

Molecular modeling of ring-chain equilibria for the ring-opening cross-metathesis of *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene with ethylene at $T = 298.15 \text{ K}$

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Abstract

The molecular modeling of ring-opening cross-metathesis of *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene (1,5-DM-COD), *cis,cis*-1,6-dimethyl-cycloocta-1,5-diene (1,6-DM-COD) and *cis,cis*-cycloocta-1,5-diene (COD) with ethylene (ethenolysis) at $T = 298.15 \text{ K}$ using the B3LYP/6-31G(d,p) level of theory reveals that ring-chain equilibrium constants are dependent on the nature of cyclic diene. The ring-chain equilibria for the ethenolysis of 1,5-DM-COD is completely shifted to the formation of monomeric 2-methyl-hexa-1,5-diene.

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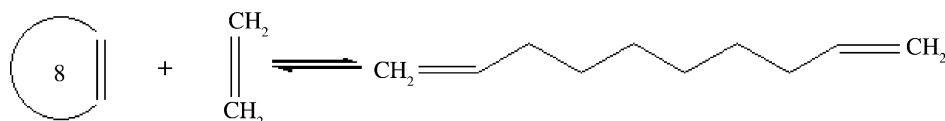
Keywords: *Ab initio* calculations; Ring-opening cross-metathesis; *cis,cis*-1,5-Dimethyl-cycloocta-1,5-diene; Equilibrium concentrations

1. Introduction

The main feature of the metathesis is the conservation of the total number and types of the chemical bonds during the reaction. The reaction leads to equilibrium between all species formed during the exchange of the double bonds and thermodynamic data can be used for the prediction and calculations of equilibrium products distributions in the system. Thus, the equilibrium distribution of the alkylidene species has been calculated for the metathesis of simple linear olefins [1]. The theoretical estimations of the distribution ring-chain products for the ring-opening metathesis polymerization (ROMP) of cycloolefins have recently been published [2]. The distributions of cyclic and linear oligomers for the intra- and intermolecular metathesis degradation of 1,4-polybutadiene and 1,4-polyisoprene using it *ab initio* approach have been studied by authors [3,4].

ROMP of cycloolefins in the presence of acyclic olefin as a chain transfer agent (CTA) leads to linear products with controlled molecular weights and functionalities [5] (scheme 1). Thus, ROMP of 1,5-cyclooctadiene in the presence of a CTA resulted in polybutadiene end capped with amino, hydroxy, carboxy and allyl chloride functional groups [5]. The end-functionalized polymers (tel-echelics) are very useful as intermediates in the synthesis of block copolymers, polymeric networks and cross-linking agents. ROMP of cycloolefins in the presence of ethylene as a CTA (ethenolysis) yields α,ω -diolefins which can be used as cross-linking agents and starting compounds in the production of fine chemicals [5]. Few reports are related to ROMP of substituted cyclooctadiene and its cross-metathesis with olefins. This may be due to the fact that these cyclic dienes participate in ROMP slower compared to unsubstituted cycloolefins [5]. Hence, cycloolefins with tri-substituted unsaturations require long time stable and high selective catalysts. The development of new generation highly active and long-lived metal-alkylidene catalysts opens new possibilities in olefin metathesis and its application to

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SCHEME 1. Ring-opening cross-metathesis of cycloolefin via ethenolysis.

polymer synthesis and degradation [5,6]. Thus, ROMP of sterically hindered *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene (1,5-DM-COD) to polyisoprene by well-defined ruthenium alkylidene catalyst has recently been reported [7]. The polymerizability via ROMP of COD having methyl, ethyl and chloro-groups has also been published [8–11]. The preparation of substituted polyalkenamers and telomers with well-defined end groups (telechelic polymers) has attracted much attention. For example, perfectly alternating copolymer of isoprene and butadiene can be prepared by ROMP of 1-methyl-cycloocta-1,5-diene [8]. Ring-opening cross-metathesis of COD and cyclododeca-1,5,9-triene with ethylene has been exploited commercially for the preparation of high-purity hexa-1,5-diene [5]. The ethenolysis of 1,5-DM-COD produced by isoprene cyclooligomerization could be a promising route for the preparation of substituted hexa-1,5-diene in the near future. It is important to note, that 1,5-DM-COD contains *cis,cis*-1,6-dimethyl-cycloocta-1,5-diene (1,6-DM-COD) isomer (about 20%) as an inseparable mixture.

The aim of this study is to model ring-chain equilibria for the ring-opening cross-metathesis of 1,5-DM-COD, 1,6-DM-COD and COD with ethylene using the *ab initio* approach and to compare the results of calculations with the experiment.

2. Computational details

All geometry optimizations were run using the Gaussian 98 [12] revision A9 package without any symmetry restriction. Lowest energy conformers were located using a Monte Carlo algorithm as implemented in the Titan package version 1.0.5 [13]. Lowest energy conformers found were used as initial structures for the geometry optimization using Becke's parameter functional (B) [14] in combination with the Lee, Yang and Parr (LYP) correlation function [15] and 6-31G(d,p) standard basis set. The molecular geometries of the all calculated molecules were optimized to a global minimum at B3LYP/6-31G(d,p) level of theory followed by frequency calculations at $T = 298.15$ K. All thermodynamic quantities were calculated by standard statistical mechanical approaches as implemented in the Gaussian 98 programme. The equilibrium constants were calculated according to

$$\Delta G^\circ = -RT \ln K, \quad (1)$$

where R is the universal gas constant, T is the absolute temperature and ΔG° is the standard free energy reaction difference. The equilibrium concentrations of *trans*- and *cis*- $C_{12}H_{20}$, *trans*- $C_{10}H_{16}$, *cis,cis*- $C_{10}H_{16}$, *cis,cis*- C_8H_{12} , 2-methyl-hexa-1,5-diene (C_7H_{12}), hexa-1,5-diene (C_6H_{10}) and ethylene molecules were calculated assuming the equilibria shown in tables 4 and 5 solving the following systems of equations (*trans*- and *cis* have been abbreviated to *t*- and *c*-, respectively):

$$\begin{aligned} [c-C_{12}H_{20}] / ([cc-C_{10}H_{16}][C_2H_4]) &= K_1, \\ [t-C_{12}H_{20}] / ([cc-C_{10}H_{16}][C_2H_4]) &= K_2, \\ [C_{12}H_{20}] + [cc-C_{10}H_{16}] + [C_2H_4] &= 1, \\ [C_7H_{12}]^4 / ([cc-C_{10}H_{16}][c-C_{12}H_{20}][C_2H_4]^3) &= K_3, \\ [C_7H_{12}]^2 / ([c-C_{12}H_{20}][C_2H_4]) &= K_4, \\ [C_7H_{12}] + [cc-C_{10}H_{16}] + [c-C_{12}H_{20}] + [C_2H_4] &= 1, \quad (2) \\ [t-C_{10}H_{16}] / ([cc-C_8H_{12}][C_2H_4]) &= K_5, \\ [C_6H_{10}]^4 / ([cc-C_8H_{12}][t-C_{10}H_{16}][C_2H_4]^3) &= K_6, \\ [C_6H_{10}] + [cc-C_8H_{12}] + [C_{10}H_{16}] + [C_2H_4] &= 1, \\ [C_6H_{10}]^2 / ([t-C_{10}H_{16}][C_2H_4]) &= K_7, \\ [C_6H_{10}] + [C_{10}H_{16}] + [C_2H_4] &= 1, \end{aligned}$$

where K_1 to K_7 are respective equilibrium constants.

3. Results

The ethenolysis of 1,5-DM-COD proceeds via the formation of *cis*- and *trans*-2,6-dimethyl-deca-1,5,9-triene isomers which are participated in the further cross-metathesis with ethylene to form 2-methyl-hexa-1,5-diene. Scheme 2 presents the possible distributions of products for the ring-opening cross-metathesis of 1,5-DM-COD with ethylene. Table 1 shows the calculated thermodynamic parameters of cyclic and linear molecules for the cross-metathesis of 1,5-DM-COD, 1,6-DM-COD and COD with ethylene at $T = 298.15$ K. It is seen that the formation of *trans*-butadiene molecules becomes more preferable compared to *cis*-isomers when the difference in the standard free energies between *cis*- and *trans*-isomers is about $8.4 \text{ kJ} \cdot \text{mol}^{-1}$. In the case of 1,5-DM-COD ethenolysis, the formation of *cis*- and *trans*-isoprene oligomers is equally likely. The identical standard energy terms for the *cis*- and *trans*-isomers are related to the effect of the methyl substituents [3,16]. Figure 1 shows the calculated minimum energy conform-

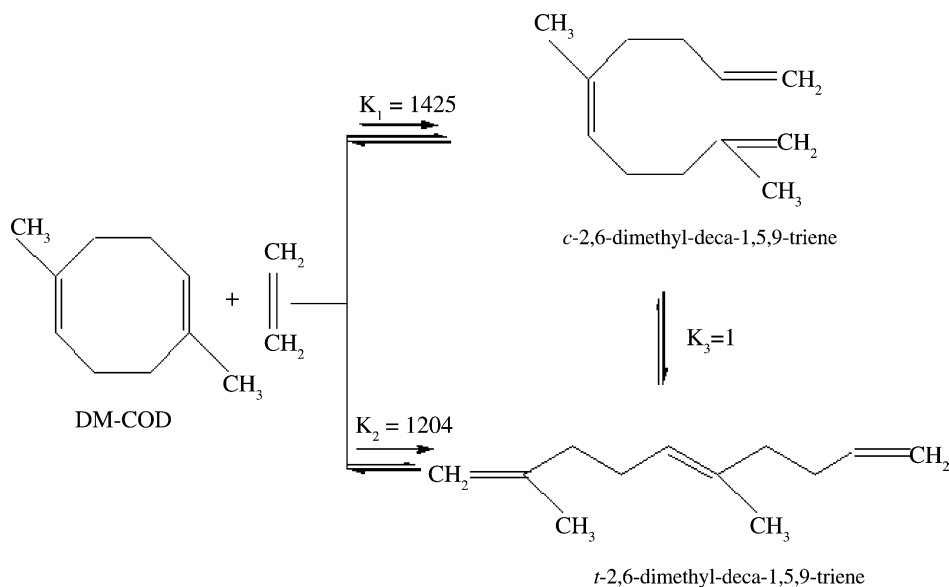
SCHEME 2. Ring-opening cross-metathesis of 1,5-DM-COD with ethylene to *cis*- and *trans*-2,6-dimethyl-deca-1,5,9-triene.

TABLE 1

Calculated standard free energy (G°), enthalpy (H) and entropy (S) of cyclic and linear molecules for the ring-opening cross-metathesis of *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene (1,5-DM-COD), *cis,cis*-1,6-dimethyl-cycloocta-1,5-diene (1,6-DM-COD) and *cis,cis*-cycloocta-1,5-diene (COD) with ethylene at $T = 298.15$ K

Compound	Formula	$10^{-5}G^\circ$ (kJ · mol ⁻¹)	$10^{-5}H$ (kJ · mol ⁻¹)	S (kJ · K ⁻¹ · mol ⁻¹)
COD	C ₈ H ₁₂	-8.1889	-8.1879	351.5
1,5-DM-COD	1,5-C ₁₀ H ₁₆	-10.2521	-10.2508	412.5
1,6-DM-COD	1,6-C ₁₀ H ₁₆	-10.2522	-10.2510	411.7
<i>c</i> -Deca-1,5,9-triene	C ₁₀ H ₁₆	-10.2516	-10.2502	458.2
<i>t</i> -Deca-1,5,9-triene	C ₁₀ H ₁₆	-10.2517	-10.2503	465.3
<i>c</i> -2,6-Dimethyl-deca-1,5,9-triene	C ₁₂ H ₂₀	-12.3149	-12.3134	524.7
<i>t</i> -2,6-Dimethyl-deca-1,5,9-triene	C ₁₂ H ₂₀	-12.3149	-12.3134	518.4
<i>c</i> -2,5-Dimethyl-deca-1,5,9-triene	C ₁₂ H ₂₀	-12.3149	-12.3133	510.0
<i>t</i> -2,5-Dimethyl-deca-1,5,9-triene	C ₁₂ H ₂₀	-12.3149	-12.3134	517.9
2-Methyl-hexa-1,5-diene	C ₇ H ₁₂	-7.1889	-7.1877	381.6
Hexa-1,5-diene	C ₆ H ₁₀	-6.1572	-6.1561	348.9
Ethylene	C ₂ H ₄	-2.0627	-2.0620	224.7

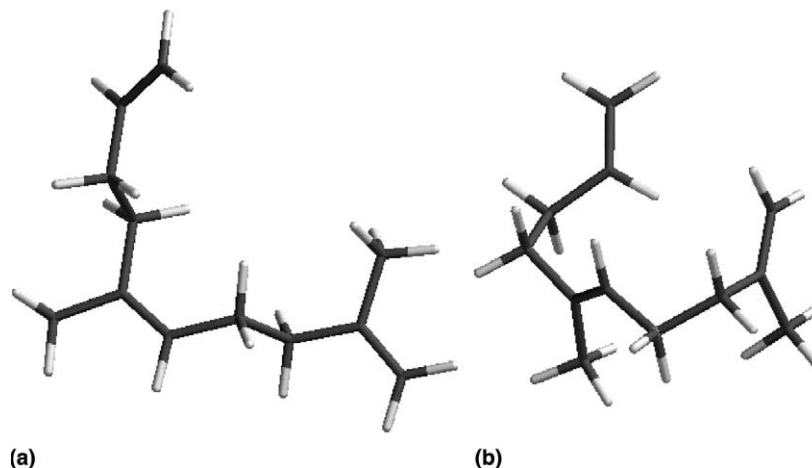
FIGURE 1. Lowest energy conformers of *cis*- (a) and *trans*- (b) isomers of 2,6-dimethyl-deca-1,5,9-triene.

TABLE 2

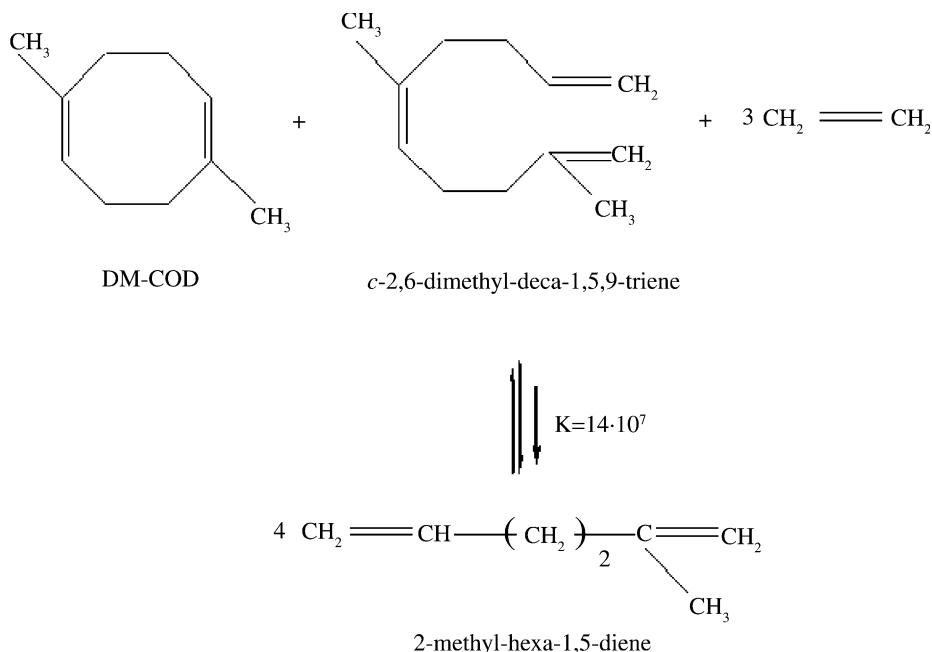
Standard free energy (ΔG°), enthalpy (ΔH) and entropy (ΔS) differences of cyclic diene-linear molecules equilibrium for the ring-opening cross-metathesis of 1,5-DM-COD, 1,6-DM-COD and COD with ethylene at $T = 298.15$ K

Entry	Reaction	ΔG° (kJ · mol ⁻¹)	ΔH (kJ · mol ⁻¹)	ΔS (J · K ⁻¹ · mol ⁻¹)
1	1,5-C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons <i>c</i> -C ₁₂ H ₂₀ ^a	-18.0	-51.5	-106.3
2	1,5-C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons <i>t</i> -C ₁₂ H ₂₀ ^a	-17.6	-52.7	-118.8
3	1,5-C ₁₀ H ₁₆ + <i>c</i> -C ₁₂ H ₂₀ + 3C ₂ H ₄ \rightleftharpoons 4C ₇ H ₁₂ ^b	-46.4	-72.4	-84.9
4	<i>c</i> -C ₁₂ H ₂₀ + C ₂ H ₄ \rightleftharpoons 2C ₇ H ₁₂ ^c	-14.2	-10.5	13.8
5	<i>t</i> -C ₁₂ H ₂₀ + C ₂ H ₄ \rightleftharpoons 2C ₇ H ₁₂ ^c	-14.6	-8.8	20.1
6	1,6-C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons <i>c</i> -C ₁₂ H ₂₀ ^d	5.9	-31.4	-224.7
7	1,6-C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons <i>t</i> -C ₁₂ H ₂₀ ^d	1.7	-33.1	-216.3
8	C ₈ H ₁₂ + C ₂ H ₄ \rightleftharpoons <i>t</i> -C ₁₀ H ₁₆ ^e	-7.1	-40.2	-110.9
9	C ₈ H ₁₂ + <i>t</i> -C ₁₀ H ₁₆ + 3C ₂ H ₄ \rightleftharpoons 4C ₆ H ₁₀ ^f	-13.0	-41.8	-94.9
10	<i>t</i> -C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons 2C ₆ H ₁₀ ^g	-4.2	-0.4	8.4

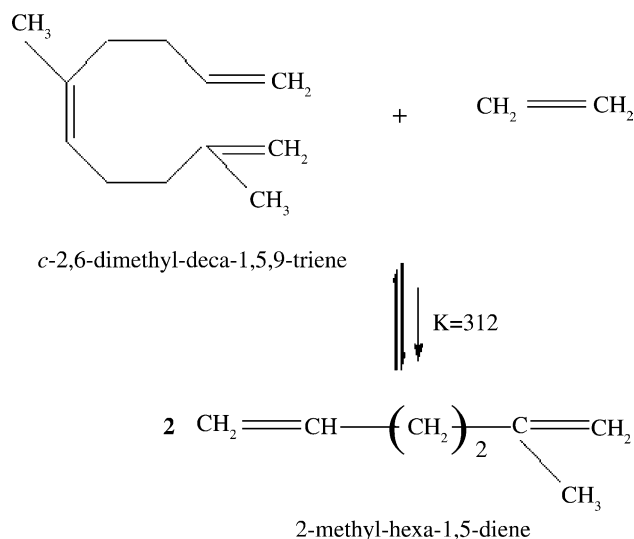
^a Scheme 2.^b Scheme 3.^c Scheme 4.^d Scheme 5.^e Scheme 6.^f Scheme 7.^g Scheme 8.

mations for the *cis*- and *trans*-isoprene molecules (C₁₂H₂₀). Table 2 presents the calculated standard free energy (ΔG°), enthalpy (ΔH) and entropy (ΔS) differences of the ring-linear molecules equilibrium for the cross-metathesis of 1,5-DM-COD, 1,6-DM-COD and COD with ethylene at $T = 298.15$ K. As seen, the formation of *cis*- and *trans*-2,6-dimethyl-deca-1,5,9-triene isomers for the ring-opening cross-metathesis of 1,5-DM-COD with ethylene at $T = 298$ K is equally likely (scheme 2). Table 2 (entries 3, 4 and 5) presents the values of ΔG° energies for the ethenolysis of 1,5-DM-COD and α,ω -vinyl-ter-

minated oligomers to 2-methyl-hexa-1,5-diene (schemes 3 and 4). The values of ΔG° for the 1,6-DM-COD ring-opening cross-metathesis with ethylene are positives at $T = 298.15$ K (table 2, entries 6 and 7, scheme 5). When substituted groups are in the 1,5 position, ΔG° for the ring-opening of eight membered ring is more negative as a result of an increased strain energy in this monomer (table 2). It is seen that 1,5-DM-COD has a much higher strain energy ($\Delta H = 12.6$) compared with 1,6-DM-COD ($\Delta H = 7.9$). Table 2 (entries 8, 9 and 10) also presents the thermodynamics for the ethenolysis of COD and



SCHEME 3. Ethenolysis of 1,5-DM-COD to 2-methyl-hexa-1,5-diene.

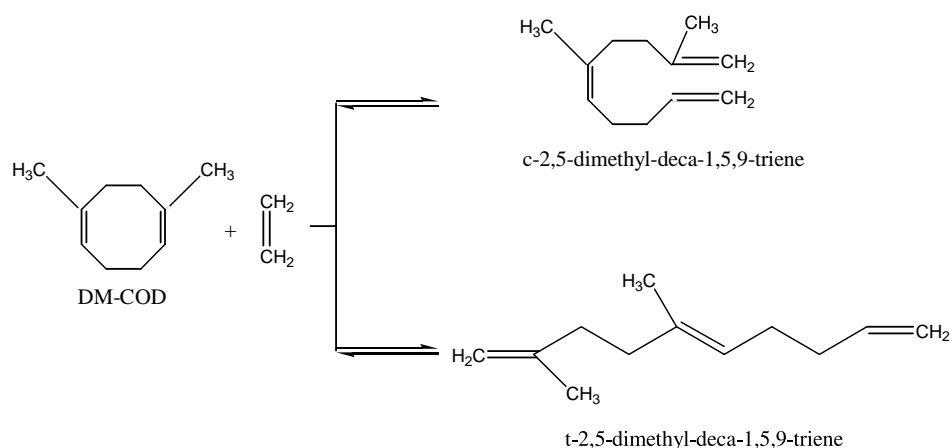


SCHEME 4. Ethenolysis of *trans*-2,6-dimethyl-deca-1,5,9-triene to 2-methyl-hexa-1,5 diene.

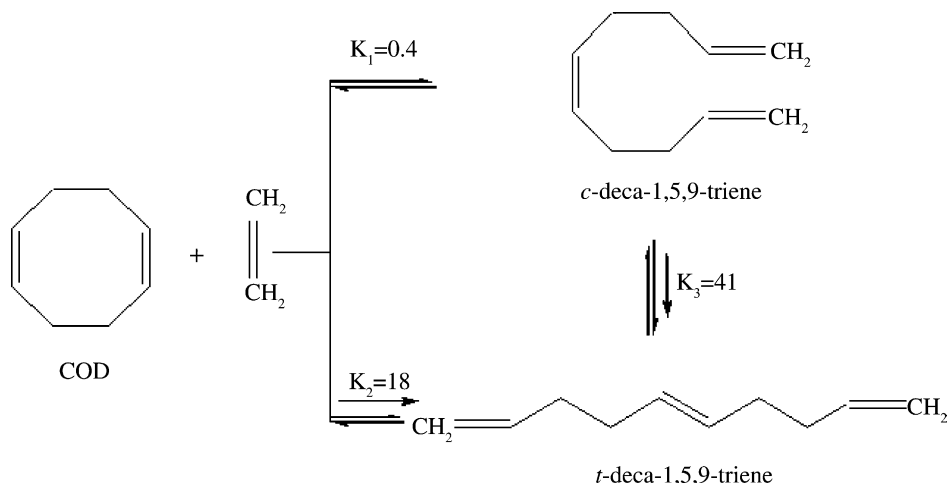
α, ω -vinyl-terminated $t\text{-C}_{10}\text{H}_{16}$ to 1,5-hexadiene (schemes 6 to 8).

For the ring-chain equilibrium, the enthalpic change (ΔH) corresponds to the strain energy of ring, since the reaction is an isodesmic one. The reaction enthalpy in this case is only a function of ring strain and *cis/trans* isomerization energy. The calculated enthalpy change (ΔH) for the ring-opening cross-metathesis of cyclic dienes with ethylene will correspond to the strain energy of these monomers. Thus, the value of ΔH for the cross-metathesis of COD with ethylene to *trans*- $\text{C}_{10}\text{H}_{16}$ is $-40.1 \text{ kJ} \cdot \text{mol}^{-1}$. The experimentally obtained value of ΔH for conversion of COD into *trans*-polybutadiene at $T = 298 \text{ K}$ is $-33.0 \text{ kJ} \cdot \text{mol}^{-1}$ [17]. It is seen that the agreement is very reasonable.

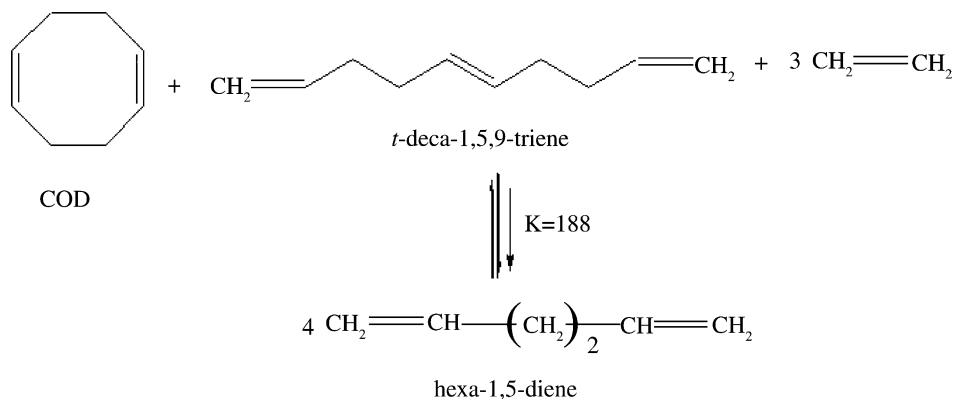
Table 3 summarizes the calculated standard free energy differences (ΔG°) and equilibrium constants (K) for the ring-opening cross-metathesis of 1,5-DM-COD, 1,6-DM-COD and COD with ethylene at $T = 298.15 \text{ K}$.



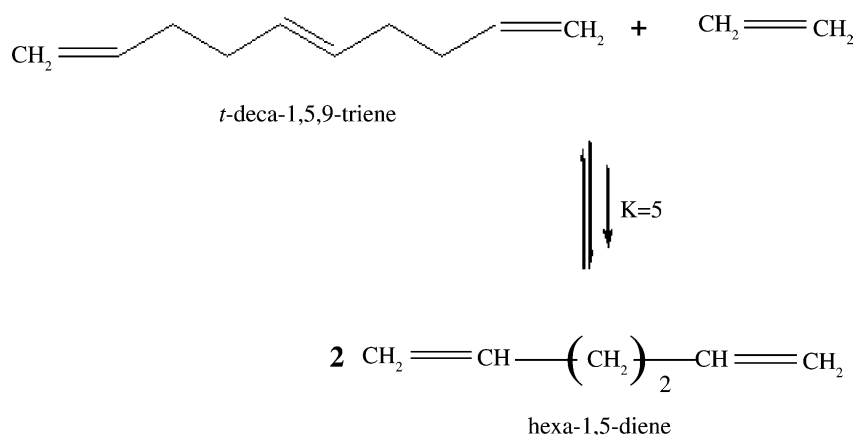
SCHEME 5. Ring-opening cross-metathesis of 1,6-DM-COD with ethylene to *cis*- and *trans*-2,5-dimethyl-deca-1,5,9-triene.



SCHEME 6. Ring-opening cross-metathesis of COD with ethylene to *cis*- and *trans*-deca-1,5,9-triene.



SCHEME 7. Ethenolysis of COD to hexa-1,5-diene.

SCHEME 8. Ethenolysis of *trans*-deca-1,5,9-triene to hexa-1,5-diene.

The results show that ring-linear molecules equilibria for the ethenolysis of 1,5-DM-COD and COD is shifted to 2-methyl-hexa-1,5-diene and hexa-1,5-diene, respec-

tively, and its concentrations depend on the nature of used cyclooctadiene. Thus, the equilibrium constants for the ethenolysis of 1,5-DM-COD and COD are $14 \cdot 10^7$

TABLE 3

Standard free energy differences (ΔG°) and equilibrium constants (K) of cyclic diene-linear molecules equilibrium for the ring-opening cross-methathesis of 1,5-DM-COD, 1,6-DM-COD and COD with ethylene at $T = 298.15 \text{ K}$

Entry	Reaction	ΔG° (kJ · mol ⁻¹)	K
1	$1,5\text{-C}_{10}\text{H}_{16} + \text{C}_2\text{H}_4 \rightleftharpoons c\text{-C}_{12}\text{H}_{20}^a$	-18.0	1425
2	$1,5\text{-C}_{10}\text{H}_{16} + \text{C}_2\text{H}_4 \rightleftharpoons t\text{-C}_{12}\text{H}_{20}^a$	-17.6	1204
3	$1,5\text{-C}_{10}\text{H}_{16} + c\text{-C}_{12}\text{H}_{20} + 3\text{C}_2\text{H}_4 \rightleftharpoons 4\text{C}_7\text{H}_{12}^b$	-46.4	14×10^7
4	$c\text{-C}_{12}\text{H}_{20} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{C}_7\text{H}_{12}^c$	-14.2	312
5	$1,6\text{-C}_{10}\text{H}_{16} + \text{C}_2\text{H}_4 \rightleftharpoons c\text{-C}_{12}\text{H}_{20}^d$	5.9	0.1
6	$1,6\text{-C}_{10}\text{H}_{16} + \text{C}_2\text{H}_4 \rightleftharpoons t\text{-C}_{12}\text{H}_{20}^d$	4.6	0.5
7	$\text{C}_8\text{H}_{12} + \text{C}_2\text{H}_4 \rightleftharpoons t\text{-C}_{10}\text{H}_{16}^e$	-7.1	18
8	$\text{C}_8\text{H}_{12} + t\text{-C}_{10}\text{H}_{16} + 3\text{C}_2\text{H}_4 \rightleftharpoons 4\text{C}_6\text{H}_{10}^f$	-13.0	188
9	$t\text{-C}_{10}\text{H}_{16} + \text{C}_2\text{H}_4 \rightleftharpoons 2\text{C}_6\text{H}_{10}^g$	-4.2	5

^a Scheme 2.^b Scheme 3.^c Scheme 4.^d Scheme 5.^e Scheme 6.^f Scheme 7.^g Scheme 8.

TABLE 4

Calculated cyclic and linear molecules distributions for the ethenolysis of 1,5-DM-COD at $T = 298.15$ K

Reaction	Mole fraction in % of			
	<i>cc</i> -C ₁₀ H ₁₆	C ₁₂ H ₂₀	C ₂ H ₄	C ₇ H ₁₂
<i>cc</i> -C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons <i>c</i> -C ₁₂ H ₂₀ ^a	2.7	94.8	2.7	
<i>cc</i> -C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons <i>t</i> -C ₁₂ H ₂₀ ^a	2.8	94.4	2.8	
<i>cc</i> -C ₁₀ H ₁₆ + <i>c</i> -C ₁₂ H ₂₀ + 3C ₂ H ₄ \rightleftharpoons 4C ₇ H ₁₂ ^b	1.0	1.0	15.4	82.6
<i>c</i> -C ₁₂ H ₂₀ + C ₂ H ₄ \rightleftharpoons 2C ₇ H ₁₂ ^c		5.1	5.1	89.8

^a Scheme 2.^b Scheme 3.^c Scheme 4.

TABLE 5

Calculated cyclic and linear molecules distributions for the ethenolysis of COD at $T = 298.15$ K

Reaction	Mole fraction in % of			
	<i>cc</i> -C ₈ H ₁₂	C ₁₀ H ₁₆	C ₂ H ₄	C ₆ H ₁₀ ^a
<i>cc</i> -C ₈ H ₁₂ + C ₂ H ₄ \rightleftharpoons <i>t</i> -C ₁₀ H ₁₆ ^b	11	78	11	
<i>cc</i> -C ₈ H ₁₂ + <i>t</i> -C ₁₀ H ₁₆ + 3C ₂ H ₄ \rightleftharpoons 4C ₆ H ₁₀ ^c	10	10	30	50
<i>t</i> -C ₁₀ H ₁₆ + C ₂ H ₄ \rightleftharpoons 2C ₆ H ₁₀ ^d		27	27	46

^a The values of experimentally observed yield of hexa-1,5-diene (C₆H₁₀) for the ethenolysis of COD [19] (ethylene/COD = 2) and *cis*-PB [20] (30 psig C₂H₄ pressure) were 50 and 43 mol%, respectively.^b Scheme 6.^c Scheme 7.^d Scheme 8.

and 188, respectively (entries 3 and 8, table 3). Table 4 presents the calculated distributions of cyclic and linear species for the ethenolysis of 1,5-DM-COD (schemes 2 to 4). The ring-opening cross-metathesis of this cyclic diene is completely shifted towards the *cis*- or *trans*-2,6-dimethyl-deca-1,5,9-triene (scheme 3). The cross-metathesis of linear isoprene oligomers with ethylene proceeds with high selectivity to form 2-methyl-hexa-1,5-diene. It follows that the ethenolysis of 1,4-polyisoprene will result with high yield in monomeric isoprene diene. Thus, the expected 2-methyl hexa-1,5-diene was detected during the ethenolysis of *trans*-polyisoprene by a tungsten carbene catalyst [18]. The calculations show that the ethenolysis of 1,5-DM-COD to monomeric diene can be realized with high selectivity without the need for large excess of CTA. Table 5 shows the calculated distributions of cyclic and linear species for the ethenolysis of COD. The concentration of hexa-1,5-diene at equilibrium with COD and *trans*-C₁₀H₁₆ is of 46 mol%. The results of calculations are in agreement with experimental data on the ethenolysis of COD by rhenium based catalysts [19] and 1,4-polybutadiene using a well-defined ruthenium alkylidene catalyst [20].

Acknowledgements

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