the total flow rate at pyrolysing temperature $\dot{V}^*_{PT}$ with the help of the following equation (2):

$$\dot{V}_{PT} = \dot{V}_{RT} \cdot \frac{273.15 + T_r}{298.15} \qquad (2)$$

T_r - reaction temperature / °C

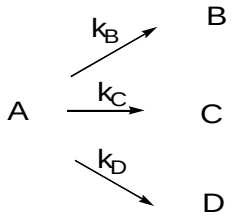
After determining the heated reactor volume V_R, the average residence time can be calculated as depicted in the following equation (3):

$$\bar{\tau} = \frac{V_R}{\dot{V}_{PT}} \qquad (3)$$

V_R - heated reactor volume / L

Calculation procedure for kinetic model: First-order kinetics was chosen for the kinetic model of the isomerisation reaction. Consecutive reactions of the products were neglected and the according parts in the reaction mixture were added to the respective primary formed product. The model of parallel first-order reactions was chosen to describe the thermal behaviour of the monoterpenes investigated (Figure 1).

Figure 1: General reaction scheme for the kinetic investigations



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

The integration of the generalised rate equations for the conversion of the educt (4) and the formation of the products (5) give equation (6) and (7).

$$\frac{d[A]}{d\tau} = -k[A] \quad (4) \quad \Rightarrow [A] = [A_0] \cdot e^{-k\tau} \quad (6)$$

$$\frac{d[P]}{d\tau} = k_P[A] \quad (5) \quad \Rightarrow [P] = [P_0] + \frac{k_P[A_0]}{k} \cdot \left(1 - e^{-k\tau}\right) \quad (7)$$

The rate constant k in equation (4-7) is the sum of all rate constants for the formation of the products (8). At every time of the reaction, the mass balance (9) has to be fulfilled. The calculation procedure for the residence time t is described in equation (1-3).

$$k = k_B + k_C + \ldots \quad (8)$$

$$[A_0] + [B_0] + [C_0] = [A] + [B] + [C] \quad (9)$$

The temperature dependency of each rate constant can be calculated with the help of the Arrhenius equation (10) and the calculated Arrhenius parameters given in Table 2 of the paper.

$$k_T = A \cdot e^{-\frac{E_A}{R \cdot T}} \quad (10)$$

The bicyclic educts used in this work had a purity higher than 98 % and no isomerisation products were detectable in the starting material. Due to this fact, it was assumed for the simulation that $[A_0]$ is 1 and the initial concentration of the products is 0. Mass balance (9) can be simplified to (11).

$$[A_0] = [A] + [B] + [C] \quad (11)$$

The reactor volume used for the calculation of the residence time (1-3) in case of the simulation was: V_R = 0.023 L. The concentration of the educt in the total gas flow was disregarded because of the low effect on average residence time. With the help of these boundary conditions we were able to calculate the reaction mixture composition in dependency of the reaction temperature. The composition was calculated with equation (12-14) for α-pinene, pinane and nopinone.

$$[A]_T = e^{-k_T \tau} \quad (12)$$

$$[B]_T = \frac{k_{B,T}}{k_T}\left(1 - e^{-k_T \tau}\right) \quad (13)$$

$$[C]_T = 1 - [A]_T - [B]_T \quad (14)$$

The composition of the reaction mixture for β-pinene, where three products were formed, was calculated with the help of the additional equation (15) and equation (14) was modified to (16).

$$[C]_T = \frac{k_{C,T}}{k_T}\left(1 - e^{-k_T \tau}\right) \quad (15)$$

$$[D]_T = 1 - [A]_T - [B]_T - [C]_T \quad (16)$$