KINETICS OF CYCLOADDITION REACTIONS OF CONJUGATED C5 DIENES

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Abstract

The kinetics of the formation of isomeric dimers and codimers via thermal dimerization and codimerization between 1,3-cyclopentadiene, isoprene, *cis*-1,3-pentadiene and *trans*-1,3-pentadiene were studied. The laboratory experiments were carried out in a batch reactor in a cyclohexane solution at different temperatures. Measured concentrations of the reactants and 1:1 Diels-Alder adducts were fitted to the kinetic model. Kinetic parameters for formation of the individual isomeric products and the summary reactions were determined. It was found that the activation energies of dimerizations of acyclic C5 dienes are by 20-40 kJ/mol higher than that of the dimerization of cyclopentadiene, and the activation energies of the formation of codimers of cyclopentadiene with 1,3-pentadienes are higher by 10-20 kJ/mol.

Key words: kinetics; Diels-Alder reactions; dimerization; codimerization; activation energy; cyclopentadiene; isoprene; 1,3-pentadiene; pyrolysis gasoline.

1. Introduction

This work is a part of our broader research focused on the kinetics of the thermal cyclo-addition reactions of dienes contained in the pyrolysis gasoline. The study was motivated by the need of kinetic data for the development of a complex mathematical model, enabling one to predict the changes of the concentrations of individual reactive components of the pyrolysis gasoline in the dependence on the operation conditions during its processing (in a series of rectification columns, dimerization reactors etc. [1]).

Pyrolysis gasoline is one of the liquid products from steam cracking of various hydrocarbon feedstocks. It consists of C5-C12 hydrocarbons and contains substantial amounts of dienes and olefins. C10 hydrocarbons in pyrolysis gasoline are mainly products of thermal cyclo-addition reactions of 1,3-cyclopentadiene (CPD), isoprene (ISP) and *cis*- and *trans*-1,3-pentadienes (cP, tP). Intentionally, not the term "Diels-Alder reactions" but "cycloaddition reactions" is used because, in addition to the [4+2]-cycloaddition reaction products, i.e., the so called Diels-Alder reaction, also the [4+4]- or [2+2]-cycloaddition reaction products of dienes can be present in pyrolysis gasoline [2]. For the sake of brevity, the term dimer is used for the product of the cycloaddition reaction of two identical molecules of a diene while the term codimer is applied for that of two unequal molecules. The corresponding reactions are simplifiedly called "dimerization" and "codimerization". Usually, the thermal dimerization of a particular diene or the codimerization reactions of a diene pair yield a higher number of isomeric adducts.

In the preceding paper [3] published in this journal we have presented results of our study of the thermal dimerization kinetics of cyclopentadiene, methylcyclopentadienes and of their codimerizations. The present study is focused on the kinetics of the cycloaddition reactions of conjugated C5 dienes, namely, 1,3-cyclopentadiene, isoprene and *cis*- and *trans*-1,3-pentadiene. So far, no summarizing kinetic study of this topic is available in the literature. Existing studies deal especially with the structural analysis and identification of the isomeric dimers or codimers formed, or with the determination of their chromatographic characteristics. Papers quantifying the kinetics are less frequent. The largest set of kinetic data is available for the cyclopentadiene dimerization which proceeds spontaneously already at room temperature and represents one of the best known examples of the Diels-Alder reactions of dienes (as reviewed in detail in [3]). Also, overall kinetic parameters of the

dimerizations of isoprene and *cis*- and *trans*-1,3-pentadiene, related to the diene consumption or to the formation of all isomeric adducts, are known [4 and the references cited therein]. Till now, however, the kinetics of the formation of individual dimers and codimers for cycloaddition C5 diene reactions was not assessed. The kinetic study by Muja *et al.* [5], in which the authors assessed the kinetic parameters of the formation of two dominant codimers of cyclopentadiene with isoprene, represents an exception. It is the aim of the present study to determine kinetic parameters of the C5 diene reactions mentioned above, especially those related to the formation of individual isomeric products.

2. Experimental

The kinetics of the reactions were measured in the liquid phase under isothermal conditions at several temperatures with cyclohexane present as solvent. Stainless steel pressure vessels of 2.7-ml volume, equipped with stainless steel covers with screw tops sealed with Teflon, were used. The vessels were filled with a scaled quantity of starting liquid mixture up to two-thirds of their inner volume. A set of several vessels filled with the same reaction mixture was concurrently immersed in an oil or water bath mixed using a magnetic stirrer. The bath was pre-heated to the required reaction temperature, which was then maintained by a thermostat. At certain pre-set intervals individual vessels were removed in successive steps from the bath and immediately cooled in a mixture of acetone and dry ice; the cooled reaction mixture was immediately chromatographically analysed. The first sample was taken out after 15 minutes; experimentally, this time is sufficient to equilibrate the temperatures of the reaction mixtures in the reactors with the temperature of the bath. The composition of this sample was regarded as the initial composition of the reaction mixture. The kinetic model enabled processing of the kinetic data even if the product concentrations in the reaction mixture at time t=0 were not zero.

The starting mixture for measuring the kinetics of dimerizations was a solution of an individual diene in cyclohexane. The starting mixture for measuring the kinetics of codimerizations was a mixture of CPD, an acyclic diene and cyclohexane.

CPD was prepared by thermal decomposition of 99.5% *endo*-dicyclopentadiene (*endo*-DCPD) by reflux under a distillation column with 18 theoretic plates. The distillate of pure CPD was cooled at the column head using a mixture of acetone and dry ice and was then kept at –20°C. Cyclohexane, isoprene, *cis*-1,3-pentadiene and *trans*-1,3-pentadiene were of commercial origin (Sigma–Aldrich–Fluka).

Quantitative analysis of reaction mixtures was based on gas chromatography (SHIMADZU GC-17 A version 3) with a flame ionization detector. The data obtained were processed using the integration software CSW. All samples were analysed on a 50-m-long HP-PONA capillary column with a temperature program of 40 °C for 5 min, increasing at 7 °C min^{-1} to 250 °C, held for 5 min. Retention times of studied isomeric products on the HP-PONA capillary column are given in our previous study [2].

It was found experimentally that the substances present in the reaction mixtures (including the solvent – cyclohexane) provide the same chromatographic response (within the limits of the measurement accuracy) and, therefore, their response factors are not significantly different from 1. The percentages of the peak areas of particular components in the chromatographic traces were therefore considered equivalent to weight percentages.

For the evaluation of the rate parameters according to the kinetic models used in this study, the mass fractions of the reaction mixture components were converted to molar concentrations. This procedure was described in detail in our study [3]. The identification of the chemical structures of the isomeric products formed by the dimerizations and codimerizations studied was the subject of our previous study [2].

3. Regression analysis of kinetic data

The regression analysis of experimental data was performed using the ERA (Easy Regression Analysis) software [6]. The software has tools for evaluation of the statistical significance and reliability of the parameters estimated. The values of the molar concentrations (in mmol/l) of the reaction components as a function of time were input parameters; estimated parameters were rate constants at the reference temperature of 120°C and activation energy E_a. The dependence of rate constant k_i on temperature was expressed by the Arrhenius relation:

$$k_i = k_{i0} \exp\left(\frac{E_{ai}(T - T_0)}{RTT_0} \right) \tag{1}$$

where T_0 is a reference temperature, k_i and k_{i0} are the rate constants of reaction i at temperature T or T_0, E_{ai} is the activation energy of reaction i and R is the universal gas constant.

A reference temperature was used in order to eliminate the strong correlation between the pre-exponential factor (frequency factor) A_{i0} and the activation energy E_{ai} in the non-modified Arrhenius equation. Significantly lesser correlation between the rate constant k_{i0} and the activation energy E_{ai} is characteristic of the modified relation (1).

The software has a graphical user interface that allows continuous visual control of the cogency of the computed concentration dependences to the experimental points during the optimization process. The differential equations in the model were solved numerically by Merson modification of the Runge-Kutta method of 4th order with variable lengths of the integration step. The values of the kinetic parameters were obtained by a modified optimization algorithm of adaptive random search. The sum of residual squares or weighted sum of residual squares was utilized as an objective function by the algorithm. In the case of the squares sum, the Diels-Alder reaction products with low rate constants are weighted less than those with large rate constants. In the case of the weighted squares sum all products are considered equally, yet the result can be strongly influenced by large errors when determining small concentrations. It was proved that the estimations of kinetic parameters obtained in accordance with both modifications of optimization criteria are satisfactorily congruent.

4. Results and Discussion

All kinetic measurements were made isothermally in temperature ranges where the Diels-Alder reactions studied can be considered irreversible [7-8]. The dependence of the component concentrations in the reaction mixtures on reaction time was monitored at selected temperatures.

4.1. Cyclopentadiene dimerization

In our studies, dimerization of CPD serves as a referential reaction. Its kinetics has been measured and assessed already in our preceding study [3]. Unlike the works referring till now to the kinetics of the CPD dimerization, our kinetic model takes into account, in addition to the formation of *endo*-dicyclopentadiene (*endo*-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoindene), also the formation of the minority *exo*-isomer (*exo*-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoindene). Activation energies E_{ai} and rate constants k_i for the equations of the type $r_i = k_i c^2_{CPD}$ at a referential temperature of 120 °C were determined. Kinetic parameters of both parallel reactions thus obtained are given in Table 1.

Table 1. Results of the regression analysis of the CPD dimerization kinetic model [3]

Reaction / Parameter	$k_{i(120°C)} \cdot 10^3$ [l.mol^{-1}.min^{-1}]	E_{ai} [kJ.mol^{-1}]
CPD $\rightarrow$ 0.5 *endo*-DCPD	67.5	70.6
CPD $\rightarrow$ 0.5 *exo*-DCPD	0.603	80.2

4.2. Dimerization of *trans*-1,3-pentadiene

Kinetics of the dimerization of *trans*-1,3-pentadiene was followed at 100, 120, 140 and 180°C. Experimental data are presented in Table 2. Formation of 7 dimers was observed in the temperature interval mentioned. In the following text they will be denoted as DtP 1 through DtP 7 and characterized by their retention time in the HP-PONA chromatographic column, as given in Table 3. The components DtP 1 and DtP 2 correspond to some of the geometrical isomers of 3,5-dimethyl-4-vinylcyclohexene and/or 3,4-dimethyl-5-vinyl-cyclohexene. The components DtP 3 and DtP 6 were unequivocally identified as *trans*- and *cis*-3-methyl-4-[(1*E*)-prop-1-en-1-yl]cyclohexene. The components DtP 4 and DtP 5 are *cis/trans* isomers of 3-methyl-5-[(1*E*)-prop-1-en-1-yl]cyclohexene but it is impossible to assign them specifically. The component DtP 7 is one of the geometric isomers of 3,4- or 3,7-dimethyl-cycloocta-1,5-diene [2].

The regression model of the dimerization of *trans*-1,3-pentadiene was constructed on the base of the following reaction scheme, taking into account the formation of six dimers:

tP $\rightarrow$ 0.5 DtP 1   (2)

tP $\rightarrow$ 0.5 DtP 2   (3)

tP $\rightarrow$ 0.5 DtP 3   (4)

tP → 0.5 DtP 4-5   (5)

tP → 0.5 DtP 6   (6)

Table 2 Experimental data from the kinetic measurements of *trans*-1,3-pentadiene dimerization. *Composition of the reaction mixtures in mmol/L in relation to the reaction time and reaction temperature*

t (min) X1	T (K) X2	c_{tP} (mmol.l^{-1}) Y1	c_{DtP1} (mmol.l^{-1}) Y2	c_{DtP2} (mmo.l^{-1}) Y3	c_{DtP3} (mmol.l^{-1}) Y4	c_{DtP4-5} (mmol.l^{-1}) Y5	c_{DtP6} (mmol.l^{-1}) Y6
0	373.15	609.7	0.15	0.00	0.57	0.00	0.72
510	373.15	596.2	0.21	0.15	0.72	0.26	1.08
1680	373.15	593.8	0.30	0.26	0.98	0.31	1.34
5830	373.15	534.5	0.41	0.36	2.16	0.77	2.58
0	393.15	1907.3	0.00	0.00	0.30	0.00	0.35
335	393.15	1816.6	0.60	0.45	3.04	1.00	3.54
1365	393.15	1708.9	2.29	1.75	10.23	3.15	12.22
2880	393.15	1608.1	5.54	4.04	26.89	7.88	32.13
4620	393.15	1536.3	7.48	5.54	37.97	11.32	50.30
0	413.15	713.5	0.0	0.0	1.1	0.0	0.0
120	413.15	711.8	0.3	0.2	1.7	0.4	2.1
245	413.15	705.6	0.5	0.3	2.4	0.6	2.8
1290	413.15	609.2	1.9	1.4	9.6	2.8	11.3
1680	413.15	551.7	2.1	1.5	9.9	2.9	11.5
0	453.15	712.5	0.3	0.3	1.6	0.4	2.0
60	453.15	671.6	1.7	1.2	8.2	2.7	9.3
120	453.15	624.4	2.4	1.7	11.3	3.6	12.5
275	453.15	524.5	3.7	2.5	18.0	5.5	19.7
1445	453.15	324.6	11.9	8.4	64.0	18.3	78.9

Due to the fact that the elution peaks of *cis/trans* isomers of 3-methyl-5-[(1*E*)-prop-1-en-1-yl]cyclohexene, that is, the components DtP 4 and DtP 5, partially overlap, the kinetics of their formation were evaluated together. The formation of the minority dimer DtP 7 having the cyclooctadiene skeleton was neglected in this model because its concentrations were too low to allow one to evaluate its kinetic reliably.

Model of the isothermal batch reactor included the equations (1) and (7) – (17).

$r_1 = k_1 c^2_{tP}$ (7)

$r_2 = k_2 c^2_{tP}$ (8)

$r_3 = k_3 c^2_{tP}$ (9)

$r_4 = k_4 c^2_{tP}$ (10)

$r_5 = k_5 c^2_{tP}$ (11)

$$\frac{dc_{tP}}{dt} = -r_1 - r_2 - r_3 - r_4 - r_5 \tag{12}$$

$$\frac{dc_{DtP1}}{dt} = 0.5 r_1 \tag{13}$$

$$\frac{dc_{DtP2}}{dt} = 0.5 r_2 \tag{14}$$

$$\frac{dc_{DtP3}}{dt} = 0.5 r_3 \tag{15}$$

$$\frac{dc_{DtP4-5}}{dt} = 0.5 r_4 \tag{16}$$

$$\frac{dc_{DtP6}}{dt} = 0.5 r_5 \tag{17}$$

where **c** and **k_{1-5}** represent molar concentrations and rate constants of reactions, respectively. Initial conditions for mass balance were:

$t = 0$, $c_{tP} = c^0_{tP}$, $c_{DtP1} = c^0_{DtP1}$, $c_{DtP2} = c^0_{DtP2}$, $c_{DtP3} = c^0_{DtP3}$, $c_{DtP4-5} = c^0_{DtP4-5}$, $c_{DtP6} = c^0_{DtP6}$ (18)

In the regression model, the dependence of rate constants on temperature was described by relation (1). The dimerization of *trans*-1,3-pentadiene was described by kinetic equations for second order reactions, (7) to (11). Since the kinetics of the cycloaddition reactions was measured in an excess of the solvent (cyclohexane), we assumed that in the reaction system the molar concentrations of the components are close to their activities.

Estimated values of the kinetic parameters $k_{i(120°C)}$ and E_{ai} obtained by optimizing the regression model are shown in Table 3 (E_{ai}) and in Fig. 1 ($k_{i(120°C)}$). Individual columns in the figure represent isomeric products, the heights of the columns correspond to the values of rate constants of the product formation, measured at the referential temperature 120°C, and the chemical structure is depicted above the columns. The model having the kinetic parameters mentioned above fitted well the temporal dependences of concentrations of the dimers formed within the whole temperature interval 100-180 C. This is illustrated by Fig. 2. For the sake of lucidity, only concentration profiles of two dominant isomers (DtP 3 and DtP 6) are shown.

The results of the measurements showed that, in the temperature range around 120°C, the overall rate of the *trans*-1,3-pentadiene dimerization (expressed as a sum of kinetic constants of the individual dimers formation) is by 3-4 orders of magnitude lower than that of the cyclopentadiene dimerization yielding *endo*-DCPD.
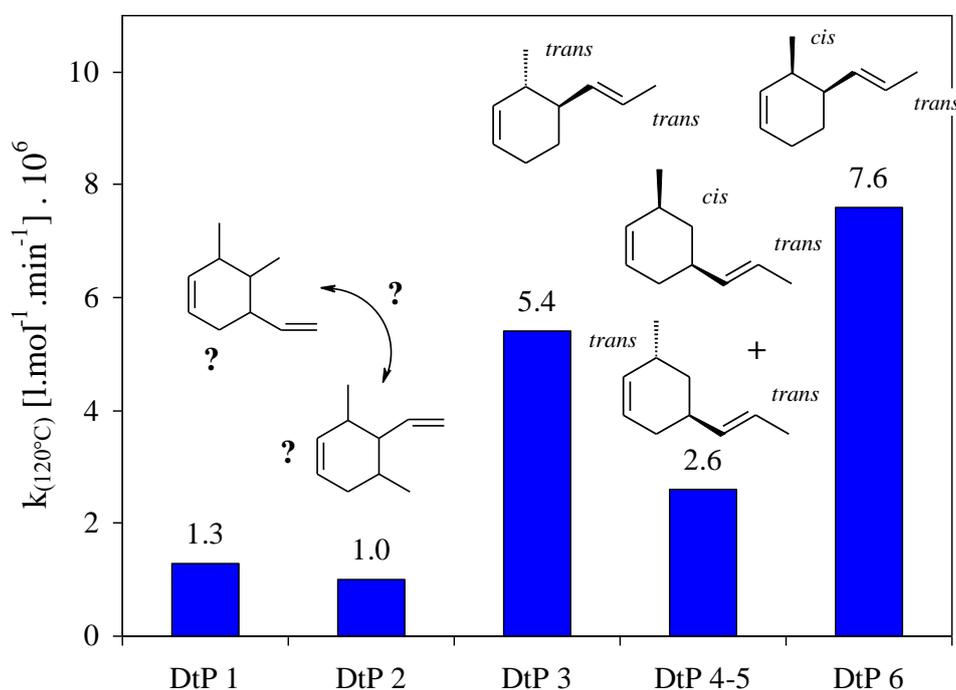
Fig. 1. Results of the regression analysis of the *trans*-1,3-pentadiene dimerization model. *Rate constants of the formation of individual dimers at 120 °C*

Table 3 Results of the regression analysis of the *trans*-1,3-pentadiene dimerization model. *Estimated values of activation energies of individual reactions*

Reaction	RT [min] of dimer product on HP-PONA[*]	E_{ai} [kJ.mol⁻¹]
tP → 0.5 DtP 1	*16.56*	101.4
tP → 0.5 DtP 2	*17.14*	90.9
tP → 0.5 DtP 3	*18.02*	102.0
tP → 0.5 DtP 4-5	*18.21 + 18.27*	87.5
tP → 0.5 DtP 6	*18.60*	99.5

*) retention time on a HP-PONA capillary column under the temperature programme
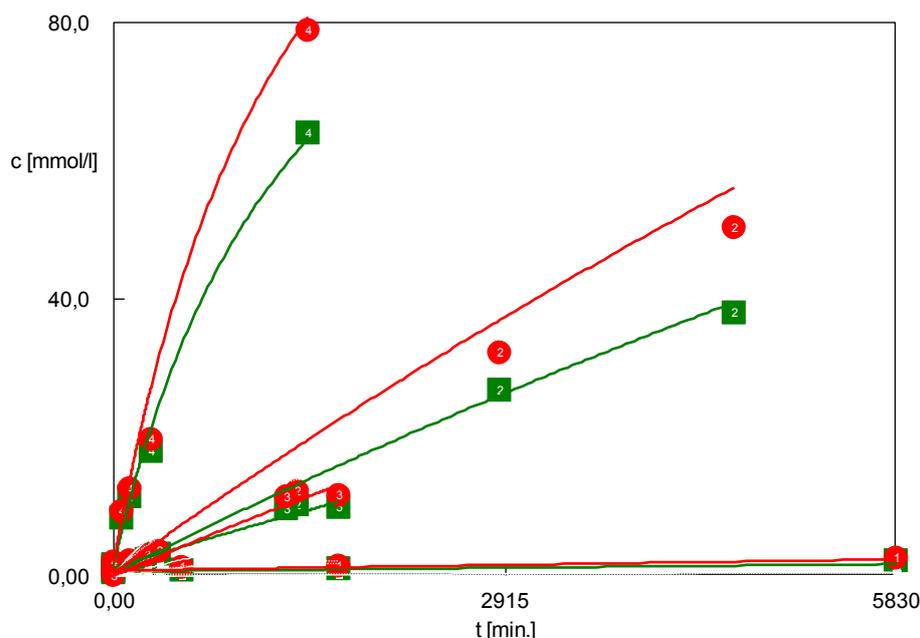
• − c_{DtP6}, ■ − c_{DtP3}, (1) − 100°C, (2) − 120°C, (3) − 140°C, (4) − 180°C

Fig. 2. Comparison of experimental data of *trans*-1,3-pentadiene dimerization with the results of the model. *Concentration profiles of dominant isomers DtP 3 and DtP 6 (curves represent concentration dependences yielded by the model)*

4.3. Cycloaddition reactions in the system cyclopentadiene/*trans*-1,3-pentadiene

Kinetic measurements were performed at 60, 100, 120 and 140 C. At these temperatures the reaction mixtures contained dimers of cyclopentadiene, dimers of *trans*-1,3-pentadiene and 5 components corresponding to codimers of CPD and *trans*-1,3-pentadiene (further CPD-tP). Retention characteristics of codimers are shown in Table 5. The codimers CPD-tP 3 to 5 are *endo*- and *exo*-5-[(1*E*)-prop-1-en-1-yl]-2-norbornene and 4-methyl-3a, 7,7a-tetrahydro-1H-indene, respectively. The codimers CPD-tP 1 and 2 are *endo*-/*exo*-isomers of 5-methyl-6-vinyl-2-norbornene but their resolution was not possible [2].

Under the conditions of kinetic measurements (dilute solutions, temperatures up to 140 C), the relative content of codimers CPD-tP in the reaction mixtures did not virtually change with reaction times and temperature. Nevertheless, orientation kinetic experiments with *undiluted* starting reactants and long reaction times, performed at 140°C and above, proved that *endo*-5-[(1*E*)-prop-1-en-1-yl]-2-norbornene (CPD-tP 3) can rearrange to 4-methyl-3a, 4,7,7a-tetrahydro-1*H*-indene (CPD-tP 5). The concentration of CPD-tP 5 increased with reaction time at a simultaneous decrease of the concentration of the codimer CPD-tP 3; and CPD-tP 5 gradually prevailed over the other codimers. Apparently, this is the thermal sigmatropic shift [*3,3*], known as the Cope rearrangement [9]. Due to the fact that, under the given conditions of the kinetic measurements of cycloaddition reactions of CPD with *trans*-1,3-pentadiene when the Cope rearrangement of CPD-tP 3 to CPD-tP 5 virtually does not take place and the predominant reaction route of the codimer CPD-tP 3 formation is the cycloaddition of CPD with *trans*-1,3-pentadiene, the rearrangement under discussion was not included into the kinetic model.

It is incorrect to construct the kinetic scheme of the codimerization reactions under the assumption that the reactions are isolated. The cycloaddition reactions in a system of two or more dienes (i.e., dimerizations and codimerizations) are competitive and parallel and must therefore be solved together.

To calculate kinetic parameters of the codimerization reactions of CPD with *trans*-1,3-pentadiene, a model was constructed on the basis of the following reaction scheme:

CPD → 0.5 DCPD	(19)	CPD + tP → CPD-tP 4	(22)
CPD + tP → CPD-tP 1-2	(20)	CPD + tP → CPD-tP 5	(23)
CPD + tP → CPD-tP 3	(21)		
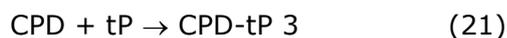
Since the difference in the reaction rates between the formation of codimers and dimers of *trans*-1,3-pentadiene was more than one order of magnitude, it was possible to neglect the dimerization of *trans*-1,3-pentadiene and thus simplify the model. The formation of *exo*-DCPD was included into the reaction (19). The kinetic of the minority isomers CPD-tP 1 and CPD-tP 2 was evaluated jointly. The regression model was constructed using relationship (1) and the following balanced equations:

$$r_1 = k_1 c^2_{CPD} \qquad (24) \qquad\qquad r_4 = k_4 c_{CPD} . c_{tP} \qquad (27)$$

$$r_2 = k_2 c_{CPD} . c_{tP} \qquad (25) \qquad\qquad r_5 = k_5 c_{CPD} . c_{tP} \qquad (28)$$

$$r_3 = k_3 c_{CPD} . c_{tP} \qquad (26)$$

$$\frac{dc_{CPD}}{dt} = -r_1 - r_2 - r_3 - r_4 - r_5 \qquad\qquad (29)$$

$$\frac{dc_{tP}}{dt} = -r_2 - r_3 - r_4 - r_5 \qquad\qquad (30)$$

$$\frac{dc_{DCPD}}{dt} = 0.5\, r_1 \qquad\qquad (31)$$

$$\frac{dc_{CPD-tP1-2}}{dt} = r_2 \qquad\qquad (32)$$

$$\frac{dc_{CPD-tP3}}{dt} = r_3 \qquad\qquad (33)$$

$$\frac{dc_{CPD-tP4}}{dt} = r_4 \qquad\qquad (34)$$

$$\frac{dc_{CPD-tP5}}{dt} = r_5 \qquad\qquad (35)$$

In the model, experimental data given in Table 4 were used. The results of the regression analysis of the model are presented in Table 5 (E_{ai}) and in Fig. 3 ($k_{i(120°C)}$). The model fits the data well and the statistical analysis showed that the kinetic parameters estimates are reliable. Activation energies of the formation of individual codimers of CPD-tP do not differ significantly and are by approx. 10-20 kJ/mol higher than those of the formation of *endo*-DCPD.

Table 4. Experimental data from the kinetic measurements of the reaction system cyclo-pentadiene – *trans*-1,3-pentadiene.

t	T	c_{tP}	c_{CPD}	$c_{CPD-tP3}$	$c_{CPD-tP4}$	$c_{CPD-tP5}$	c_{DCPD}	$c_{CPD-tP1-2}$
(min)	(K)	(mmol.l^{-1})	(mmol.l^{-1})	(mmol.l^{-1})	(mmol.l^{-1})	(mmol.l^{-1})	(mmol.l^{-1})	(mmol.l^{-1})
X1	X2	Y1	Y2	Y3	Y4	Y5	Y6	Y7
0	373.15	887.8	422.1	1.51	0.00	0.00	320.0	0.00
30	373.15	886.5	358.1	2.10	0.22	0.21	363.3	0.09
120	373.15	885.9	226.0	2.88	0.94	0.95	426.4	0.22
423	373.15	746.4	83.3	4.92	1.57	1.52	482.6	0.57
0	393.15	761.0	576.2	0.90	0.20	0.00	275.8	0.05
13	393.15	765.4	359.3	2.70	0.70	0.50	370.7	0.25
60	393.15	776.9	172.5	5.50	1.40	1.10	474.4	0.45
150	393.15	746.9	84.9	8.00	2.00	1.70	517.3	0.70
360	393.15	767.7	46.6	10.80	3.20	2.50	536.9	1.00
0	413.15	949.7	373.2	12.73	3.67	2.74	1354.0	1.35
13	413.15	945.7	222.4	14.93	4.31	3.43	1441.9	1.78
30	413.15	937.9	134.7	19.24	5.43	4.26	1477.1	2.02
65	413.15	930.1	97.7	23.35	6.41	5.24	1500.8	2.51
135	413.15	911.4	83.7	26.14	7.98	6.64	1513.9	2.82
0	333.15	2526.1	2318.1	0.44	0.00	0.00	73.9	0.00
60	333.15	2524.1	2070.1	1.08	0.21	0.23	250.3	0.11
170	333.15	2523.7	1652.1	1.93	0.33	0.44	464.1	0.27
1030	333.15	2509.6	543.8	7.65	1.77	2.04	945.5	0.92
3010	333.15	2507.4	240.1	11.70	2.76	3.18	1109.8	1.36

Table 5 The results of the regression analysis of the kinetic model comprising the reactions (19)-(23). *Estimates of the activation energy values of the formation of individual codimers CPD-tP.*

Reaction	RT [min] of codimer on HP-PONA	E_{ai} [kJ.mol^{-1}]
CPD + tP → CPD-tP 1-2	*16.09 + 16.16*	81.6
CPD + tP → CPD-tP 3	*18.10*	87.0
CPD + tP → CPD-tP 4	*18.20*	90.4
CPD + tP → CPD-tP 5	*19.46*	86.1
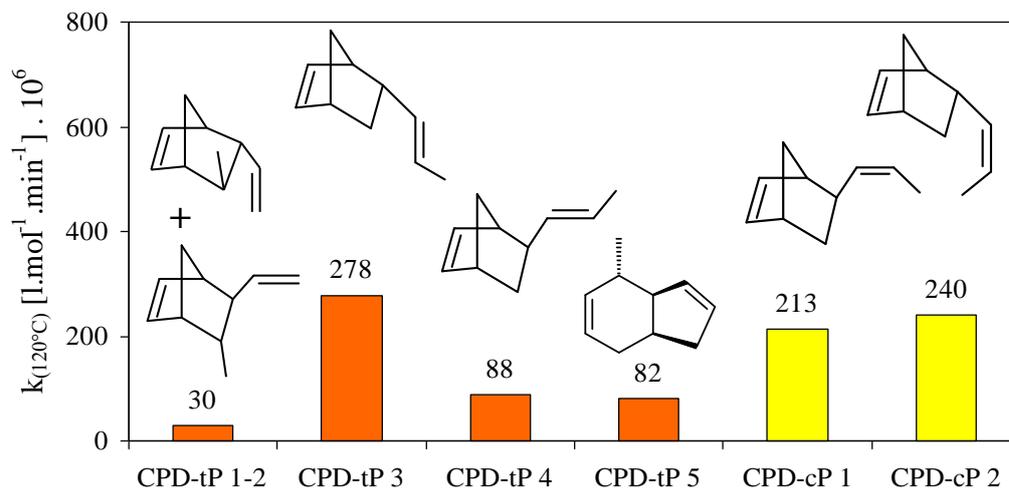
Fig. 3. The results of the regression analyses of the kinetic models for the systems cyclopentadiene – *trans*-1,3-pentadiene and cyclopentadiene – *cis*-1,3-pentadiene. *Rate constants of the formation of the codimers of cyclopentadiene with cis- and trans-1,3-pentadiene at 120°C.*

4.4. Dimerization of *cis*-1,3-pentadiene

In the corresponding reaction mixtures, 7 compounds (DcP 1-7) having molar mass of 136 g/mol were found which corresponds to that of the *cis*-1,3-pentadiene dimers. Their retention times in the chromatographic column HP-PONA are presented in our preceding paper [2]. There was not enough information to identify unambiguously the structures of the products. Estimates of the structures are shown in Fig. 4. The dimer DcP 3, dominating during measurements at 120 C, was the only structure which was unequivocally determined, namely as *trans*-1,2-di[(1*Z*)-prop-1-en-yl]cyclobutane [2]. Kinetic measurements of the *cis*-1,3-pentadiene dimerization were performed at 120 and 175°C. The experiments showed that the reaction temperature affects dramatically distribution of the products. At 120°C, isomers with the cyclobutane skeleton, i.e., DcP 3 and DcP 5, prevailed in the reaction mixture whereas at 175 ^{o}C the same was true for isomers with the cyclohexene and cyclo-octadiene skeleton, namely DcP 4, DcP 6 and DcP 7. Temporal concentration profiles of the components DcP 3 and DcP 5 had a shape characteristic for intermediates (concentration maximum). Thus it is obvious that the kinetic model of the reactions of *cis*-1,3-pentadiene proceeding at elevated temperatures must include also the Cope rearrangements of the products DcP 3 and DcP 5, and cannot be correctly assessed without their separate kinetic measurements. Pure *cis*-1,3-pentadiene is presently unavailable commercially and the disposable amount of this substance was so small that it did not allow us to perform such experiments. The estimates of the "activation energies" of the formation of individual isomers of DcP, obtained by solving the model not including the Cope rearrangements of the products, would not be physically substantiated. Hence, only the rate constants of the formation of the individual isomers of DcP were evaluated from the kinetic data at 120 C (Table 6), when the extent of the rearrangements of the dimers can be neglected (Fig. 4). Long reaction times (days), very low concentrations of the products in the reaction mixtures and a small number of experimental points resulted in a higher experimental error and, consequently, the rate constant values obtained should be considered as orientation estimates only (the reliability of the determination of k_i is within one order of magnitude). Nevertheless, to make a concept of the extent of the *cis*-1,3-pentadiene

dimerization, these data are sufficient. The rate of the *cis*-1,3-pentadiene formation, as compared with that of the products of the cycloaddition reactions of other C5 dienes, is the lowest (at 120 C, it is by 4 orders of magnitude lower than the rate of CPD dimerization). The rate constant of a summary reaction of the *cis*-1,3-pentadiene dimers formation at 175 C was evaluated as well and amounts to 7.8×10^{-5} L.mol^{-1}.min^{-1}.

Table 6 Experimental data from the kinetic measurements of *cis*-1,3-pentadiene dimerization.

t (min)	T (K)	c_{cP} (mol.l^{-1})	c_{DcP1} (mol.l^{-1})	c_{DcP2} (mol.l^{-1})	c_{DcP3} (mol.l^{-1})	c_{DcP4} (mol.l^{-1})	c_{DcP5} (mol.l^{-1})	c_{DcP6} (mol.l^{-1})	c_{DcP7} (mol.l^{-1})
X1	X2	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8
0	393.15	2178.4	0.0	0.00	0.1	0.0	0.0	0.0	0.0
440	393.15	2172.6	0.2	0.05	2.7	0.3	0.9	0.3	0.3
1500	393.15	2165.4	0.4	0.18	9.7	0.6	1.9	0.9	1.0
3370	393.15	2105.2	1.2	0.40	27.3	1.4	4.7	1.6	1.5
6319	393.15	2027.8	2.2	0.99	50.9	3.0	9.4	3.1	3.2
0	448.15	1405.2	0.13	0.00	1.76	0.00	0.57	1.32	0.00
60	448.15	1387.9	0.57	0.18	7.66	0.57	1.41	0.71	1.01
120	448.15	1355.4	0.83	0.28	10.19	1.01	1.74	1.24	1.88
240	448.15	1349.9	1.46	0.52	14.46	2.59	2.36	3.35	6.03
1440	448.15	1217.0	1.95	0.56	10.90	15.18	1.68	18.79	38.98
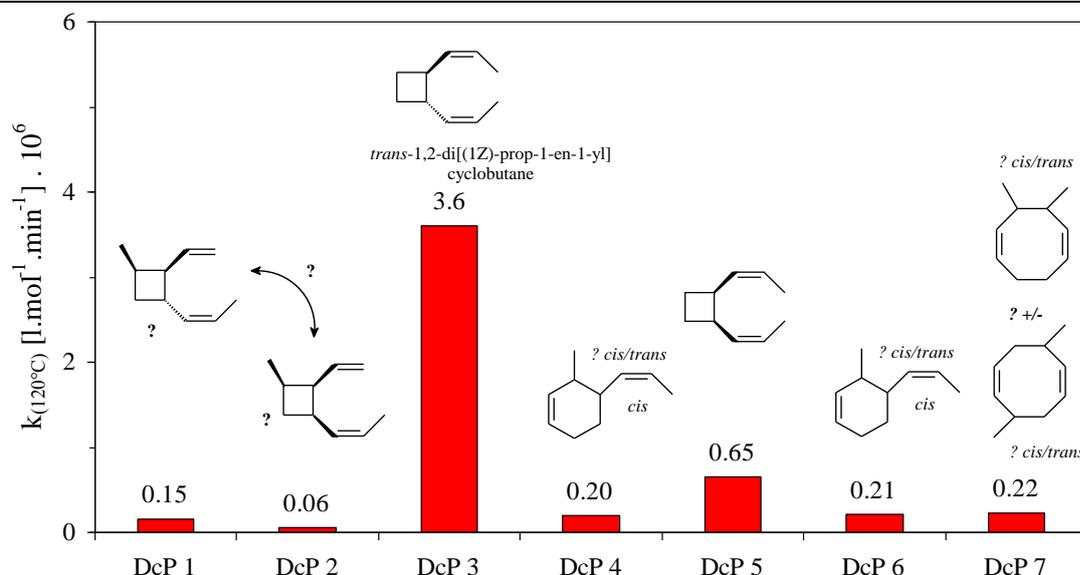
Fig. 4. Results of the regression analysis of the model of *cis*-1,3-pentadiene dimerization. *Rate constants of the dimer formation at 120°C*

4.5. Cycloaddition reactions in the system cyclopentadiene/*cis*-1,3-pentadiene

Kinetic measurements were performed at 80, 100, 120 and 140 C. Experimental data obtained are given in Table 7. In addition to *exo*- and *endo*-DCPD and the *cis*-1,3-pentadiene dimers, also a non-negligible concentrations of two codimers of cyclopentadiene with *cis*-1,3-pentadiene (further CPD-cP) were found in the reaction mixture. They were identified as *exo*- and *endo*- isomers of 5-[(1*Z*)-prop-1-en-1-yl]-2-norbornene [3].

In the temperature range under study (80 to 140 C), no isomerizations of the products formed were observed and the kinetic model was therefore constructed on the basis of the following reaction scheme:

CPD → 0.5 DCPD   (36)

CPD + cP → CPD-cP 1 (*exo*-5-[(1*Z*)-prop-1-en-1-yl]-2-norbornene)   (37)

CPD + cP → CPD-cP 2 (*endo*-5-[(1*Z*)-prop-1-en-1-yl]-2-norbornene)   (38)

CPD + cP → Σ other products   (39)
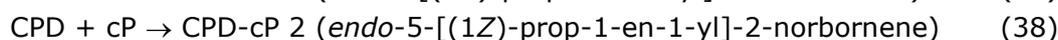
The formation of *exo*-DCPD was included into the reaction (36). The formal reaction (39) in the model took into account the depletion of the reactants through other reactions (trimerization of CPD, dimerization of cP and the formation of minority codimers CPD-cP)

and thus increased the reliability of kinetic parameters determination of the CPD-cP 1 and CPD-cP 2 formation. The balance equations in the regression model were constructed in analogy to preceding cases.

Table 7 Experimental data from the kinetic measurements of the reaction cyclopentadiene-*cis*-1,3-pentadiene.

t (min) X1	T (K) X2	c_{cP} (mmol.l^{-1}) Y1	c_{CPD} (mmol.l^{-1}) Y2	$c_{CPD-cP1}$ (mmol.l^{-1}) Y3	$c_{CPD-cP2}$ (mmol.l^{-1}) Y4	c_{DCPD} (mmol.l^{-1}) Y5
0	353.15	1000.1	720.7	0.0	0.0	149.4
45	353.15	999.7	616.6	0.4	0.5	201.9
95	353.15	998.4	523.3	0.7	0.8	243.7
150	353.15	994.4	424.4	0.9	1.1	264.9
570	353.15	994.6	195.7	2.5	2.7	408.6
1190	353.15	992.1	116.2	3.3	3.7	444.3
0	373.15	972.7	631.9	0.0	0.0	176.6
21	373.15	969.0	501.1	0.8	1.0	242.5
40	373.15	963.0	424.4	1.2	1.3	265.3
130	373.15	962.8	230.9	2.4	2.7	349.9
285	373.15	962.1	129.5	3.7	4.1	401.2
455	373.15	961.8	86.3	4.6	5.0	423.1
0	393.15	894.5	556.0	0.5	0.2	148.8
25	393.15	882.1	294.0	2.4	2.7	282.5
50	393.15	880.2	196.9	3.5	3.8	328.3
80	393.15	879.2	140.8	4.4	4.8	354.2
172	393.15	878.2	76.9	6.1	6.6	385.3
425	393.15	872.1	38.8	8.3	9.0	403.1
0	413.15	939.4	406.1	1.8	2.1	264.6
10	413.15	934.7	228.5	3.8	4.2	359.8
25	413.15	931.1	140.8	5.7	6.2	385.3
40	413.15	928.4	102.8	6.8	7.3	414.8
70	413.15	925.9	60.2	8.6	9.4	446.3
145	413.15	921.5	29.7	13.6	14.9	444.0

The results of the model regression analysis are summarized in Table 8 (E_{ai}) and in Fig. 3 ($k_{i(120°C)}$). The estimates of the parameters are relatively reliable and the model fits well the data measured, as seen in Fig. 5. Activation energies of the formation of both majority codimers CPD-cP do not virtually differ from each other and are approx. by 10 kJ/mol higher than that of the formation of *endo*-DCPD. Although at around 120 C *cis*-1,3-pentadiene dimerizes much slower than the *trans* isomer, overall rates of codimerizations of both isomers with cyclopentadiene are comparable in this temperature range.

Table 8. Results of the regression analysis of the kinetic model comprising the reactions (36)-(39). *Estimates of the activation energies of the individual codimers CPD-cP formation.*

Reaction	**RT** [min] of codimer on HP-PONA	E_{ai} [kJ.mol^{-1}]
CPD + cP → CPD-cP 1	*18.19*	82.8
CPD + cP → CPD-cP 2	*18.36*	81.6

From the structures of the products in Fig. 3 it can be concluded:

1. During the codimerization of cyclopentadiene with 1,3-pentadienes, norbornene-type adducts are kinetically preferred, i.e., cyclopentadiene reacts as a diene substantially more quickly than 1,3-pentadiene (and also isoprene, see Fig. 6).
2. *Trans*-1,3-pentadiene behaves both as a diene and a dienophile, whereas *cis*-1,3-pentadiene serves only as a dienophile of cyclopentadiene (i.e., does not yield tetrahydro-indene adducts).
3. Outer double bond of 1,3-pentadiene undergoes cycloaddition more easily than the inner one.

Ishii *et al.* arrived at the same conclusions [10].
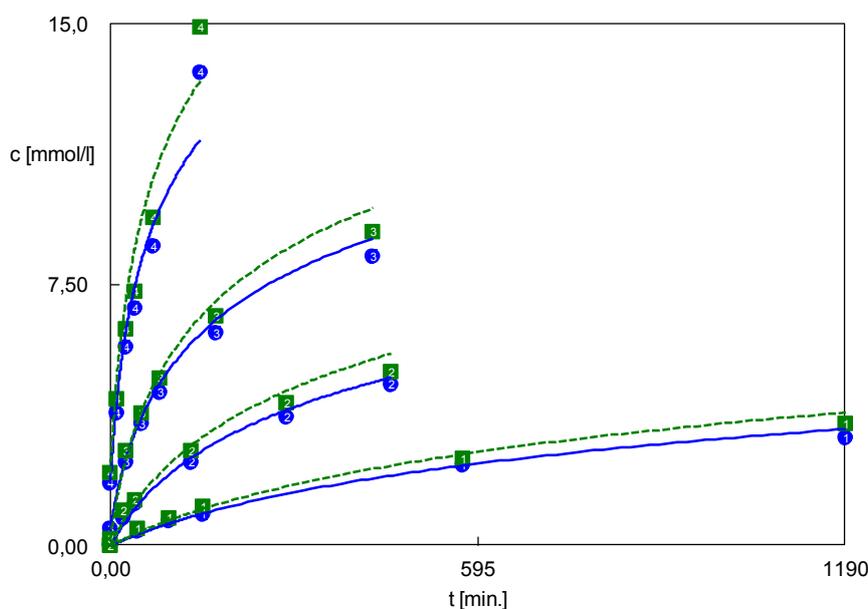
● − $c_{CPD-cP1}$, ■ − $c_{CPD-cP2}$, (1) − 80°C, (2) − 100°C, (3) − 120°C, (4) − 140°C

Fig. 5 Comparison of the experimental data of the CPD/*cis*-1,3-pentadiene codimerization with the results of the model. Concentration profiles of codimers of CPD-cP 1 and CPD-cP 2 *(the curves are evaluated concentration dependences)*

4.6. Isoprene dimerization

The kinetics of isoprene dimerization was measured at 100, 140, 160, 180 and 220 C. Kinetic measurements were performed with isoprene containing 200 ppm of a radical polymerization inhibitor (2,6-di-*tert*-butyl-*p*-cresol) and with distilled isoprene containing no inhibitor. Chromatographic analyses of the reaction mixtures yielded the same results for both cases. This is in accordance with published data [11-12], according which the oxidation inhibitors preventing peroxides formation and thus inhibiting radical polymerizations do not influence the rate of the Diels-Alder reactions. Experimental results showed that, in case of using the "unstabilized" isoprene, the content of chromatographically undetectable in the reaction products (i.e., in this case, products of radical polymerizations) is negligible up to 160 C. At higher temperatures and reaction times above 4 hrs the undetectable portion constitutes a few units of wt.%.

It followed from the kinetic measurements that, in the temperature interval under study (100-220°C), seven isomeric isoprene dimers are formed in non-negligible concentrations by a dimerization of isoprene. These isomers will be denoted as DISP 0 to DISP 6 in the following text. The structures of the isomers DISP 3 (diprene), DISP 4 (limonene) and DISP 0 (1-methyl-1-vinyl-2-isopropenyl-cyclobutane) were unequivocally proved. For DISP 0, the relative configuration of the substituents is unknown. The structure of the components DISP 1 and 2 corresponds to dimethyl-substituted vinylcyclohexenes while that of DISP 5 and 6 to dimethyl-substituted cyclroocta-1,5-dienes [2]. The formation of dimers with the cyclobutane and cyclooctadiene skeletons indicates that, on heating, isoprene undergoes not only the Diels-Alder reaction but also the cycloaddition reaction of the type [2+2] and [4+4].

The mathematical model of the reaction kinetics was constructed on the basis of the following reaction scheme and took into account the formation of six isomers.

ISP → 0.5 DISP 1   (40)

ISP → 0.5 DISP 2   (41)

ISP → 0.5 DISP 3 (diprene)   (42)

ISP → 0.5 DISP 4 (limonene)   (43)

ISP → 0.5 DISP 5-6(diMe-cycloocta-1,5-dienes)   (44)
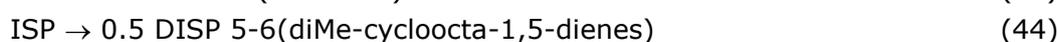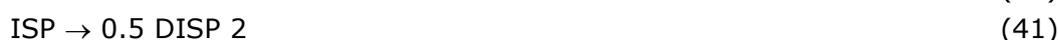
The formation of the minority isomer DISP 0 having the structure of a cyclobutane derivative was neglected. It was observed at as high temperatures as 140-180°C only and its concentrations in the reaction mixtures were too low to enable one to evaluate the kinetics of its formation. Under the conditions of the chromatographic analyses, the

elution peaks of the isoprene dimers DISP 5 and DISP 6, differing in the position of the methyl substituents on the cyclooctadiene skeleton, overlapped partially and did not allow one to determine precisely the concentrations of the mentioned isomers. Due to that, the kinetic of their formation was assessed together. In the model, the measured experimental data given in Table 9 were used. The balance equations in the regression model were constructed in analogy to the model of *trans*-1,3-pentadiene dimerization.

Table 9. Experimental data from the kinetic measurements of isoprene dimerization.

t (min) X1	T (K) X2	c_{ISP} (mmol.l^{-1}) Y1	c_{DISP1} (mmol.l^{-1}) Y2	c_{DISP2} (mmol.l^{-1}) Y3	c_{DISP3} (mmol.l^{-1}) Y4	c_{DISP4} (mmol.l^{-1}) Y5	$c_{DISP5-6}$ (mmol.l^{-1}) Y6
0	373.15	1698.2	0.0	0.0	0.0	0.0	0.0
85	373.15	1680.1	0.0	0.0	0.7	0.3	
253	373.15	1655.6	0.0	0.0	1.6	0.9	
465	373.15	1625.4	0.3	0.5	2.6	1.3	
1317	373.15	1560.2	0.8	1.5	7.4	3.6	
0	413.15	1579.9	0.0	0.0	2.0	1.2	0.0
30	413.15	1496.1		1.5	4.6	2.9	
60	413.15	1463.5	1.0	2.2	6.9	4.4	
200	413.15	1301.6	2.7	5.8	19.0	12.2	3.1
415	413.15	1155.6	5.0	10.7	37.9	23.3	5.5
1380	413.15	801.7	15.9	32.2	159.2	100.3	22.7
0	433.15	1462.5	0.9	1.9	5.0	3.5	0.9
31	433.15	1400.6	2.2	4.6	12.7	8.9	2.4
60	433.15	1317.7	3.7	7.9	23.8	15.7	4.4
160	433.15	1113.1	7.6	15.8	57.5	40.0	11.1
395	433.15	821.5	18.4	37.3	145.9	105.2	25.4
501	433.15	719.6	30.7	52.1	190.9	135.1	28.8
0	453.15	1372.9	1.5	3.1	6.6	5.3	1.4
30	453.15	1208.0	5.8	11.6	29.9	22.6	7.4
60	453.15	1071.1	8.4	16.5	42.0	32.8	10.5
120	453.15	847.1	15.2	29.6	71.4	56.3	14.7
220	453.15	655.4	19.9	38.3	120.7	77.3	23.7
366	453.15	464.1	30.0	58.2	169.1	135.9	40.5
0	493.15	535.2	29.0	53.7	126.4	80.3	26.3
30	493.15	323.5	36.1	70.3	137.6	123.7	36.2
70	493.15	189.4	45.6	86.0	164.4	150.3	42.3
120	493.15	124.5	51.2	89.5	175.3	158.6	44.1
190	493.15	57.3	51.4	91.1	192.3	169.3	45.3
240	493.15	49.2	51.8	91.8	192.9	177.0	46.4

Results of the model regression analysis are presented in Table 10 (E_{ai}) and in Fig. 6 ($k_{i(120°C)}$). The kinetic model with optimized parameters k_{i0} and E_{ai} fitted well the concentration-time dependences of the reaction components at the reaction temperatures between 100 and 180 °C. The agreement between the calculated and experimental data of the kinetic measurement at 220°C was markedly poorer because, probably, the model does not reflects possible mutual conversions of the dimers through the Cope rearrangement which may take place at higher temperatures (e.g., 220 °C). Statistical analysis suggested that there are strong correlations between the pairs k_{i0} – E_{ai} and the estimates of these parameters are relatively less reliable. The reliability of the rate constant determinations lies within one order of magnitude. However, the combination of the calculated estimates of both parameters k_{i0} – E_{ai} enables one to describe very well, for the technically interesting tempe-rature interval 100-180 °C, the dependences of the reaction components concentrations on temperature. Thus the model yields a clear concept on the extent of the reactions leading to the individual isoprene dimers formation and on mutual relations of the corres-ponding reaction rates in the dependence on the reaction temperature. Similarly, a lower reliability of the estimations of the k_{i0} – E_{ai} pairs was observed also for the model of the *trans*-1,3-pentadiene dimerization. Thus, in case of dimerizations of both mentioned dienes,

this fact hampers the extrapolation of the kinetic model to temperatures far from measured range.

Table 10 Results of the regression analysis of the model of the isoprene dimerization. *Estimates of the activation energy values for individual reactions.*

Reaction	RT [min] of dimer on HP-PONA	E_{ai} [kJ.mol^{-1}]
ISP → 0.5 DISP 1	16.99	109.1
ISP → 0.5 DISP 2	17.06	110.0
ISP → 0.5 DISP 3 (diprene)	18.91	99.3
ISP → 0.5 DISP 4 (limonene)	19.00	108.8
ISP → 0.5 DISP 5-6	20.22 + 20.28	111.0

It can be seen from Table 10 that the activation energies E_a of the formation of the isoprene dimers range around 110 kJ.mol^{-1}, only E_a of the diprene formation is by 10 kJ.mol^{-1} lower which is in agreement with the general opinion that diprene is a "kinetically preferred" product of the isoprene dimerization [13-14].
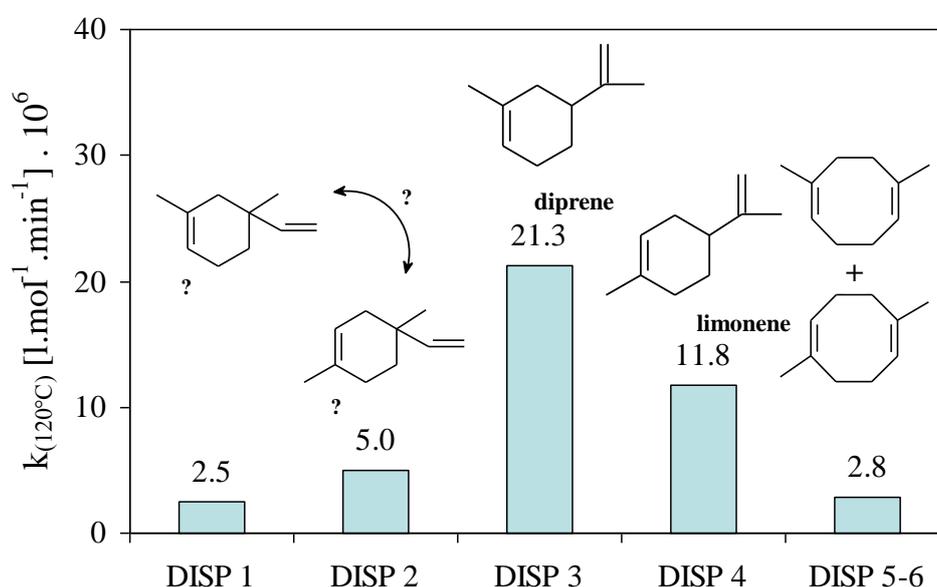
Fig. 6. Results of the regression analysis of the model of the isoprene dimerization. *Rate constants of the formation of isoprene dimers at 120°C.*

5. Conclusions

Kinetics of the thermal dimerizations of isoprene and *cis-* and *trans-*pentadiene and that of codimerization reactions of reactive cyclopentadiene with *cis-* and *trans-*pentadiene was measured, and the kinetic parameters k_{i0}, E_{ai} related to the formation of individual isomeric products were determined. It was found that, when compared to the cyclopentadiene dimerization, the activation energies of dimerizations of the acyclic C5 dienes are higher by 20-40 kJ.mol^{-1} and the activation energies of the formation of the cyclopentadiene codimers with 1,3-pentadienes are higher approx. by 10-20 kJ.mol^{-1}. In comparison to the rate of cyclopentadiene dimerization, the overall rate of the isoprene dimerization at around 120 C is by three orders of magnitude lower, the rate of the *trans-*1,3-pentadiene dimerization by 3-4 orders of magnitude lower and the rate of *cis-*1,3-pentadiene dimerization by four orders of magnitude lower.

Kinetics of the codimerization of cyclopentadiene with isoprene will be the subject of an independent study. The reason is a larger extent of this study under preparation which is due to the fact that the kinetic model of the reaction system cyclopentadiene-isoprene includes both the cycloaddition reactions of dienes and the Cope rearrangement of the dominant codimer (*endo-*5-isopropenyl-2-norbornene) to the thermodynamically more stable codimer (5-methyl-3a,4,7,7a-tetrahydro-1*H*-indene).

Acknowledgements

Symbols and abbreviations

c	molar concentration
c^0	initial molar concentration
CPD	1,3-cyclopentadiene
cP	*cis*-1,3-pentadiene
CPD-cP	codimer of cyclopentadiene with *cis*-1,3-pentadiene
CPD-tP	codimer of cyclopentadiene with *trans*-1,3-pentadiene
DcP	dimer of *cis*-1,3-pentadiene
DCPD	dicyclopentadiene, 3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene
DISP	dimer of isoprene
DtP	dimer of *trans*-1,3-pentadiene
E_{ai}	activation energy of the *i*-th reaction
ISP	isoprene, 2-methyl-1,3-butadiene
k_i	rate constant of the *i*-th reaction
k_{i0}	rate constant of the *i*-th reaction at the reference temperature
$k_{i(120°C)}$	rate constant of the *i*-th reaction at the reference temperature of 120°C
r_i	reaction rate of the *i*-th reaction
RT	retention time under the given analysis conditions
T	temperature, K
T_0	reference temperature, K
t	reaction time
tP	*trans*-1,3-pentadiene
X	independent variable
Y	dependent variable

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