Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 52 (4) 290-306, 2010

KINETICS OF THERMAL DIMERIZATIONS OF CYCLOPENTADIENE AND METHYLCYCLOPENTADIENES AND THEIR CODIMERIZATION

Jiří Krupka

Department of Organic Technology, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic, e-mail: Jiri.Krupka@vscht.cz

Received November 4, 2010, Accepted November 15, 2010

Abstract

The kinetics of the formation of isomeric dimers and codimers via thermal dimerization and codimerization between cyclopentadiene, 1-methyl-1,3-cyclopentadiene and 2-methyl-1,3-cyclopentadiene 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. The overall rates of cyclopentadiene and methylcyclopentadiene dimerizations and their mutual codimerization were found to be identical throughout the temperature range in which the reactions are kinetically controlled. The presence of a methyl group on the cyclopentadiene ring does not decrease the reactivity of the monomer in the Diels-Alder reaction. The reactivities of both methylcyclopentadiene isomers are the same.

Key words: kinetics; Diels-Alder reactions; dimerization; codimerization; activation energy; methyldicyclopentadiene; dimethyldicyclopentadiene; *exo*-dicyclopentadiene.

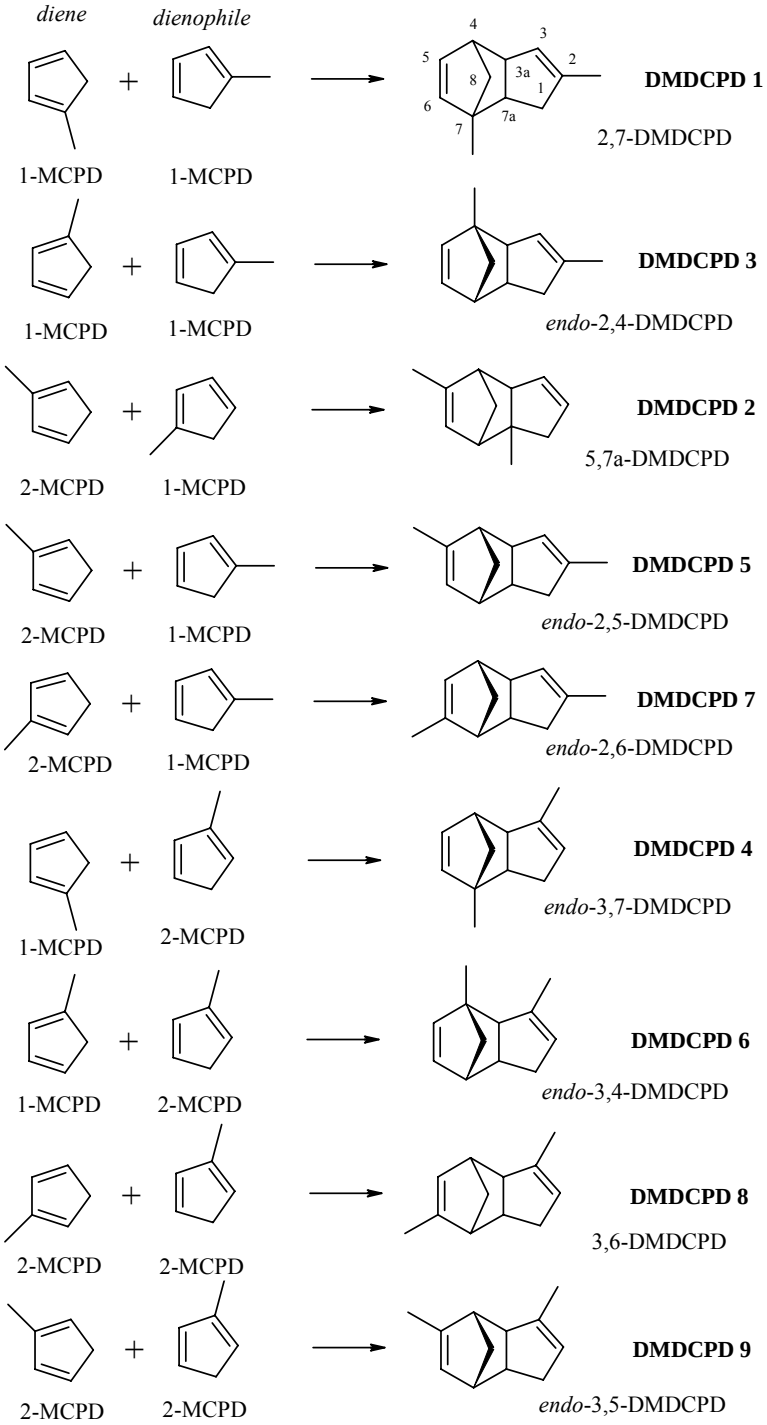
1. Introduction

Three methyl-1,3-cyclopentadiene (MCPD) positional isomers exist: 1-methyl-, 2-methyl- and 5-methyl-1,3-cyclopentadiene (1-MCPD, 2-MCPD and 5-MCPD, respectively). Their dimers and mutual 1:1 Diels-Alder adducts may in short be referred to as dimethyl-dicyclopentadienes (DMDCPD). According to the systematic nomenclature, they are positional and geometric isomers of dimethyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene. Codimers of 1,3-cyclopentadiene (CPD) with MCPD isomers are called methyldicyclo-pentadienes (MDCPD) or, systematically, methyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindenes. 1-MCPD and 2-MCPD are present among the products of steam cracking of petroleum fractions or other similar hydrocarbon mixtures. The amount of 5-MCPD is usually insignificant. [1–3] Both CPD and MCPD undergo Diels-Alder reactions easily and, therefore, the steam cracking condensates contain mixtures of MDCPD and DMDCPD isomers. Owing to the large-scale accessibility, low price and high synthetic potential of MDCPD and DMDCPD mixtures, the literature offers a significant number of papers focused on the characterization, separation and identification of the isomeric components present and their physicochemical characteristics as well as papers focused on their formation.[3–16] Based on these papers it is possible to propose a scheme for the thermal dimerization and codimerization reactions that take place in mixtures of CPD, 1-MCPD and 2-MCPD (Fig. 1-2). Diels-Alder reactions of MCPD can theoretically provide numerous adducts with an *endo*- or *exo*-DCPD skeleton. However, it is generally accepted that *endo* forms are preferentially formed.[1]

Although numerous papers have discussed MCPD thermal behaviour and structural analysis of MCPD dimerization products, thus far the kinetics of MCPD dimerization and codimerization of MDCPD with CPD have not been quantified. On the other hand, kinetic data on the dimerization of CPD to *endo*-dicyclopentadiene (*endo*-DCPD) have been investigated in many studies. The published (second order) kinetic data on cyclopentadiene dimerization are summarized in Table 1. The majority of the studies do not specify which form of dimer the kinetic parameters relate to. However, it emerges from the context that these parameters relate to the reaction forming *endo*-DCPD which, up to a temperature of approximately 150°C, is almost the only dimerization product. E*xo*-DCPD is formed in larger quantities only at higher temperatures; according to Wassermann [17], its activation

energy of formation is 88.76 kJ.mol^{-1}. The CPD dimerization rates and Arrhenius parameters are roughly the same magnitude in both the gas phase and solution – in nonpolar solvents. The type of solvent (carbon tetrachloride, nitrobenzene, ethanol etc.) does not have a significant influence on the CPD dimerization rate.[17]

Figure 1 Overview of the dimerization and codimerization reactions of 1-MCPD and 2-MCPD that appreciably take place at temperatures below 120°C



Generally, Diels-Alder reactions are reversible and exothermic and, therefore, an increase in temperature shifts the equilibrium in favour of diene and dienophile. They do not require a catalyst and are not affected by the presence of the oxidation inhibitors with which dienes are often treated in order to avoid the formation of peroxides. Wassermann [17–22] was the first to systematically study the kinetics of diene addition and its reverse reaction. Wasserman's kinetic data showed that it is possible to consider diene addition as a homogenous reaction of second order and to describe it by the kinetic equation: *rate* = k_1*[diene][dienophile].*

Figure 2: Overview of the codimerization reactions of CPD with 1-MCPD and 2-MCPD that appreciably take place at temperatures below 120°C

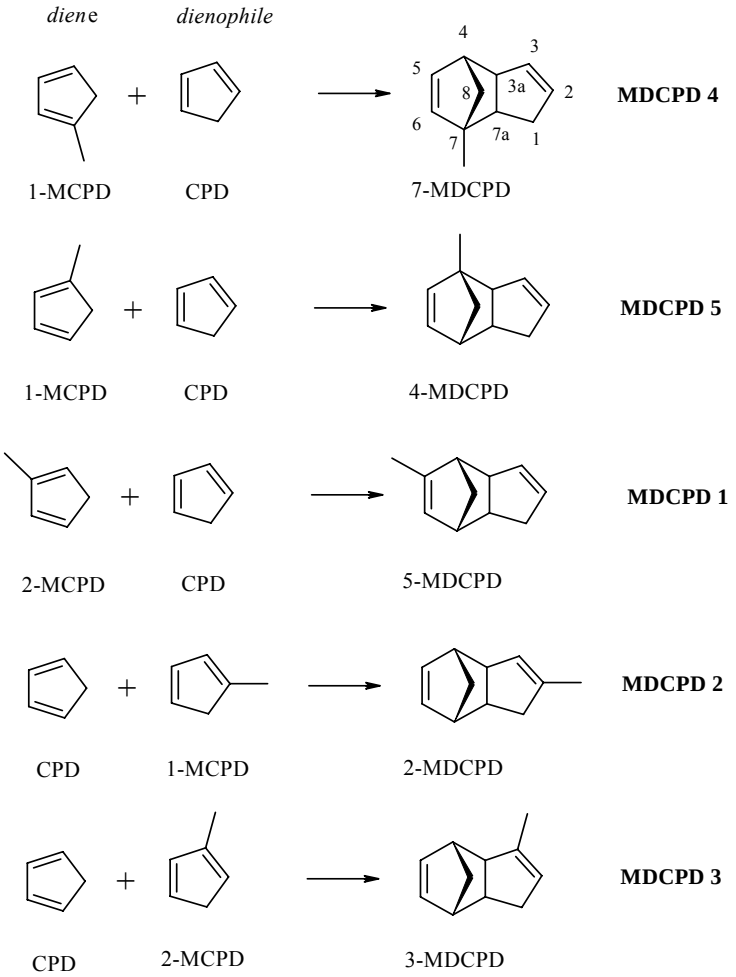


Table 1: Overview of cyclopentadiene dimerization kinetic parameters from the literature

Literature	k [l mol^{-1} s^{-1}]	A_0 .10^{-6} [l mol^{-1} s^{-1}]	E_a [kJ mol^{-1}]	Reaction conditions
(ref. 24)	k(100°C)= 2.67 . 10^{-4}	1.94	68.7	hydrocarbon fraction C5, 60–120°C
(ref. 18, 20–22)		1.2	69.9	gas phase, 80–150°C
(ref. 18)		6.29	72.8	alkane mixture, 0–172°C
(ref. 25)		0.792 (?)	68.3	gas phase
(ref. 26)	k(100°C)= 5.50 . 10^{-4}	1.406	67.9	toluene, 80–130°C
(ref. 27)	k(25°C)= 8.33 . 10^{-7}	2.46	71.2	liquid phase, without solvent, 0–40°C
(ref. 28)	k(20°C)= 5.53 . 10^{-7}	10.5	74.5	liquid phase, a) without solvent, b) in isoprene, 10–20°C
(ref. 29)	k(180°C)= 2.03 . 10^{-2}	3.36	71.3	decalin, 30–190°C
(ref. 30)	k(25°C)= 8.32 . 10^{-7}			liquid phase, without solvent
(ref. 31)	k(150°C)= 3.0 . 10^{-3}		62.4	benzene

Kinetic parameters relate to the equation in the form CPD → 0.5 DCPD;
Values converted to SI units

The present paper is focused on the description of the kinetics of the thermal dimerizations of CPD and MCPD and their codimerization. The motivation for the study came from the need for kinetic data in order to develop a complex mathematical model that would allow prediction of the concentration changes of individual reactive components in pyrolysis gasoline during its processing in a series of rectification columns. The kinetics description was focused on the temperature range 40–120°C, within which the Diels-Alder reactions can be considered irreversible. Whilst the equilibria of dimerizations and codimerizations of acyclic C5-conjugated dienes are entirely shifted towards the products even at temperatures

of 300°C, the equilibria governing CPD and MCPD dimerizations are completely shifted towards the product only up to temperatures of around 130°C [23]. The activation energies of decomposition (monomerization) of DCPD, MDCPD and DMDCPD are not significantly different.

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 and 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 CPD dimerization was a solution of CPD in cyclohexane. The starting mixture for measuring the kinetics of MCPD dimerization was a mixture of 1-MCPD, 2-MCPD and cyclohexane, and the starting mixture for measuring the kinetics of CPD–MCPD codimerizations was a mixture of CPD, 1-MCPD, 2-MCPD and cyclohexane.

CPD was prepared by thermal decomposition of 99.5% 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. The mixture of MCPD isomers was prepared analogously using a commercial DMDCPD mixture derived from pyrolysis gasoline.

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.

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 according to the relation

$$c_i = \frac{x_i \rho}{M_i} \qquad (1)$$

where c_i is the molar concentration, x_i is the mass fraction and M_i is the molar weight of component i in the mixture and ρ is the density of the mixture at the reaction temperature.

As the reaction kinetics were measured in the presence of excess solvent, so that the absolute concentration of the reaction components mostly did not exceed wt. 10%, the reaction mixture density change with reaction conversion was neglected in the kinetic models. It was experimentally proved that the density change during the reaction is less than the experimental error in the kinetic measurements. The changes in reaction mixture density with temperature are significant and were included in the analysis. The process went as follows: at the laboratory temperature both before the kinetic experiment and after the reaction the reaction mixture was weighed and its volume was measured. The reaction mixture densities at the beginning and at the end of the experiment were computed from these parameters. The arithmetic mean of these parameters corresponded to the average reaction mixture density at the laboratory temperature and was recorded on a graph of the known cyclohexane density-temperature dependence. Assuming that the dependence of the reaction mixture density (which contains mainly cyclohexane) on temperature is

the same as the dependence of pure cyclohexane, a polynomial function duplicating the curve of the cyclohexane density-temperature dependence was fitted through the plotted point of the real density. The reaction mixture densities for the individual temperatures at which the kinetic measurements took place were then read from the transposed curve.

The identification of the chemical structures of the isomeric products formed by the dimerizations and codimerizations studied was the subject of our previous study. [32]

3. Regression analysis of kinetic data

The regression analysis of experimental data was performed using the ERA (Easy Regression Analysis) software [33]. 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:

$$k_i = k_{i0} \exp\left(\frac{E_{ai}\left(T - T_0\right)}{RTT_0} \right) \qquad (2)$$

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 poorer correlation between the rate constant k_{i0} and the activation energy E_{ai} is characteristic of the modified relation (2).

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.

3. Results and discussion

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

3.1. Cyclopentadiene dimerization

CPD dimerization was studied as a reference reaction at temperatures of 40, 60, 80, 100 and 120°C. The chromatographic analysis of the reaction mixtures showed that a small quantity of *exo*-DCPD was produced besides a large quantity of *endo*-DCPD in the tested temperature range. In addition, a few hundredths wt. % of CPD trimer appeared in the reaction mixture at 120°C. However, its low concentration allowed omission of the trimerization reaction from the kinetic model. The data measured (time dependence of the molar concentrations of CPD, *endo*-DCPD and *exo*-DCPD) are listed in Table 2. A certain discrepancy in mass balance is caused by the fact that the concentrations of reaction components are statistically independent variables and they were not processed relatively (i.e. with post-calculation of the concentration of the last component according to the mass balance) but were measured absolutely. Data analysis showed the concentration values in the tables are not subject to systematic error but only to random error. Larger errors in the values measured include not only the errors inherent in the assay of reaction concentrations but mainly the experimental error caused by manipulation of small amounts of the reaction mixture during kinetic measurements.

The mathematic model of the reaction kinetics was based on the following reaction scheme:

CPD → 0.5 *endo*-DCPD (3)

CPD → 0.5 *exo*-DCPD (4)

In contrast to papers on CPD dimerization kinetics published thus far, the model considered the formation of the minor *exo*-isomer as well as that of *endo*-DCPD. The model of isothermal batch reactor included equations (2) and (5)–(9).

$r_1 = k_1 c^2_{CPD}$ (5)

$r_2 = k_2 c^2_{CPD}$ (6)

$$\frac{dc_{CPD}}{dt} = -r_1 - r_2 \quad (7)$$

$$\frac{dc_{endo-DCPD}}{dt} = 0.5 r_1 \quad (8)$$

$$\frac{dc_{exo-DCPD}}{dt} = 0.5 r_2 \quad (9)$$

where *c* represents molar reaction concentrations and k_1, k_2 are the rate constants of CPD dimerization to *endo*- and *exo*-DCPD, respectively. Initial conditions for the mass balance were:

$t = 0 \quad c_{CPD} = c^0_{CPD} \quad c_{endo\text{-}DCPD} = c^0_{endo\text{-}DCPD} \quad c_{exo\text{-}DCPD} = c^0_{exo\text{-}DCPD}$ (10)

The dependence of the rate constants on temperature was expressed in the regression model by relation (2). The CPD dimerization was described by kinetic equations for reactions of second order (5) – (6). Considering the fact that the kinetics of the Diels-Alder reactions were measured in excess solvent (cyclohexane), it was assumed that the molar concentrations of the components in the reaction system approached the component activities.

Table 3: Regression analysis results of the CPD dimerization model

Parameter / Reaction	$k_{i(120°C)} \cdot 10^3$ [l.mol^{-1}.min^{-1}]		E_{ai} [kJ.mol^{-1}]	
	Value	95% conf. limits	Value	95% conf. limits
CPD → 0.5 *endo*-DCPD	67.51	56.81 – 79.96	70.62	66.35 – 72.20
CPD → 0.5 *exo*-DCPD	0.6033	0.4510 – 0.7937	80.16	72.73 – 87.26

$A_{1,0} = 1{,}63.10^8$ l.mol^{-1}.min^{-1}, $A_{2,0} = 2{,}70.10^7$ l.mol^{-1}.min^{-1}

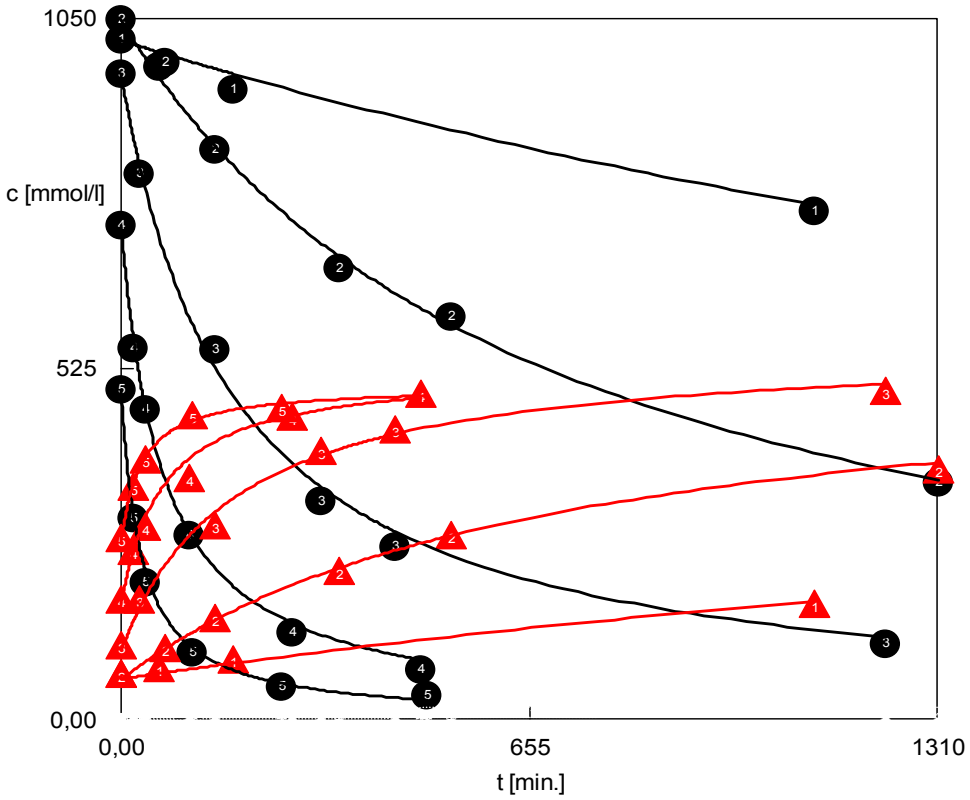
The regression analysis results are shown in Table 3, which also provides confidence limits for the estimated values of the kinetic parameters. This approach substitutes confidence intervals, works with a real confidence region and is asymmetric according to the optimal value. The values of residual variance do not exceed the estimation of the kinetic measurements variance, which shows that the model describes the data measured adequately. The congruence of computed and measured data is clear from Figures 3a and 3b. The values determined for the rate constants of *endo*- and *exo*-DCPD formation for the measured temperature intervals are shown in Table 4. The results reflect the fact that the Diels-Alder reaction of CPD to form *exo*-DCPD is, in the temperature interval from 40°C to 120°C, two or three orders of magnitude slower than the reaction of CPD to *endo*-DCPD. The kinetic parameters are of solid congruence with published data (Table 5 or Table 1).

Table 4: The values of the rate constants for *endo*- and *exo*-DCPD formation for the measured temperature intervals [l mol^{-1} min^{-1}]

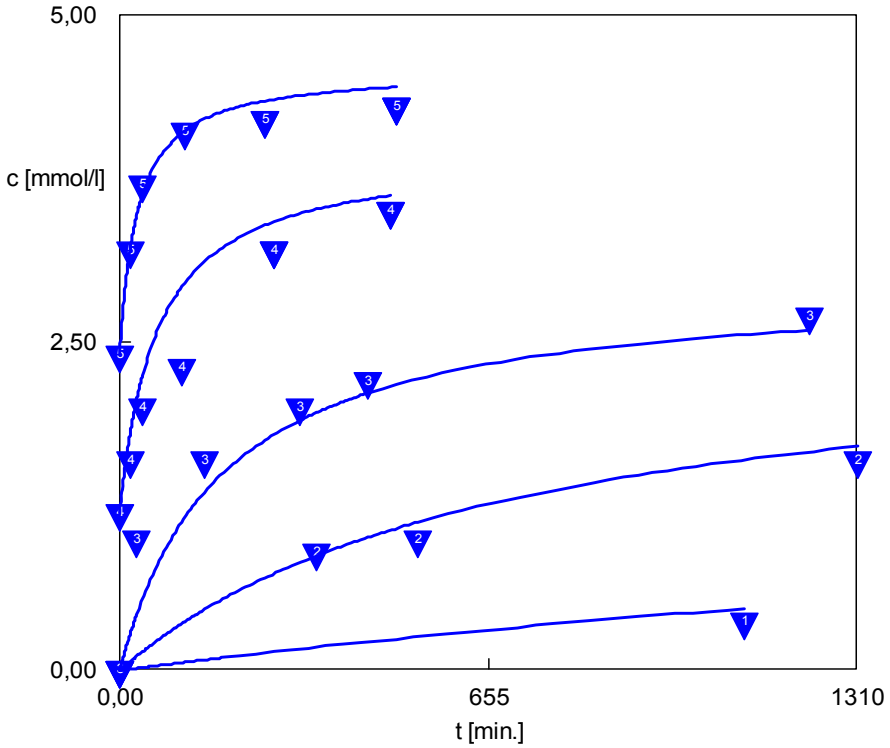
temperature /reaction	40°C	60°C	80°C	100°C	120°C
CPD → 0.5 *endo*-DCPD	2.71E-04	1.38E-03	5.84E-03	2.12E-02	6.75E-02
CPD → 0.5 *exo*-DCPD	1.15E-06	7.28E-06	3.75E-05	1.62E-04	6.03E-04

Table 5: Comparison of the measured rate constants of CPD dimerization with literature values (at 120°C; l mol^{-1} min^{-1})

reaction /rate constant	*measured*	Bělohlav (ref. 29)	Muja (ref. 26)	Wassermann (ref. 18)	Szekeres (ref. 24)
CPD → 0.5 *endo*-DCPD	6.75E-02	6.78E-02	9.6E-02	8.0E-02	5.00E-02
CPD → 0.5 *exo*-DCPD	6.03E-04				



a



b

Fig. 3 CPD dimerization – comparison of the experimental data (points) with the model (solid lines), ● – c_{CPD}, ▲ – $c_{endo\text{-}DCPD}$ ▼– $c_{exo\text{-}DCPD}$, (1)–40°C, (2)–60°C, (3)–80°C, (4)–100°C, (5)–120°C

Table 2: Experimental data from the kinetic measurements of CPD 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_{CPD} (mmol.l^{-1}) Y1	$c_{endo\text{-}DCPD}$ (mmol.l^{-1}) Y2	$c_{exo\text{-}DCPD}$ (mmol.l^{-1}) Y3
0	313.15	1017.1	61.8	0.0
60	313.15	976.8	69.7	
180	313.15	942.7	84.2	
1110	313.15	731.9	166.6	0,4
0	333.15	1047	61.0	0.0
70	333.15	984	100	
150	333.15	853	145	
350	333.15	676	217	0.9
530	333.15	602	269	1.0
1310	333.15	354	367	1.4
0	353.15	966	104	0.0
30	353.15	816	173	1.0
150	353.15	553	284	1.6
320	353.15	327	396	2.0
440	353.15	258	427	2.2
1225	353.15	114	486	2.7
0	373.15	739	174	1.2
20	373.15	555	245	1.6
40	373.15	465	282	2.0
110	373.15	275	355	2.3
275	373.15	130	446	3.1
480	373.15	74.0	482	3.2
0	393.15	494	265	2.4
20	393.15	301	343	3.2
40	393.15	206	382	3.7
115	393.15	101	449	4.1
258	393.15	49.0	459	4.2
490	393.15	36.0		4.3

3.2. Methylcyclopentadiene dimerization

The methylcyclopentadiene positional isomers in pure form were not available for the study of MCPD dimerization reactions, only a mixture of 1-methyl and 2-methyl isomers in a 56:44 weight ratio prepared by thermal decomposition of a commercial mixture of DMDCPD isomers. The mixture of 1-MCPD and 2-MCPD is not separable by rectification. Dimerization and codimerization reactions of 5-MCPD were not included in this study because this isomer is rarely present among pyrolysis products. [1–3] Although, when a mixture of 1-MCPD and 2-MCPD is heated, homo-dimers as well as mixed codimers of 1-MCPD + 2-MCPD are formed, the simplified term 'MCPD dimerization' will be used throughout this paper.

The reactions were observed at temperatures of 60, 80, 100 and 120°C. In the observed temperature interval, nine DMDCPD isomers were produced in appreciable quantities. In this paper they are labelled as DMDCPD 1 – 9. Their structures and chromatographic characteristics are shown in Table 6. There are two isomers that clearly dominate the others: *endo*-2,5-dimethyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene (*endo*-2,5-DMDCPD, or DMDCPD 5) and *endo*-3,5-dimethyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene (*endo*-3,5-DMDCPD, or DMDCPD 9). Based on the evaluation of the kinetic experiments, on the identification of the products formed and on information from the literature, a scheme of the reactions taking place in the 1-methyl- and 2-MCPD mixture in the observed temperature interval of 60-120°C was constructed.

(diene) (dienophile)

1-MCPD + 1-MCPD → 2,7-DMDCPD (DMDCPD 1) (11)

1-MCPD + 1-MCPD → *endo*-2,4-DMDCPD (DMDCPD 3) (12)

2-MCPD + 1-MCPD → 5,7a-DMDCPD (DMDCPD 2) (13)

2-MCPD + 1-MCPD → *endo*-2,5-DMDCPD (DMDCPD 5) (14)

2-MCPD + 1-MCPD → *endo*-2,6-DMDCPD (DMDCPD 7) (15)

1-MCPD + 2-MCPD → *endo*-3,7-DMDCPD (DMDCPD 4) (16)

1-MCPD + 2-MCPD → *endo*-3,4-DMDCPD (DMDCPD 6) (17)

2-MCPD + 2-MCPD → 3,6-DMDCPD (DMDCPD 8) (18)

2-MCPD + 2-MCPD → *endo*-3,5-DMDCPD (DMDCPD 9) (19)

endo-3,4-DMDCPD (DMDCPD 6) → *endo*-2,5-DMDCPD (DMDCPD 5) (20)

The time dependences of the *endo*-3,4-dimethyl-DCPD concentrations during the kinetic measurements revealed that this product is formed by Diels-Alder reaction of 2-MCPD and 1-MCPD, but at temperatures above 80°C it isomerizes to *endo*-2,5-DMDCPD (*endo*-3,4-DMDCPD concentration maximum observed). The concentrations of other DMDCPD isomers grow monotonically with time and their mutual concentration ratios barely change over time. Ratios of their concentrations also do not significantly change with reaction temperature (within the studied temperature range of 60–120°C). It was observed that, within experimental error, the concentration ratio of the two monomers remains constant throughout the whole reaction (2-MCPD / 1-MCPD ~ 1.3). This suggests the reactivity of both MCPD isomers is congruent for Diels-Alder reactions.

The regression analysis of the kinetic model constructed according to the aforementioned reaction scheme showed that the quality and amount of experimental data obtained from the kinetic measurements of the 'dimerization' of the 1-MCPD and 2-MCPD mixture do not allow reliable setting of kinetic parameters for reactions (11) – (20). The data would have to be supplemented by separate kinetic measurements of *endo*-3,4-DMDCPD (DMDCPD 6) isomerization to *endo*-2,5-DMDCPD (DMDCPD 5) and by an individual measurement of pure 1-MCPD or 2-MCPD dimerization, or alternatively by a measurement of 'dimerization' of a mixture containing a different initial molar ratio of monomers.

For that reason, only kinetic parameters of the 'MCPD dimerization' summary reaction were evaluated according to the scheme:

Σ MCPD → 0.5 Σ DMDCPD (21)

and, furthermore, formal kinetic parameters of the three 'pseudo-dimerization reactions' according to the simplified scheme (below) which includes individual reactions for production of the two dominant DMDCPD components (chromatographic peaks) which, in the reaction mixtures, represent 6/7 of the mass of all DMDCPD isomers:

Σ MCPD → 0.5 DMDCPD 5+6 *(1st dominant peak)* (22)

Σ MCPD → 0.5 DMDCPD 9 *(2nd dominant peak)* (23)

Σ MCPD → 0.5 Σ other DMDCPD (24)

The experimental data used in the model are shown in Table 7. The experimental finding that the reactivity of both isomer monomers is congruent and the activation energy of the formation of individual DMDCPD isomers is not dramatically different (molar ratio of DMDCPD isomers barely changes with temperature) was useful for the simplification of the reaction system to the form of equation (21).

The three-equation model, (22) – (24), does not depend on individual DMDCPD 5 and DMDCPD 6 isomer concentrations but only on their sum; therefore, their mutual isomerization did not have to be considered. These two isomers appear to be equivalent forms of matter from the outside because they have the same boiling point and usually share a common chromatographic peak in the GC-analysis. On HP-PONA both isomers create a common peak as well. The left sides of equations (22) and (23) are not fully in accordance with the reaction mechanism because they do not reflect the fact that DMDCPD 9 arises solely via 2-MCPD dimerization and the DMDCPD 5-6 isomers arise via reaction of 2-MCPD with 1-MCPD. The kinetic parameters evaluated in this way are therefore only valid under the condition that the ratio of 2-MCPD/1-MCPD ~ 1.3. This requirement is satisfied regarding pyrolysis gasoline and other technological streams originating from pyrolysis products. Such a relation is sufficient for prediction of the production of the two main DMDCPD isomers based on the knowledge of the MCPD summary concentration in a particular technological stream.

The regression analysis results of both simplified models of the 'MCPD dimerization' are shown in Tables 8 and 9. The first model included, apart from the summary equation of MCPD dimerization (21), also a formal equation considering the decrease in concentration

of MCPD caused by other reactions (trimerization, codimerization with residual CPD etc.). The balanced equations in both regression models were constructed analogously to the case of CPD dimerization. The cogency of the summary kinetic model to the experimental points is illustrated in Figure 4. From the results in the tables it is clear that the MCPD dimerization rate is absolutely congruent with the CPD dimerization and the presence of a methyl group on the cyclopentadiene ring does not decrease monomer reactivity for the Diels-Alder reaction. That explains also the observed congruent reactivities of both methyl-cyclopentadiene isomers. The activation energies of CPD and MCPD dimerization are also identical and, as Table 9 shows, neither differs from the E_a of the individual DMDCPD isomers' formation. The formation rates of the two dominant DMDCPD components are equivalent.

Table 8 Regression analysis results of the MCPD dimerization summary model

Parameter	$k_{(120°C)} \cdot 10^3$ [l.mol^{-1}.min^{-1}]		E_a [kJ.mol^{-1}]	
Reaction	Value	95% conf. limits	Value	95% conf. limits
Σ MCPD → 0,5 Σ DMDCPD	64.56	57.83 – 71.86	70.50	67.43 – 73.51

Table 9 Regression analysis results of the MCPD dimerization simplified summary model, considering the formation of the two dominant components of DMDCPD

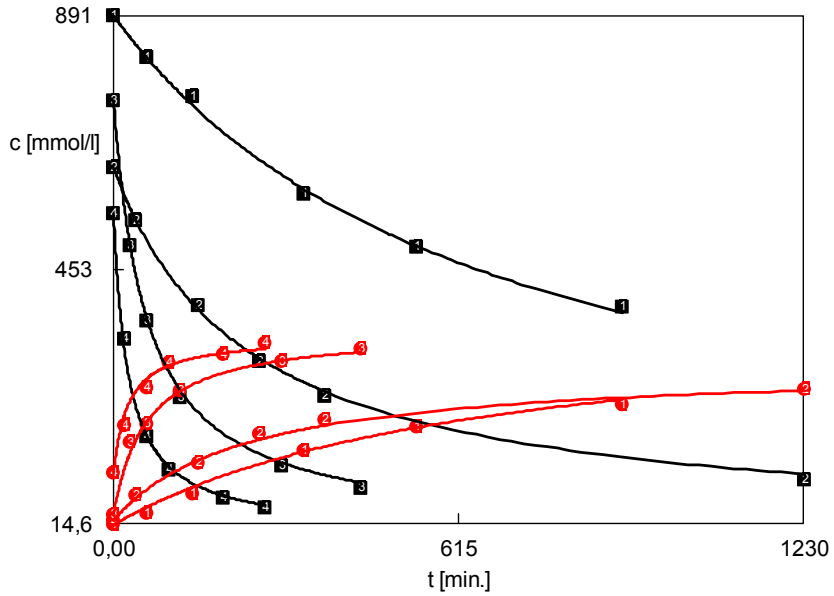
Parameter	$k_{i(120°C)} \cdot 10^3$ [l.mol^{-1}.min^{-1}]		E_{ai} [kJ.mol^{-1}]	
Reaction	Value	conf. limits	Value	conf. limits
Σ MCPD → 0,5 DMDCPD 5-6	30.5	24.2 – 38.2	73.9	67.5 – 80.2
Σ MCPD → 0,5 DMDCPD 9	29.0	23.0 – 36.4	71.3	64.9 – 77.6
Σ MCPD → 0,5 Σ other DMDCPD	10.8	8.46 – 13.6	77.1	70.5 – 83.4

95%- confidence limits

Table 7 Experimental data from the kinetic measurements of the reaction system 1-MCPD – 2-MCPD

t (min) X1	T (K) X2	$c_{\Sigma\ MCPD}$ (mmol.l^{-1}) Y1	$c_{DMDCPD\ 5\text{-}6}$ (mmol.l^{-1}) Y2	$c_{DMDCPD\ 9}$ (mmol.l^{-1}) Y3	$c_{\Sigma\ other\ DMDCPD}$ (mmol.l^{-1}) Y4
0	333.15	890.6	6.1	6.5	2.1
60	333.15	817.5	14.6	15.4	5.0
140	333.15	705.9	28.9	30.8	8.9
340	333.15	582.5	67.6	77.4	19.2
540	333.15	491.3	69.2	74.0	21.2
905	333.15	389.8	92.8	99.3	28.7
0	353.15	628.6	9.4	10.1	3.1
40	353.15	538.3	27.3	29.6	9.2
150	353.15	392.4	49.8	52.7	16.8
260	353.15	296.5	73.9	78.3	24.6
375	353.15	235.6	83.6	87.3	28.2
1230	353.15	92.5	99.9	105.1	33.4
0	373.15	744.7	13.5	13.9	5.1
30	373.15	493.8	65.3	66.8	24.0
60	373.15	364.9	79.0	80.4	29.0
120	373.15	233.9	102.9	103.9	37.7
300	373.15	114.6	124.5	123.9	45.8
440	373.15	76.8	138.6	137.6	51.0
0	393.15	549.6	43.2	42.1	18.1
20	393.15	333.9	78.6	76.1	30.7
60	393.15	166.0	101.7	97.1	41.9
100	393.15	108.9	124.0	118.0	50.4
195	393.15	59.4	130.9	123.2	53.0
270	393.15	44.4	144.2	135.7	57.0

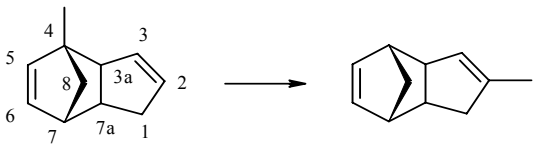
Figure 4 MCPD dimerization – comparison of the experimental points with the results of summary kinetic model (solid lines)



● – $C_{\Sigma\ DMDCPD}$, ■ – $C_{(1\text{-}MCPD\ +\ 2\text{-}MCPD)}$, *(1) – 60°C, (2) – 80°C, (3) – 100°C, (4) – 120°C, (The curves represent evaluated concentration dependencies.)*

3.3. Codimerization of cyclopentadiene with methylcyclopentadienes

In order to evaluate the kinetics of codimerization of cyclopentadiene with the methyl-cyclopentadienes, reaction kinetics of a system composed of CPD + 1-MCPD + 2-MCPD at temperatures of 50, 70, 100 and 120°C were observed. In accordance with the data from the literature, five MDCPD isomers appeared in significant volumes from the initial dienes in question. The reaction scheme for their formation is shown in Figure 2. Furthermore, the reaction mixtures contained other Diels-Alder products: DMDCPD isomers and *endo*- and *exo*-DCPD. Although the structural analysis did not confirm that the resulting MDCPD isomers have *endo*-structures, it is possible to consider them, based on prior knowledge of Diels-Alder reaction kinetics, as methyl-derivates of *endo*-DCPD. An interesting finding is that 6-MDCPD is not present among the isomers formed. This is probably due to the polarization of the double bond by the methyl group in the 2-MCPD molecule, which causes a pre-reaction orientation of the 2-MCPD and CPD molecules such that reaction leads to the formation of the 5-methyl- isomer. A similar tendency can be observed in the case of 2-MCPD dimerization. Among the resulting DMDCPD isomers are minor components with the methyl in position 6. A completely new finding was observed when studying CPD with MCPD codimerization kinetics: 4-MDCPD (MDCPD 5) isomerizes at temperatures below 120°C to 2-MDCPD (MDCPD 2).



4-MDCPD **MDCPD 5** → 2-MDCPD **MDCPD 2** (25)

The kinetics of this [*3,3*]-sigmatropic rearrangement were measured and quantified. They are part of a separate study. [34,23]

It would be incorrect to solve the kinetics of CPD – MCPD codimerization reactions as isolated reactions. Diels-Alder reactions in a system of two or more dienes (i.e. dimerization and codimerization) have competitive – parallel character and, in the kinetic model, they must be solved together. To evaluate the kinetics, a model was constructed on the basis of the following reaction scheme:

reaction 1: CPD → 0.5 DCPD (26)

reaction 2: 1-MCPD + CPD → 7-MDCPD (MDCPD 4) (27)

reaction 3: 1-MCPD + CPD → 4-MDCPD (MDCPD 5) (28)

reaction 4: 2-MCPD + CPD → 5-MDCPD (MDCPD 1) (29)

reaction 5: 1-MCPD + CPD → 2-MDCPD (MDCPD 2) (30)

reaction 6: 2-MCPD + CPD → 3-MDCPD (MDCPD 3) (31)

reaction 7: 1-MCPD → Σ other (32)

reaction 8: 2-MCPD → Σ other (33)

reaction 9: 4-MDCPD (MDCPD 5) → 2-MDCPD (MDCPD 2) (34)

The model considered 4-methyl-DCPD isomerization and the experimental data from the isomerization kinetic measurements [35] were included in the model. The 'formal summary equations' (32) and (33) describe the decrease of MCPD on DMDCPD, or potentially on all other products except CPD-MCPD codimers. The regression model included the relationship (2) and the following balanced equations:

$$r_1 = k_1 c^2_{CPD} \quad (35)$$

$$r_2 = k_2 c_{CPD} . c_{1\text{-}MCPD} \quad (36)$$

$$r_3 = k_3 c_{CPD} . c_{1\text{-}MCPD} \quad (37)$$

$$r_4 = k_4 c_{CPD} . c_{2\text{-}MCPD} \quad (38)$$

$$r_4 = k_5 c_{CPD} . c_{1\text{-}MCPD} \quad (39)$$

$$r_6 = k_6 c_{CPD} . c_{2\text{-}MCPD} \quad (40)$$

$$r_7 = k_7 c^2_{1\text{-}MCPD} \quad (41)$$

$$r_8 = k_8 c^2_{2\text{-}MCPD} \quad (42)$$

$$r_9 = k_9 c_{4\text{-}MDCPD} \quad (43)$$

$$\frac{dc_{CPD}}{dt} = -r_1 - r_2 - r_3 - r_4 - r_5 - r_6 \quad (44)$$

$$\frac{dc_{1-MCPD}}{dt} = -r_2 - r_3 - r_5 - r_7 \quad (45)$$

$$\frac{dc_{2-MCPD}}{dt} = -r_4 - r_6 - r_8 \quad (46)$$

$$\frac{dc_{DCPD}}{dt} = 0.5\, r_1 \quad (47)$$

$$\frac{dc_{7-MDCPD}}{dt} = r_2 \quad (48)$$

$$\frac{dc_{4-MDCPD}}{dt} = r_3 - r_9 \quad (49)$$

$$\frac{dc_{5-MDCPD}}{dt} = r_4 \quad (50)$$

$$\frac{dc_{2-MDCPD}}{dt} = r_5 + r_9 \quad (51)$$

$$\frac{dc_{3-MDCPD}}{dt} = r_6 \quad (52)$$

The experimental data used in the model are given in Table 10. The results of the regression analysis of the model are presented in Table 11. The estimates of parameters are relatively reliable and the model describes the measured data well. The activation energies of formation of the individual CPD-MCPD codimers do not, within experimental error, differ from and are practically the same as the *endo*-DCPD formation activation energy.

Apart from the evaluation of the kinetic parameters for the formation of the individual codimers, the kinetic parameters of the overall reactions (53) – (55) were evaluated according

to a simplified model that does not depend on 1-MCPD and 2-MCPD concentrations but only on their sum.

$$CPD \rightarrow 0.5\ DCPD \quad (53)$$

$$CPD + \Sigma\ MCPD \rightarrow \Sigma\ MDCPD \quad (54)$$

$$\Sigma\ MCPD \rightarrow 0.5\ \Sigma\ DMDCPD \quad (55)$$

The results of the regression analysis of this summary model (Table 12) show clearly that the rates of dimerizations of CPD and MCPD and their mutual codimerization are congruent within the entire temperature interval tested where the reactions are kinetically controlled.

Table 11 The results of regression analysis of the kinetic model including reactions (26) – (34)

Parameter / Reaction	$k_{i(120°C)} \cdot 10^3$ [l.mol^{-1}.min^{-1}]		E_{ai} [kJ.mol^{-1}]	
	Value	conf. limits	Value	conf. limits
CPD → 0,5 *endo*-DCPD	77.0	69.9 – 140.0	71.2	66.3 – 88.4
1-MCPD + CPD → 7-methyl-DCPD	3.67	2.43 – 6.00	77.6	69.2 – 87.9
1-MCPD + CPD → 4-methyl-DCPD	19.2	12.1 – 29.1	77.0	67.7 – 86.1
2-MCPD + CPD → 5-methyl-DCPD	44.9	28.5 – 67.8	75.9	66.6 – 85.0
1-MCPD + CPD → 2-methyl-DCPD	20.9	12.9 – 35.0	73.5	63.9 – 84.2
2-MCPD + CPD → 3-methyl-DCPD	41.3	25.3 – 63.5	71.3	61.4 – 80.6
	$k_{i(120°C)} \cdot 10^3$ [min^{-1}]			
4-methyl-DCPD → 2-methyl-DCPD	4.32	2.98 – 4.61	124.5	107 – 131

The optimized parameters of formal equations (32)-(33) are not noted in the table; 95% confidence limits

Table 12 The regression analysis results of the CPD–MCPD codimerization summary model

Parameter / Reaction	$k_{i(120°C)} \cdot 10^3$ [l.mol^{-1}.min^{-1}]		E_{ai} [kJ.mol^{-1}]	
	Value	conf. limits	Value	conf. limits
CPD → 0.5 DCPD	77.3	57.4 – 104.0	71.1	65.1 – 77.3
CPD + Σ MCPD → Σ MDCPD	69.1	56.1 – 85.1	71.6	67.2 – 76.3
Σ MCPD → 0.5 Σ DMDCPD	63.2	45.1 – 87.9	68.7	61.5 – 76.3

95% confidence limits

It is necessary to point out that the rate constant $k_{(120°C)}$ of the summary reaction (54) does not correspond to the rate constant sum $k_{(120°C)}$ for the formation of individual MDCPD isomers shown in Table 11 because reaction equation (54) is defined differently (concentrations of 1-MCPD and 2-MCPD *vs.* Σ MCPD).

Table 6 Overview of the nomenclature and retention times for the dimers and codimers

Diels-Alder product	Compound name	RT [min] HP-PONA temp. prog.	RI * HP-PONA 100°C
MDCPD 4	7-MDCPD*, (7-methyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene)	19.44	1042.4
MDCPD 5	4-MDCPD	19.55	1046.5
MDCPD 1	5-MDCPD	20.62	1084.3
MDCPD 2	2-MDCPD	20.81	1090.7
MDCPD 3	3-MDCPD	21.04	1098.9
DMDCPD 1	2,7-DMDCPD**	21.22	1104.2
DMDCPD 3	*endo*-2,4-DMDCPD	21.26	1104.8
DMDCPD 4	*endo*-3,7-DMDCPD	21.35	1108.6
DMDCPD 5	*endo*-2,5-DMDCPD	21.48	1112.8
DMDCPD 6	*endo*-3,4-DMDCPD	22.08	1134.4
DMDCPD 7	*endo*-2,6-DMDCPD	22.11	1134.4
DMDCPD 8	3,6-DMDCPD	22.60	1154.1
DMDCPD 9	*endo*-3,5-DMDCPD	22.83	1160.8

) ref. 32. **) Position numbering in accordance with IUPAC rule A-34 (3a,4,7,7a-tetrahydro-1H-4,7-methanoindene). *) The endo/exo stereoisomeric configuration was not confirmed for some isomers; however, based on current knowledge it is possible to consider them compounds with an endo-DCPD skeleton*

4. Conclusions

The kinetics of the mutual Diels-Alder reactions of CPD, 2-MCPD and 1-MCPD were studied in the liquid phase in the temperature range of 40–120°C. In the cases of CPD dimerization and codimerization of CPD with 1-MCPD and 2-MCPD, kinetic parameters for the formation of the individual isomeric products were evaluated. In the case of 1-MCPD and 2-MCPD dimerization, the experimental data did not allow the evaluation of kinetic parameters related to the formation of individual DMDCPD isomers and, thus, the kinetic description was simplified. The kinetic parameters of MCPD dimerization and its codimerization with CPD have not been published in any study thus far and, in this regard, this paper presents original results. The description of cyclopentadiene dimerization kinetics as previously known was extended with the formation of the minor *exo*-dicyclopentadiene product.

It was observed that, during the mutual Diels-Alder reactions of 1-MCPD and 2-MCPD, the concentration ratio of the two monomers remains constant over the course of reaction. It can be deduced that the reactivity of both methylcyclopentadiene isomers is congruent for Diels-Alder reactions.

The overall rates of CPD dimerization, MCPD dimerization and their mutual codimerizations consist only of the rates of the formation of products with an *endo*-dicyclopentadiene skeleton. The formation of *exo*-isomers effectively has a negligible impact on the rate of decrease of reactant concentrations. The mentioned overall rates were found to be congruent throughout the entire temperature range in which the reactions are kinetically controlled. Thus, the presence of a methyl group on the cyclopentadiene ring does not decrease the reactivity of the monomer for Diels-Alder reaction. That also explains the observed congruent reactivity of both methylcyclopentadiene isomers. The activation energies of the CPD and MCPD dimerizations are identical. Nor is there any difference - within the limits of measurement error – in the activation energies of formation of the individual DMDCPD and MDCPD '*endo*-isomers', which correspond to the activation energy of *endo*-DCPD formation. In comparison with the dimerizations of acyclic C5 conjugated dienes and codimerizations of CPD with these acyclic dienes [23,35], the rates of the reactions studied here are significantly higher.

Symbols and abbreviations

1-MCPD	1-methyl-1,3-cyclopentadiene
2-MCPD	2-methyl-1,3-cyclopentadiene
A_{i0}	frequency factor of the *i*-th reaction
c	molar concentration
c^0	initial molar concentration
conf.	confidence
CPD	1,3-cyclopentadiene
DCPD	dicyclopentadiene; 3a,4,7,7a-tetrahydro-1*H*-4,7-methanoindene
DMDCPD	isomers of dimethyldicyclopentadienes
E_a	activation energy
E_a	activation energy of the *i*-th reaction
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
MCPD	isomers of methyl-1,3-cyclopentadienes
MDCPD	isomers of methyldicyclopentadienes
r_i	reaction rate of the *i*-th reaction
RI	Kovats retention index on HP-PONA column at 100°C
RT	retention time under the analysis conditions described in Chapter 2
T	temperature, K
T_0	reference temperature, K
T	reaction time
Σ DMDCPD	sum of DMDCPD isomers
Σ MCPD	sum of 1-MCPD and 2-MCPD
Σ MDCPD	sum of MDCPD isomers
Σ other	sum of all Diels-Alder products except CPD-MCPD codimers

Acknowledgements

We would like to thank the Ministry of Industry and Trade of the Czech Republic for financial support through project FT-TA3/079, "Research on Progressive Chemical Products Based on Dicyclopentadiene".

References

[1] Csicsery, S. M.: J. Org. Chem. 1960, 25, 518.
[2] Alder, K., Ache, H. J.: Chem. Ber. 1962, 95, 503.
[3] Diez, M. S., Fannanas, F. J., Blanco, C. G., Bermejo J.: J. Chromatogr. 1989, 464, 93.
[4] Diez, M. S., Fannanas, F. J., Blanco, C. G., Bermejo J.: J. Chem. Technol. Biotechnol. 1990, 48, 173.
[5] Diez, M. S., Guillen, M. D., Blanco, C. G., Bermejo, J.: J. Chromatogr. 1990, 508, 363.
[6] Bermejo, J., Blanco, C. G., Diez, M. A.: Afinidad 1983, 40, 320.
[7] Lauer, J. C., Laurens, T., Schmit-Quiles, F., Nicole, D., Matlengiewicz, M., Henzel, N.: Analusis 1993, 21, 359.
[8] Laurens, T., Nicole, D., Rubini, P., Lauer, J. C., Matlengiewicz, M., Henzel, N.: Magn. Reson. Chem. 1991, 29, 1119.
[9] Schmit-Quiles, F., Laurens, T., Nicole, D., Lauer, J. C., Henzel, N.: Analusis 1993, 21, 227.
[10] Thommen, W., Pamingle, H., Schulte-Elte, K. H.: Helv. Chim. Acta 1989, 72, 1346.
[11] Zharov, V. P., Montanari, S. G., Tumanova, L. M.: Zh. Anal. Khim. 1984, 39, 551.
[12] Sergeyev, M. N., Avramenko, G. I., Korenevsky, V. A., Ustynyuk, Y. A.: Org. Magn. Reson. 1972, 4, 39.
[13] Langer, S. H., Melton, H. R., Griffit, T. D.: J. Chromatogr. 1976, 122, 487.
[14] Arefyev, O. A., Vorobyeva, N. S., Epishev, I. V., Petrov, A. A.: Neftekhimiya 1972, 12(2), 171.
[15] Musaev, M. R., Sharifova, S. M., Aliev, M. A.: Azerbaidzhanskii Khim. Zh. 1975 (5), 43.
[16] Mironov, V. A., Fadeeva, T. M., Stepanyanc, A. U., Akhrem, A. A.: Izvestiya Akad. Nauk SSSR Ser. Khim. 1967 (2), p. 434.
[17] Wassermann, A.: Diels-Alder Reactions, Elsevier Publishing Co., London, 1965.
[18] Wassermann, A.: Trans. Faraday Soc. 1938, 34, 128.
[19] Wassermann, A.: J. Chem. Soc. 1942, p. 618.
[20] Wassermann, A., Kaufmann, H.: J. Chem. Soc. 1939, p. 381.
[21] Khambata, B., Wassermann, A.: J. Chem. Soc. 1939, p. 870.
[22] Benford, G. A., Wassermann, A.: J. Chem. Soc. 1939, p. 362.
[23] Krupka, J.: Doctoral thesis, 2008, Institute of Chem. Technology, Prague, Czech Rep.
[24] Szekeres, G., Siklós, P., Nagy, L., Jelinek, L.: Periodica Polytechnica 1977, 21, 13.
[25] Howat, C. S., Swift, G. W.: Ind. Eng. Chem. Res. 1988, 27, 1487.
[26] Muja, I., Andreescu, G., Corciovei, M., Fratiloiu, R.: Revista de chimie 1975, 26, 981.
[27] Raistrick, B, Sapiro, R. H., Newitt, D. M.: J. Chem. Soc. 1939, p. 1761.
[28] Lesteva, T. M., Ogorodnikov, S. K., Morozova, A. I.: Zh. Prikl. Khim. 1967, 40, 891.
[29] Bělohlav, Z., Zámostný, P., Fulín, P., Štěpánek, K.: Chem. Biochem. Eng. Q. 2000, 14, 29.
[30] Turnbull, A. G., Hull, H. S.: Aust. J. Chem. 1968, 21 (7), 1789.
[31] Duschek, C, Pritzkow, W.: J. Prakt. Chem. 1970, Bd 312, 15.
[32] Krupka, J., Pašek, J.: "Chromatographic characteristics and identification of methyldicyclopentadiene and dimethyldicyclopentadiene isomers", Petroleum and Coal, Petroleum & Coal 52 (4) 227-234, 2010.
[33] Zámostný, P., Bělohlav, Z.: Comput. Chem. 1999, 23, 479.
[34] Krupka, J.: in preparation.

Table 10 Experimental data from the kinetic measurements of the reaction system CPD – 1-MCPD – 2-MCPD

t (min) X1	T (K) X2	c_{CPD} (mmol.l^{-1}) Y1	$c_{1\text{-}MCPD}$ (mmol.l^{-1}) Y2	$c_{2\text{-}MCPD}$ (mmol.l^{-1}) Y3	c_{DCPD} (mmol.l^{-1}) Y4	$c_{MDCPD\ 4}$ (mmol.l^{-1}) Y5	$c_{MDCPD\ 5}$ (mmol.l^{-1}) Y6	$c_{MDCPD\ 1}$ (mmol.l^{-1}) Y7	$c_{MDCPD\ 2}$ (mmol.l^{-1}) Y8	$c_{MDCPD\ 3}$ (mmol.l^{-1}) Y9	$c_{\Sigma\ DMDCPD}$ (mmol.l^{-1}) Y10
0	323.15	910.8	341.9	420.4	148.1	0.20	1.22	3.7	1.6	4.6	20.7
95	323.15	826.2	314.0	377.6	166.9	0.82	4.08	12.8	5.5	15.5	31.4
185	323.15	773.9	297.6	351.4	182.6	1.17	6.43	20.1	8.5	24.4	39.4
360	323.15	645.8	254.0	296.2	211.6	1.94	10.82	34.2	14.5	41.3	57.2
1350	323.15	349.0	131.2	160.8	271.0	3.83	21.43	68.4	28.9	82.4	94.0
1660	323.15	292.4	113.9	142.6	300.3	4.39	25.31	81.4	34.3	98.0	119.4
0	343.15	640.2	278.6	347.7	125.2	0.40	2.09	6.4	2.9	7.7	21.8
55	343.15	572.4	233.8	323.5	147.6	1.29	6.46	20.0	8.6	23.8	38.1
120	343.15	452.9	187.0	240.2	172.8	2.09	10.88	34.3	14.5	40.7	55.7
210	343.15	355.3	146.5	191.3	196.7	2.93	14.95	47.3	19.9	56.3	72.0
422	343.15	233.0	98.0	131.0	223.1	3.82	19.86	64.6	26.6	76.3	91.6
1660	343.15	109.0	33.6	65.4	332.7	4.53	27.41	91.6	37.5	107.0	125.4
0	373.15	590.3	247.8	322.0	181.7	2.11	9.74	26.1	11.6	30.5	46.1
21	373.15	378.8	161.3	212.8	229.9	4.37	20.01	54.8	23.9	63.7	80.7
50	373.15	251.6	106.4	141.3	249.7	5.32	24.64	70.4	30.6	80.7	97.1
90	373.15	121.0	71.2	95.0	272.6	6.37	28.96	84.9	36.9	96.1	115.6
175	373.15	88.5	42.3	55.9	295.8	7.00	32.43	101.1	44.4	111.2	135.6
370	373.15	41.7	20.8	27.6	308.9	7.37	32.17	113.4	51.2	117.7	149.7
0	393.15	443.0	174.5	227.7	214.1	3.51	15.21	45.9	20.7	52.2	62.8
20	393.15	184.2	76.3	100.6	255.5	5.50	23.12	75.0	34.7	81.1	96.3
41	393.15	107.0	48.5	63.8	269.0	6.47	24.32	87.7	41.1	90.7	106.0
70	393.15	62.8	32.2	42.3	285.8	7.21	24.64	100.6	48.4	94.1	120.5
150	393.15	37.1	17.1	22.4	289.3	7.67	20.30	109.5	55.1	95.7	106.4
285	393.15	21.9	9.7	12.7	292.6	8.04	16.27	118.6	62.1	98.5	129.2

Table 10 Continuing – Experimental data from the kinetic measurements of the reaction system CPD – 1-MCPD – 2-MCPD, including data on the rearrangement of MDCPD 5 to MDCPD 2 codimer

t (min) X1	T (K) X2	c_{CPD} (mmol.l^{-1}) Y1	$c_{1\text{-}MCPD}$ (mmol.l^{-1}) Y2	$c_{2\text{-}MCPD}$ (mmol.l^{-1}) Y3	c_{DCPD} (mmol.l^{-1}) Y4	$c_{MDCPD\ 4}$ (mmol.l^{-1}) Y5	$c_{MDCPD\ 5}$ (mmol.l^{-1}) Y6	$c_{MDCPD\ 1}$ (mmol.l^{-1}) Y7	$c_{MDCPD\ 2}$ (mmol.l^{-1}) Y8	$c_{MDCPD\ 3}$ (mmol.l^{-1}) Y9	$c_{\Sigma\ DMDCPD}$ (mmol.l^{-1}) Y10
0	353.15	0	0	0	0	0	1194.0	0	22.7	0	0
500	353.15	0	0	0	0	0	1157.5	0	56.8	0	0
3360	353.15	0	0	0	0	0	993.9	0	243.5	0	0
6050	353.15	0	0	0	0	0	824.6	0	366.3	0	0
15840	353.15	0	0	0	0	0	453.8	0	690.4	0	0
0	373.15	0	0	0	0	0	495.6	0	22.1	0	0
50	373.15	0	0	0	0	0	458.3	0	35.8	0	0
120	373.15	0	0	0	0	0	439.7	0	57.4	0	0
250	373.15	0	0	0	0	0	400.0	0	93.6	0	0
440	373.15	0	0	0	0	0	359.4	0	139.0	0	0
1400	373.15	0	0	0	0	0	219.7	0	312.3	0	0
0	393.15	0	0	0	0	0	440.4	0	41.6	0	0
20	393.15	0	0	0	0	0	411.6	0	87.9	0	0
40	393.15	0	0	0	0	0	384.6	0	136.8	0	0
110	393.15	0	0	0	0	0	276.8	0	261.8	0	0
275	393.15	0	0	0	0	0	156.1	0	391.9	0	0
480	393.15	0	0	0	0	0	110.7	0	414.8	0	0
0	413.15	0	0	0	0	0	349.5	0	220.0	0	0
20	413.15	0	0	0	0	0	188.8	0	369.8	0	0
40	413.15	0	0	0	0	0	138.9	0	409.5	0	0