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Molecular modeling of ring-opening cross metathesis. Distributions of products for the ethenolysis of *cis,cis*-cycloocta-1,5-diene and *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene

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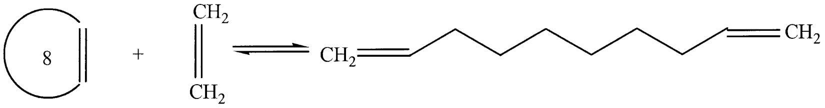
Abstract—The molecular modeling of the products distributions for the ethenolysis of *cis,cis*-cycloocta-1,5-diene and *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene at 298.15 K using the B3LYP/6-31G(d, p) level of theory reveals that the concentrations of hexa-1,5-dienes at equilibrium with cyclic and α,ω-vinyl-terminated molecules depend on the nature of cyclic diene and *cis/trans* ratio in linear butadiene oligomers. The selectivity of ring-opening cross metathesis of cycloocta-1,5-diene with *cis*-but-2-ene as chain transfer agent is higher than that with *trans*-but-2-ene. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The main feature of the metathesis is the conservation of the total number and types of the chemical bonds during the reaction. This reaction leads to equilibrium between all species formed during the exchange of the double bonds and thermodynamic data can be used for the prediction of equilibrium state of all products in the system. Thus, the equilibrium distribution of the alkylidene species has been calculated for the metathesis of simple linear olefins.[1] The theoretical estimation of ring-chain products distributions 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 *cis*-polybutadiene (*cis*-PB) and *cis*-polyisoprene (*cis*-PI) using ab initio approach have been studied by authors.[3]

It is well known that the ROMP of cycloolefins in the presence of acyclic olefin as a chain transfer agent (CTA) leads to linear products with controlled molecular weights[4] (Scheme 1). Many studies devoted to the cross-metathesis of *cis,cis*-cycloocta-1,5-diene (COD) with linear olefins have been carried out.[5–14] On the other hand, very few reports are related to ROMP of substituted COD and its cross-metathesis with olefins. The lack of information on this topic may be due to the fact that these cyclic dienes participate in ROMP slower compared to unsubstituted cycloolefins.[4] Hence, cycloolefins with trisubstituted unsaturations require long-time stable and high selective catalysts. The development of highly active and long-lived metal-alkylidene catalysts of new generation opens vast opportunities in olefin metathesis and its application to polymer synthesis.[4,15] Thus, ROMP of sterically hindered *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene (DM-COD) to polyisoprene in 90% yield by well-defined ruthenium alkylidene catalyst has recently been reported.[16] The polymerizabilty by ROMP of COD having methyl, ethyl and chloro-groups has also been investigated.[17–20] The preparation of substituted polyalkenamers and telomers with well-defined end groups has recently attracted much attention. For example, perfectly alternating copolymer of isoprene and butadiene can be



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

Keywords: ab initio calculations; ethenolysis; cycloocta-1,5-diene; products distributions; isomers; hexa-1,5-diene; selectivity.

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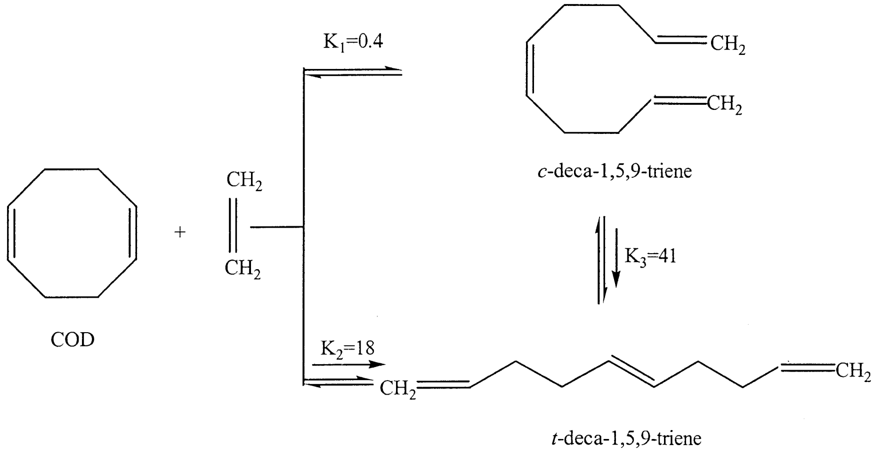


Scheme 2. Ring-opening cross-metathesis of COD with ethylene to *cis*- and *trans*-deca-1,5,9-triene.

prepared by ROMP of 1-methyl-cycloocta-1,5-diene.[17] The ROMP of cycloolefins in the presence of ethylene widely used in industry. This reaction has been exploited commercially for the preparation of high-purity hexa-1,5-diene from COD and cyclododeca-1,5,9-triene.[4] The ring-opening cross metathesis of DM-COD produced by cyclooligomerization of isoprene could be a promising route for the preparation of substituted hexa-1,5-diene in the near future.

The aims of this study is to estimate the concentrations of hexa-1,5-diene and 2-methyl-hexa-1,5-diene at equilibrium with cyclic and linear molecules for the ethenolysis of COD and DM-COD using ab initio approach.

2. Computational details

All geometry optimizations were run using Gaussian-98[21] revision A9 package without any symmetry restriction. Lowest energy conformers were located using Monte-Carlo algorithm as implemented in Titan package version 1.0.5.[22] Lowest energy conformers found were used as initial structures for the geometry optimization using Becke's parameter functional (B)[23] in combination with Lee, Yang and Parr (LYP) correlation function[24] and 6-31G(d, p) standard basis set. The molecular geometries of all calculated molecules were optimized to a global minimum at B3LYP/6-31G(d, p) level of theory followed by frequency calculations at 298.15 K. All thermodynamic quantities were calculated by a standard statistical mechanical approach as implemented in Gaussian 98 program. The equilibrium constants were calculated according to Eq. (1).

$$\Delta G = -RT \ln K \tag{1}$$

where R is the universal gas constant, T the absolute temperature and ΔG the standard free energy reaction difference. The equilibrium concentrations of *trans,trans,trans*-$C_{12}H_{20}$, *trans*- and *cis*-$C_{12}H_{20}$, *trans*- and *cis*-$C_{10}H_{16}$, *cis,cis*-$C_{10}H_{16}$, *cis,cis*-C_8H_{12}, *trans,trans*-C_8H_{14}, 2-methyl-hexa-1,5-diene (C_7H_{12}), hexa-1,5-diene (C_6H_{10}), *trans*- and *cis*-but-2-ene and ethylene molecules were calculated assuming the equilibriums shown in Tables 4–6 solving the following systems of equations (*trans*- and *cis*- have been abbreviated to *t*- and *c*-, respectively):

$$[t\text{-}C_{10}H_{16}]/([cc\text{-}C_8H_{12}][C_2H_4]) = K_1$$

$$[C_6H_{10}]^4/([cc\text{-}C_8H_{12}][t\text{-}C_{10}H_{16}][C_2H_4]^3) = K_2$$

$$[C_6H_{10}]^4/([cc\text{-}C_8H_{12}][c\text{-}C_{10}H_{16}][C_2H_4]^3) = K_3$$

$$[C_6H_{10}] + ([cc\text{-}C_8H_{12}] + [C_{10}H_{16}] + [C_2H_4]) = 1$$

$$[C_6H_{10}]^2/([t\text{-}C_{10}H_{16}][C_2H_4]) = K_4$$

$$[C_6H_{10}]^2/([c\text{-}C_{10}H_{16}][C_2H_4]) = K_5$$

$$[C_6H_{10}] + [C_{10}H_{16}] + [C_2H_4] = 1$$

$$[tt\text{-}C_8H_{14}]^4/([cc\text{-}C_8H_{12}][ttt\text{-}C_{12}H_{20}][c\text{-}C_4H_8]^3) = K_6$$

$$[tt\text{-}C_8H_{14}]^4/([cc\text{-}C_8H_{12}][ttt\text{-}C_{12}H_{20}][t\text{-}C_4H_8]^3) = K_7$$

$$[tt\text{-}C_8H_{14}] + ([cc\text{-}C_8H_{12}] + [ttt\text{-}C_{12}H_{20}] + [C_4H_8]) = 1 \tag{2}$$

$$[tt\text{-}C_8H_{14}]^2/([ttt\text{-}C_{12}H_{20}][c\text{-}C_4H_8]) = K_8$$

$$[tt\text{-}C_8H_{14}]^2/([ttt\text{-}C_{12}H_{20}][t\text{-}C_4H_8]) = K_9$$

$$[tt\text{-}C_8H_{14}] + [ttt\text{-}C_{12}H_{20}] + [C_4H_8] = 1$$

$$[c\text{-}C_{12}H_{20}]/([cc\text{-}C_{10}H_{16}][C_2H_4]) = K_{10}$$

$$[t\text{-}C_{12}H_{20}]/([cc\text{-}C_{10}H_{16}][C_2H_4]) = K_{11}$$

$$[C_{12}H_{20}] + [cc\text{-}C_{10}H_{16}] + [C_2H_4] = 1$$

$$[C_7H_{12}]^2/([c\text{-}C_{12}H_{20}][C_2H_4]) = K_{12}$$

$$[C_7H_{12}]^4/([cc\text{-}C_{10}H_{16}][c\text{-}C_{12}H_{20}][C_2H_4]^3) = K_{13}$$

$$[C_7H_{12}] + [cc\text{-}C_{10}H_{16}] + [c\text{-}C_{12}H_{20}] + [C_2H_4] = 1$$

where K_1–K_{13} are respective equilibrium constants.

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*-cycloocta-1,5-diene (COD) and *cis*,*cis*-1,5-dimethyl-cycloocta-1,5-diene (DM-COD) with ethylene (*cis*- and *trans*-but-2-ene) at 298.15 K

Compound	Formula	G (kcal mol^{-1})	H (kcal mol^{-1})	S (cal mol^{-1} K)
COD	C_8H_{12}	−195719.6401	−195694.5924	84.0
DM-COD	$C_{10}H_{16}$	−245030.3959	−245000.9858	98.6
c-Deca-1,5,9-triene	$C_{10}H_{16}$	−245018.9576	−244986.3089	109.5
t-Deca-1,5,9-triene	$C_{10}H_{16}$	−245021.1294	−244987.9900	111.2
c-2,6-Dimethyl-deca-1,5,9-triene	$C_{12}H_{20}$	−294334.4586	−294297.0797	125.4
t-2,6-Dimethyl-deca-1,5,9-triene	$C_{12}H_{20}$	−294334.3456	−294297.3972	123.9
ttt-Dodeca-2,6,10-triene	$C_{12}H_{20}$	−294338.3385	−294300.4331	127.1
tt-Octa-2,6-diene	C_8H_{14}	−196478.7044	−196448.8933	99.9
2-Methyl-hexa-1,5-diene	C_7H_{12}	−171818.8387	−171791.6625	91.2
Hexa-1,5-diene	C_6H_{10}	−147160.8014	−147135.9394	83.4
c-But-2-ene	C_4H_8	−98616.8403	−98595.3638	72.0
t-But-2-ene	C_4H_8	−98617.9956	−98596.7908	71.1
Ethylene	C_2H_4	−49299.7881	−49283.7772	53.7

3. Results

The ethenolysis of COD proceeds via the formation of *cis*- and *trans*-deca-1,5,9-triene isomers which are participated in the further cross-metathesis with ethylene to form hexa-1,5-diene. Scheme 2 presents the possible distributions of the products for the ring-opening cross metathesis of COD with ethylene. Table 1 shows the calculated thermodynamic parameters of cyclic and linear molecules for the cross-metathesis of COD and DM-COD with ethylene (*cis*- and *trans*-but-2-ene). It is seen that the formation of *trans*-butadiene molecules ($C_{10}H_{16}$) becomes more preferable compared to *cis*-isomers with the difference in the standard free energies between *cis*- and *trans*- isomers is about 2 kcal mol^{-1}. In the case of DM-COD ethenolysis the possibility of the formation of *cis*- and *trans*-isoprene oligomers is practically same. The identical standard energy terms for the *cis*- and *trans*-isomers are related to the effect of the methyl substituents.[3b] Fig. 1 shows the calculated minimum energy conformations for the *cis*-(A) and *trans*-(B) isoprene molecules ($C_{12}H_{20}$). 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 COD and DM-COD with ethylene and *cis*-but-2-ene. As seen the ring-opening cross metathesis of COD with ethylene at 298 K leads to *trans*-deca-1,5,9-triene (t-$C_{10}H_{16}$) (Scheme 2). Numerous studies showed that the ROMP of COD at room temperature led initially to 1,4-polybutadiene with high *cis* content due to one of the *cis*-double bonds is preformed. However, the *cis*-*trans*-isomerization occurs with increasing reaction time and the *trans/cis* ratio of the formed polymer approaches the equilibrium (about 80/20).[4,25] Molecular modeling shows that low stereoselectivity of the olefin metathesis is due to the close matching of activation energies for *cis*- and *trans*-isomer formation and the fast *cis*–*trans*-isomerization by catalyst leading to equilibrium mixture of the isomers.[26] According to the calculations, the value of the standard free energy differences for the isomerization of *cis*-deca-1,5,9-triene to *trans*-deca-1,5,9-triene is −2.2 kcal mol^{-1} at 298.15 K, corresponding to the equilibrium constant K=41.

For the ring-chain equilibrium the enthalpic change (ΔH) corresponds to the strain energy of ring, since the reaction is an isodesmic one. The calculated enthalpy change (ΔH) for the ROMP of COD with ethylene will correspond to the strain energy of COD. The value of ΔH of this reaction to *trans*-$C_{10}H_{16}$ is −9.6 kcal mol^{-1}. The experimentally obtained value of ΔH for conversion of COD into *trans*-polybutadiene at 298 K is −7.9 kcal mol^{-1}.[27] It is seen that the agreement is very reasonable.

Table 2 (entries 3–5) presents the values of ΔG energies for the ethenolysis of COD and α,ω-vinyl-terminated oligomers to hexa-1,5-diene (Schemes 3 and 4). The equilibrium

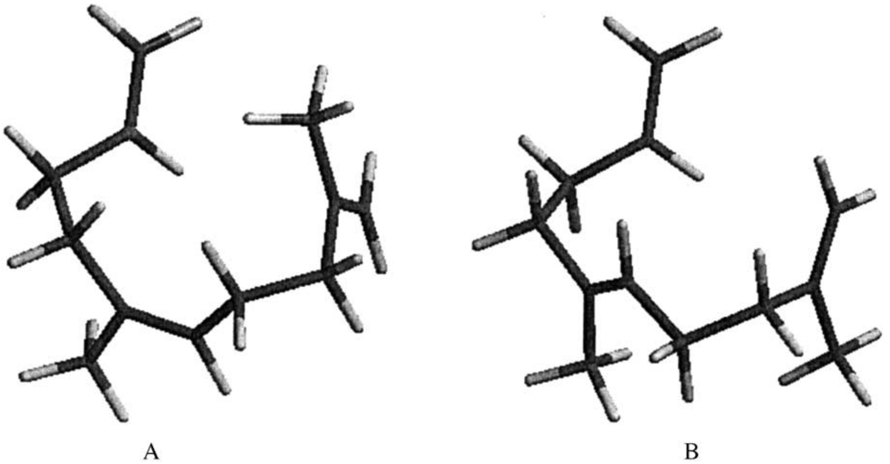


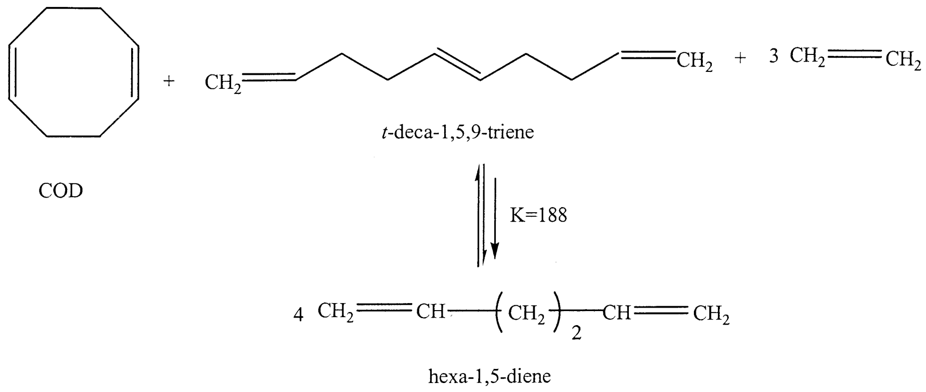
Figure 1. Lowest energy conformers of *cis*-(A) and *trans*-(B) isomers of 2,6-dimethyl-deca-1,5,9-triene.

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 COD and DM-COD with ethylene (*cis*-but-2-ene) at 298.15 K

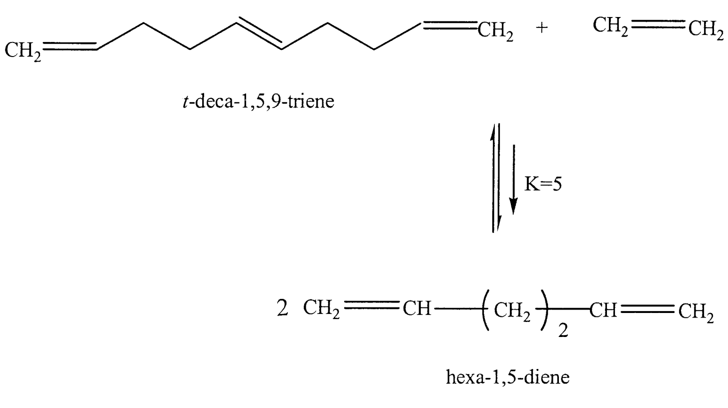
Entry	Reaction	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K)
1[a]	cc-C_8H_{12} + C_2H_4 ⇔ c-$C_{10}H_{16}$[b]	0.5	−7.9	−28.2
2	cc-C_8H_{12} + C_2H_4 ⇔ t-$C_{10}H_{16}$[b]	−1.7	−9.6	−26.5
3	cc-C_8H_{12} + t-$C_{10}H_{16}$ + $3C_2H_4$ ⇔ $4C_6H_{10}$[c]	−3.1	−10	−22.7
4	c-$C_{10}H_{16}$ + C_2H_4 ⇔ $2C_6H_{10}$[d]	−3.0	−1.8	3.6
5	t-$C_{10}H_{16}$ + C_2H_4 ⇔ $2C_6H_{10}$[d]	−1.0	−0.1	2.0
6	cc-C_8H_{12} + ttt-$C_{12}H_{20}$ + $3c$-C_4H_8 ⇔ $4tt$-C_8H_{14}[e]	−6.3	−15	−27.0
7	ttt-$C_{12}H_{20}$ + c-C_4H_8 ⇔ $2tt$-C_8H_{14}[f]	−2.2	−2.0	0.7
8	cc-$C_{10}H_{16}$ + C_2H_4 ⇔ c-$C_{12}H_{20}$[g]	−4.3	−12.3	−25.4
9	cc-$C_{10}H_{16}$ + C_2H_4 ⇔ t-$C_{12}H_{20}$[g]	−4.2	−12.6	−28.4
10	cc-$C_{10}H_{16}$ + c-$C_{12}H_{20}$ + $3C_2H_4$ ⇔ $4C_7H_{12}$[h]	−11.1	−17.3	−20.3
11	c-$C_{12}H_{20}$ + C_2H_4 ⇔ $2C_7H_{12}$[i]	−3.4	−2.5	3.3
12	t-$C_{12}H_{20}$ + C_2H_4 ⇔ $2C_7H_{12}$[i]	−3.5	−2.1	4.8

[a] ΔG of reaction calculated using B3LYP/6-311+G(2d,p) was 1.2 kcal mol^{-1}.
[b] Scheme 2.
[c] Scheme 3.
[d] Scheme 4.
[e] Scheme 5.
[f] Scheme 6.
[g] Scheme 7.
[h] Scheme 8.
[i] Scheme 9.

depends on the *cis*/*trans* ratio of linear butadiene molecules. *cis*-Deca-1,5,9-triene ($C_{10}H_{16}$) degraded to hexa-1,5-diene with higher selectivity compared with *trans*-isomer. Experimental data show that *cis*-olefins[28] participated in the metathesis reaction more easily than *trans*-olefins. Thus, it has been reported that the metathesis degradation of *cis*-PB proceeds faster than that for the *trans*-PB giving oligomers with lower molecular weight.[29] It is seen from Table 2 (entries 3 and 4) that the values of ΔG for the ethenolysis of COD (Scheme 3) and *cis*-deca-1,5,9-triene ($C_{10}H_{16}$) (Scheme 4) are same. Table 3 summarizes the calculated standard free energies differences (ΔG) and



Scheme 3. Ethenolysis of COD to hexa-1,5-diene.



Scheme 4. Ethenolysis of *trans*-deca-1,5,9-triene to hexa-1,5-diene.

Table 3. Standard free energy differences (ΔG) and equilibrium constants (K) of cyclic diene-linear molecules equilibrium for the ring-opening cross metathesis of COD and DM-COD with ethylene, *cis*- and *trans*-but-2-ene at 298.15 K

Entry	Reaction	ΔG (kcal mol^{-1})	K
1	$cc\text{-}C_8H_{12} + C_2H_4 \Leftrightarrow c\text{-}C_{10}H_{16}$[a]	0.5	0.4
2	$cc\text{-}C_8H_{12} + C_2H_4 \Leftrightarrow t\text{-}C_{10}H_{16}$[a]	−1.7	18
3	$cc\text{-}C_8H_{12} + t\text{-}C_{10}H_{16} + 3C_2H_4 \Leftrightarrow 4C_6H_{10}$[b]	−3.1	188
4	$c\text{-}C_{10}H_{16} \Leftrightarrow t\text{-}C_{10}H_{16}$	−2.2	41
5	$c\text{-}C_{10}H_{16} + C_2H_4 \Leftrightarrow 2C_6H_{10}$[c]	−3.0	164
6	$t\text{-}C_{10}H_{16} + C_2H_4 \Leftrightarrow 2C_6H_{10}$[c]	−1.0	5
7	$cc\text{-}C_8H_{12} + ttt\text{-}C_{12}H_{20} + 3c\text{-}C_4H_8 \Leftrightarrow 4tt\text{-}C_8H_{14}$[d]	−6.3	42×10^3
8	$cc\text{-}C_8H_{12} + ttt\text{-}C_{12}H_{20} + 3t\text{-}C_4H_8 \Leftrightarrow 4tt\text{-}C_8H_{14}$[d]	−3.0	164
9	$ttt\text{-}C_{12}H_{20} + c\text{-}C_4H_8 \Leftrightarrow 2tt\text{-}C_8H_{14}$[e]	−2.2	41
10	$cc\text{-}C_{10}H_{16} + C_2H_4 \Leftrightarrow c\text{-}C_{12}H_{20}$[f]	−4.3	1425
11	$cc\text{-}C_{10}H_{16} + C_2H_4 \Leftrightarrow t\text{-}C_{12}H_{20}$[f]	−4.2	1204
12	$cc\text{-}C_{10}H_{16} + c\text{-}C_{12}H_{20} + 3C_2H_4 \Leftrightarrow 4C_7H_{12}$[g]	−11.1	14×10^7
13	$c\text{-}C_{12}H_{20} \Leftrightarrow t\text{-}C_{12}H_{20}$	0.1	1
14	$c\text{-}C_{12}H_{20} + C_2H_4 \Leftrightarrow 2C_7H_{12}$[h]	−3.4	312

[a] Scheme 2.
[b] Scheme 3.
[c] Scheme 4.
[d] Scheme 5.
[e] Scheme 6.
[f] Scheme 7.
[g] Scheme 8.
[h] Scheme 9.

equilibrium constants (K) for the ring-opening cross metathesis of COD and DM-COD in the presence of ethylene, *cis*- and *trans*-but-2-ene. The results show that ring-linear molecules equilibrium for the ethenolysis is shifted to hexa-1,5-diene and 2-methyl-hexa-1,5-diene and its concentrations depend on the nature of used cyclooctadiene. Thus, the equilibrium constants for the ethenolysis of COD and DM-COD are 188 and 14×10^7, respectively (entries 3 and 12, Table 3). It can also be seen from the Table 3 that ring-chain equilibrium for the ring-opening cross-metathesis of COD depends on the nature of linear olefin used as a CTA. Ethylene and *trans*-but-2-ene behave similarly, while *cis*-but-2-ene shows much better activity as a CTA. The values of the equilibrium constants for the cross-metathesis of COD with ethylene, *trans*-but-2-ene and *cis*-but-2-ene to monomeric dienes are 188, 164 and 42×10^3, respectively (Table 3, entries 3, 7 and 8). Table 4 shows the calculated distributions of cyclic and linear species for the ethenolysis of COD. As seen butadiene oligomers-hexa-1,5-diene equilibrium depends on the isomer distributions of butadiene molecules. Thus, the concentration of hexa-1,5-diene at equilibrium with

Table 4. Calculated cyclic and linear molecules distributions for the ethenolysis of COD at 298.15 K

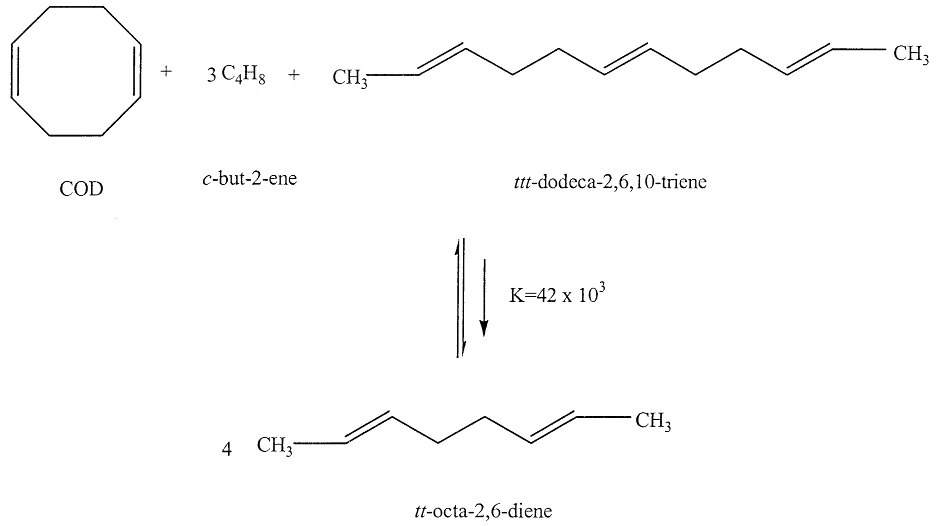
Reaction	Mole fraction in % of			
	$cc\text{-}C_8H_{12}$	$C_{10}H_{16}$	C_2H_4	C_6H_{10}[a]
$cc\text{-}C_8H_{12} + C_2H_4 \Leftrightarrow t\text{-}C_{10}H_{16}$[b]	11	78	11	
$cc\text{-}C_8H_{12} + t\text{-}C_{10}H_{16} + 3C_2H_4 \Leftrightarrow 4C_6H_{10}$[c]	10	10	30	50
$t\text{-}C_{10}H_{16} + C_2H_4 \Leftrightarrow 2C_6H_{10}$[d]		25	25	50
$c\text{-}C_{10}H_{16} + C_2H_4 \Leftrightarrow 2C_6H_{10}$[d]		7	7	86

[a] The values of experimentally observed yeild of hexa-1,5-diene (C_6H_{10}) for the ethenolysis of COD[13] (ethylene/COD=2) and *cis*-PB[25] (30 psig C_2H_4 pressure) were 50 and 43 mol%, respectively.
[b] Scheme 2.
[c] Scheme 3.
[d] Scheme 4.

Table 5. Calculated cyclic and linear molecules distributions for the ring-opening cross metathesis of COD with *cis*- and *trans*-but-2-ene at 298.15 K

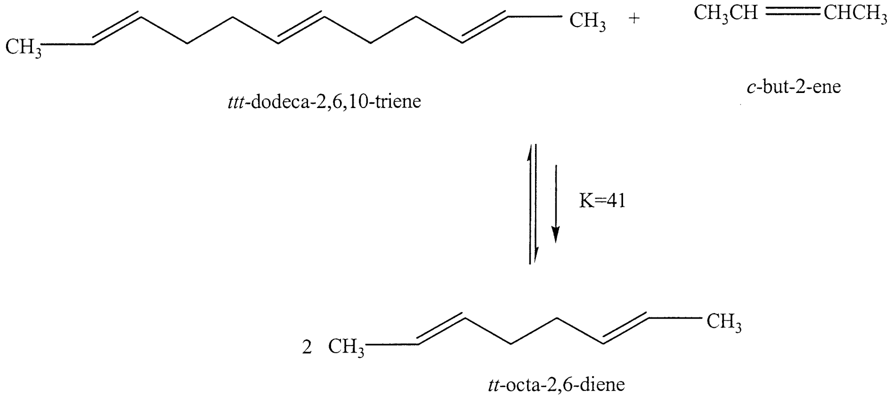
Reaction	Mole fraction in % of			
	$cc\text{-}C_8H_{12}$	$ttt\text{-}C_{12}H_{20}$	C_4H_8	$tt\text{-}C_8H_{14}$
$cc\text{-}C_8H_{12} + ttt\text{-}C_{12}H_{20} + 3c\text{-}C_4H_8 \Leftrightarrow 4tt\text{-}C_8H_{14}$[a]	5	5	14	76
$cc\text{-}C_8H_{12} + ttt\text{-}C_{12}H_{20} + 3t\text{-}C_4H_8 \Leftrightarrow 4tt\text{-}C_8H_{14}$[a]	10	10	31	49
$ttt\text{-}C_{12}H_{20} + c\text{-}C_4H_8 \Leftrightarrow 2tt\text{-}C_8H_{14}$[b]		12	12	76
$ttt\text{-}C_{12}H_{20} + t\text{-}C_4H_8 \Leftrightarrow 2tt\text{-}C_8H_{14}$[b]		24	24	52

[a] Scheme 5.
[b] Scheme 6.



Scheme 5. Ring-opening cross metathesis of COD with *cis*-but-2-ene to *trans*,*trans*-octa-2,6-diene.

trans-$C_{10}H_{16}$ is of 50 mol%, while this value for the *cis*-$C_{10}H_{16}$ is of 86 mol%. The results of calculations are in agreement with experimental data on the ethenolysis of COD by rhenium based catalysts[13] and *cis*-PB using a well-defined ruthenium alkylidene catalyst.[30] Table 5 presents the calculated cyclic and linear molecules distributions for the cross-metathesis of COD with *cis*- and *trans*-but-2-ene (Schemes 5 and 6). The ring-opening cross-metathesis of COD in the presence of *cis*-but-2-ene to monomeric diene *trans*,*trans*-octa-2,6-diene is more selective than that with *trans*-but-2-ene. The calculations show that cross-metathesis of COD and *cis*-PB to monomeric diene can be achieved without excess of CTA. Numerous investigations demonstrated that for complete ring-opening cross metathesis of cycloolefins and depolymerization of polyalkenamers, it is necessary to use a large excess of CTA.[4] It has been reported that *cis*-but-2-ene exhibited much higher selectivity in the ring-opening cross metathesis of cyclooctene compared to *trans*-but-2-ene.[28,31] This effect can be explained by the fact that *cis*-but-2-ene is thermodynamically less stable than *trans*-but-2-ene resulting in a higher yeild of monomeric diene. It is important to note that hexa-1,5-diene participates more easily in the acyclic diene metathesis oligomerization (ADMET) than octa-2,6-diene,

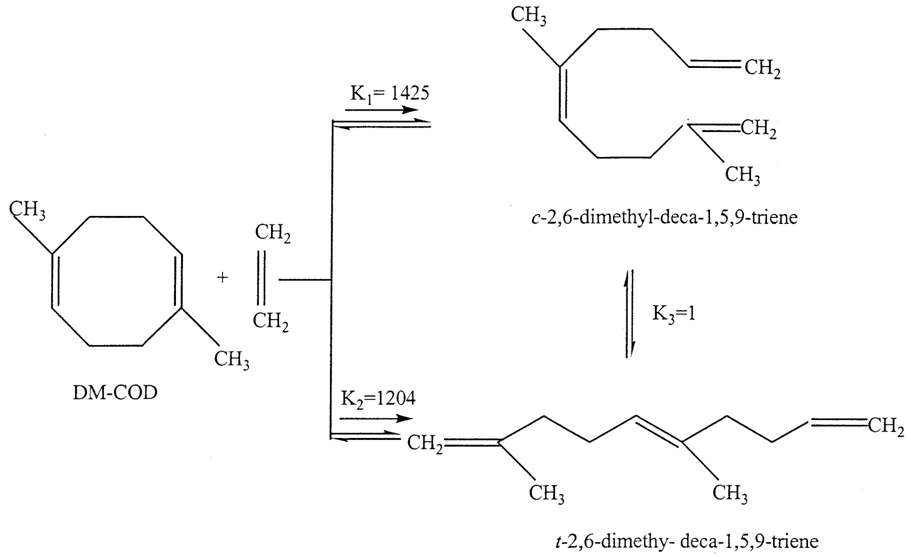


Scheme 6. Cross-metathesis of *trans*,*trans*,*trans*-dodeca-2,6,10-triene with *cis*-but-2-ene to *trans*,*trans*-octa-2,6-diene.

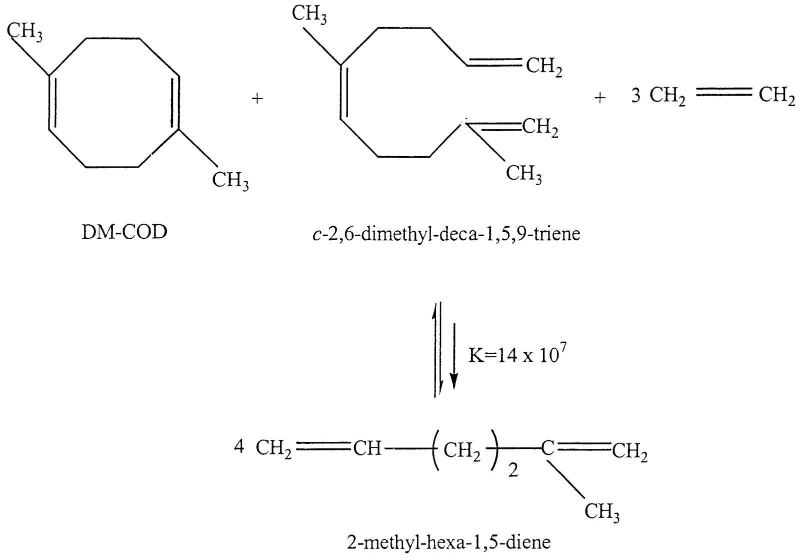
Table 6. Calculated cyclic and linear molecules distributions for the ethenolysis of DM-COD at 298.15 K

Reaction	Mole fraction in % of			
	cc-$C_{10}H_{16}$	$C_{12}H_{20}$	C_2H_4	C_7H_{12}
cc-$C_{10}H_{16}$ + C_2H_4 ⇔ *c*-$C_{12}H_{20}$[a]	2.7	94.8	2.7	
cc-$C_{10}H_{16}$ + C_2H_4 ⇔ *t*-$C_{12}H_{20}$[a]	2.8	94.4	2.8	
cc-$C_{10}H_{16}$ + *c*-$C_{12}H_{20}$ + 3C_2H_4 ⇔ 4C_7H_{12}[b]	1.0	1.0	15.4	82.6
c-$C_{12}H_{20}$ + C_2H_4 ⇔ 2C_7H_{12}[c]		5.1	5.1	89.8

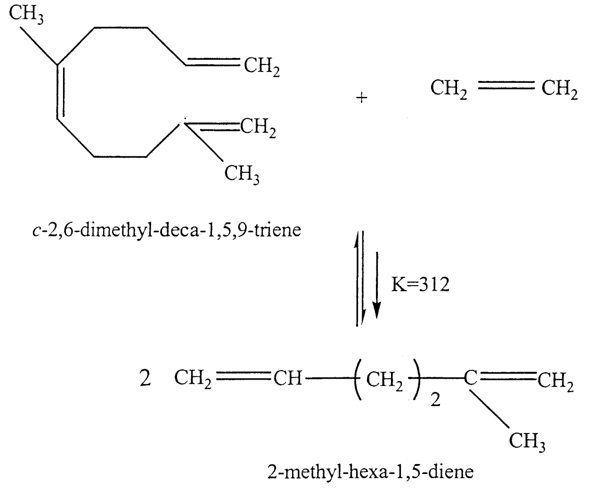
[a] Scheme 7.
[b] Scheme 8.
[c] Scheme 9.



Scheme 7. Ring-opening cross-metathesis of DM-COD with ethylene to *cis*- and *trans*-2,6-dimethyl-deca-1,5,9-triene.



Scheme 8. Ethenolysis of DM-COD to 2-methyl-hexa-1,5-diene.



Scheme 9. Ethenolysis of *cis*-2,6-dimethyl-deca-1,5,9-triene to 2-methy-hexa-1,5 diene.

again giving oligomers and ethylene (see entries 6 and 9, Table 3). Table 6 presents the calculated distributions of cyclic and linear species for the ethenolysis of DM-COD (Schemes 7–9). The ring-opening cross metathesis of DM-COD is completely shifted towards the *cis*- or *trans*-2,6-dimethyl-deca-1,5,9-triene (Scheme 7). The possibility of the formation of *cis*- or *trans*-isomers is practically the same, while the formation of *trans*-butadiene oligomers is more preferable. Early studies demonstrated that the W-containing catalyst reduced the molecular weight of *cis*-polyisoprene by 2 orders of magnitude, without any marked loss of unsaturation and *cis*-double bond content.[31] 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-poly-isoprene will result in monomeric isoprene diene with high yield. Thus, the expected 2-methyl-hexa-1,5-diene was detected during the ethenolysis of *trans*-polyisoprene by a tungsten carbene catalyst.[32] The calculations show that the ethenolysis of DM-COD to monomeric diene can be realized with high selectivity without the need for large excess of CTA.

4. Conclusions

The concentrations of hexa-1,5-diene and 2-methyl-hexa-1,5-diene for the ethenolysis of COD and DM-COD were estimated using ab initio approach. The calculations show that COD, vinyl-terminated butadiene oligomers and hexa-1,5-diene equilibrium depends on the *cis*/*trans* ratio of linear butadiene molecules. The amount of cyclic diene at equilibrium with linear molecules is small. The concentration of hexa-1,5-diene at equilibrium with *cis*-oligomers is higher than that with *trans*-butadiene molecules and ranges from 50 to 86 mol%. The results of calculations are in agreement with experimental data on the ethenolysis of COD by rhenium based catalysts and *cis*-PB using a well-defined ruthenium alkylidene catalyst. The butadiene oligomers-monomeric diene equilibrium also depends on the nature of the linear olefin used as a CTA. The selectivity of the ring-opening cross metathesis of COD with *cis*-but-2-ene is higher than that with ethylene and *trans*-but-2-ene. The ethenolysis of DM-COD is completely shifted towards the formation of 2-methyl-hexa-1,5-diene. The calculations predict that in the presence of ethylene natural rubber and *trans*-polyisoprene will depolymerize by long-lived metathesis catalysts to 2-methyl-hexa-1,5-diene with high selectivity.

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