

Kinetic modeling of the palladium-catalyzed isomerizing methoxycarbonylation of 1-decene

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Abstract

The kinetics of the Pd/DTBPMB-catalyzed isomerizing methoxycarbonylation of 1-decene in a thermomorphic solvent system were studied experimentally. Kinetic models for the methoxycarbonylation and isomerization reaction rates including inhibition effects of carbon monoxide and 1-decene were derived and parametrized for process development and optimization.

Keywords: Alkene, Homogeneous Catalysis, Kinetic Modeling, Methoxycarbonylation, Palladium

1. Introduction

The use of renewable feedstocks in the chemical industry is attractive as the limitation of fossil resources and the ecological rethinking set the economic stimulus for a technological change. The increasing worldwide demand for polymers, e.g. for methyl methacrylate (MMA), resulted in a drastic rise in price for the raw materials from 2010 to 2012 [1]. MMA is produced using the common acetone-cyanohydrin process. Lucite International developed the less expensive Alpha process [2, 3] with a production of 250 kilotons MMA per year. Herein MMA is obtained from the ester methyl propionate which is produced by the homogeneously catalyzed methoxycarbonylation of ethylene, methanol (MeOH) and carbon monoxide (CO) using a palladium catalyst modified with the bidentate phosphine ligand 1,2-bis(di-*tert*-butylphosphino-methyl)benzene (DTBPMB) [2].

Unsaturated oleochemicals from renewables like glycerides, methyl oleate and methyl 10-undecenoate (UME) have also been proven to be attractive substitutes for petrochemical substrates in the palladium-catalyzed methoxycarbonylation [4-10] producing α,ω -functionalized intermediates for the production of polyesters and polyamides [5]. For a sustainable and economic catalytic process, the reuse of the catalyst plays a key role. In this context, Gaide et al. [6, 7] successfully demonstrated the Pd/DTBPMB-catalyzed methoxycarbonylation of UME with high yields of the desired diester using a thermomorphic solvent system (TMS) to recycle the homogeneous catalyst. Thus, a temperature dependent miscibility gap enables phase separation at low temperature and an efficient reaction without mass transport limitations at elevated temperature [11].

In terms of further process development and optimization, knowledge about the reaction kinetics is of crucial importance. In this contribution the reaction kinetics of the Pd/DTBPMB-catalyzed methoxycarbonylation of 1-decene in a TMS consisting of MeOH/dodecane is investigated. 1-Decene was used as model substrate for long chain unsaturated oleochemicals. The composition of the TMS and the highly active and selective catalytic system refers to reported results of Gaide et al. [6, 7].

2. Reaction network and kinetic experiments

Methoxycarbonylation experiments were conducted in a stainless steel vessel equipped with a glass stirrer, PTFE-coated gas cylinder, flexible gas dosing, locking and evacuation system, temperature controller and pressure regulator. The catalyst solution was prepared by dissolving Pd₂(dba)₃ (0.038 mmol) and DTBPMB (1.72 mmol) in the solvent MeOH (574 mmol, >99.9 %). Subsequently, the reactor was

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filled with methane sulfonic acid (MSA, 2.67 mmol, >99.5 %) and dodecane (53 mmol, 99.0 %). The mixture was heated to the desired reaction temperature and pressurized using CO (99 %). The kinetic experiment was started with the controlled injection of 1-decene (76 mmol, 96.0 %) into the reactor. Samples were taken in discrete time increments and were analyzed using standard gas chromatography. The precision of the measurements in terms of the coefficient of variation was always ≤ 0.5 %. The reproducibility of the kinetic experiments in terms of the coefficient of variation for the yield of *n*-methyl ester after 180 min was always ≤ 3.8 %. Details to the experimental procedure and the quantitative analysis can be found in the supporting information.

In preliminary experiments the main reaction products of the Pd/DTBPMB-catalyzed methoxycarbonylation of 1-decene were identified. The desired linear *n*-methyl ester and the undesired branched *iso*-methyl esters were observed as methoxycarbonylation products. The regioselectivity of the catalyst was characterized by the linear to branched ester (*l/b*) ratio. In addition, the methoxycarbonylation was accompanied by a fast and dominant isomerization of 1-decene to 2-, 3-, 4- and 5-decene including *cis/trans*-configuration.

Thus, a reaction network was postulated including the methoxycarbonylation and isomerization of 1-decene (Fig. 1). The *iso*-methyl esters and the decene isomers were lumped together into the pseudo components *iso*-methyl esters and *iso*-decenes, respectively. In addition, the formation of *iso*-methyl esters was assumed to take place exclusively from 1-decene.

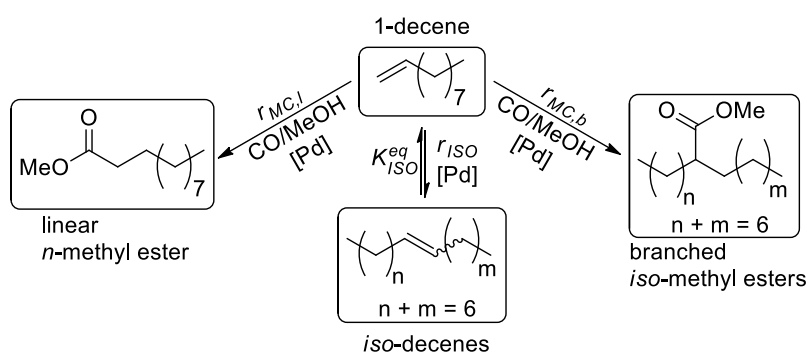


Figure 1. Reaction network of the Pd/DTBPMB-catalyzed isomerizing methoxycarbonylation of 1-decene.

3. Experimental results and reaction analysis

The influence of temperature T and CO partial pressure p_{CO} on the reaction kinetics were investigated ranging from 75 °C to 95 °C and 10 bar to 30 bar, respectively. To reduce the experimental efforts for parametrizing adequate kinetic models, a perturbation experiment was performed, applying dynamic variations of the process parameters T and p_{CO} during the experiment.

Experimental results in Tab. 1 are presented as mean values and for the yield of *n*-methyl ester the standard deviation is additionally given. An increase of the desired *n*-methyl ester yields with temperature for 30 bar CO was observed. In all experiments, the highest yield of 79 % *n*-methyl ester was determined for 5 bar CO at 95 °C after 180 min. Comparable catalytic results for terminal long chain olefins were already reported [10, 12-14]. The Pd/DTBPMB-catalyzed methoxycarbonylation is characterized by a fast isomerization of 1-decene to *iso*-decenes with respect to the *n*-selective methoxycarbonylation (Fig. 2). For all reaction conditions a constant *l/b* ratio of 94/6 was determined according to the literature [6, 7, 12, 13]. A comparison of concentration profiles for different CO pressures indicated an inhibition of the isomerization with increasing CO pressure. This resulted in temporal higher 1-decene concentrations but no significant change in the methoxycarbonylation rate was observed which indicated a significant substrate limitation.

Tab. 1: Experimental results for the methoxycarbonylation of 1-decene after 180 min.

Experiment	1	2	3	4	5 ^a
p_{CO} [bar]	5	10	30	30	20...30
T [°C]	95	75	85	95	75...95
Y [%]	79.3 ± 0.8	65.6 ± 0.9	68.8 ± 0.2	75.9 ± 1.6	76.0 ± 2.9
TON [-]	760	635	667	736	736
TOF [h ⁻¹]	253	212	222	245	245
STY [kg m ⁻³ h ⁻¹]	77	65	68	75	75

a) Perturbation experiment (for details to applied temperature and pressure profiles see Fig. 3).

4. Kinetic modeling

Based on the experimental findings semi-empirical kinetic models were derived for the rates of methoxycarbonylations $r_{MC,l}$ and $r_{MC,b}$ as well as the isomerization r_{ISO} (Eq. 1-3). A simple kinetic model including substrate inhibition was used with respect to the substrate 1-decene according to the observed substrate limitation. The overall constant l/b ratio of 94/6 was used to approximate the *iso*-selective methoxycarbonylation rate $r_{MC,b}$. In addition, for the reversible isomerization an additional inhibition effect of CO was introduced.

$$\text{Methoxycarbonylation, } n\text{-selective (MC,l): } r_{MC,l} = \frac{k_{MC,l}(T) \cdot c_{1-decene} \cdot c_{CO} \cdot c_{MeOH} \cdot c_{cat}}{1 + K_1^{inh} \cdot c_{1-decene}} \quad (1)$$

$$\text{Isomerization (ISO): } r_{ISO} = \frac{k_{ISO}(T) \cdot \left(c_{1-decene} - \frac{c_{iso-decenes}}{K_{ISO}^{eq}(T)} \right)}{1 + K_1^{inh} \cdot c_{1-decene} + K_2^{inh} \cdot c_{CO}} \cdot c_{cat} \quad (2)$$

$$\text{Methoxycarbonylation, } iso\text{-selective (MC,b): } r_{MC,b} = r_{MC,l} \cdot \frac{6}{94} \quad (3)$$

The temperature dependent equilibrium constant K_{ISO}^{eq} for the isomerization of 1-decene was calculated according to Jörke et al. [15]. A reparametrized Arrhenius equation (Eq. 4a) was used for the reaction rate constants k_j to minimize the correlation between the activation energy E_j^A and the collision factor k_j^∞ [16-18] ($T_{ref} = 85$ °C).

$$\text{Reaction rate constants: } k_j = \exp \left[A_j + B_j \left(1 - \frac{T_{ref}}{T} \right) \right] \quad (4a)$$

$$A_j = \ln(k_j^\infty) - \frac{E_j^A}{R \cdot T_{ref}} \quad (4b)$$

$$B_j = \frac{E_j^A}{R \cdot T_{ref}} \quad (4c)$$

The model of a well-mixed semi-batch reactor was applied. Henry's law (Eq. 7) was used to describe the gas solubility of CO in the liquid phase. Gas solubility experiments using the dynamic pressure-step method were performed to determine the Henry's law constant H_{CO} and the effective mass transfer coefficient β_{eff} [19] (Tab. 2). In these experiments the pressure drop of CO in the reaction mixture without catalyst was monitored. Details to the experimental procedure can be found in the supporting

information. For both parameters no significant temperature dependence was found in the temperature range from 75 °C to 95 °C.

$$\frac{dp_{CO}}{dt} = \beta_{eff} (p_{CO}^* - p_{CO}) - \text{div}(j_{CO}) \quad (5)$$

$$\frac{dc_i}{dt} = \beta_{eff} (c_i^* - c_i) + \sum_{j=1}^{N_R} \nu_{i,j} \cdot r_j \quad (6)$$

$$p_{CO}^* = c_{CO}^* \cdot H_{CO} \quad (7)$$

Table 2. Gas solubility and mass transfer parameters for CO in the TMS 1-decene/dodecane/MeOH (details are given in supporting information).

Parameter	Mean value \pm standard deviation
β_{eff} [s^{-1}]	$(25.3 \pm 6.6) \times 10^{-3}$
H_{CO} [bar L mol^{-1}]	180.6 ± 6.3

5. Parameter estimation and discussion

The kinetic parameters in Eq. (8) were estimated using the Matlab R2015b function *lsqnonlin* with trust-region-reflective algorithm and central finite differences for the optimization problem defined in Eq. 9. The system of ordinary differential equations (Eq. 5-6) was solved using the solver *ode15s*.

Parameter vector:
$$\bar{\theta} = \{A_{MC,I}, B_{MC,I}, A_{ISO}, B_{ISO}, K_1^{inh}, K_2^{inh}\} \quad (8)$$

$$Obj = \min_{\theta} NRSS = \sum_{i=1}^{N_C} \sum_{m=1}^{N_{exp}} \sum_{n=1}^{N_{sp}} \left[\frac{c_{i,m}^{exp}(t_n) - c_{i,m,n}^{mod}(t_n, \bar{\theta})}{c_{i,m}^{exp}} \right]^2 \quad (9)$$

The experimental results and simulations are illustrated in Fig. 2. In addition, the results of all fitted experiments were condensed in a parity plot (Fig. 3). The final kinetic parameters are summarized in Tab. 3.

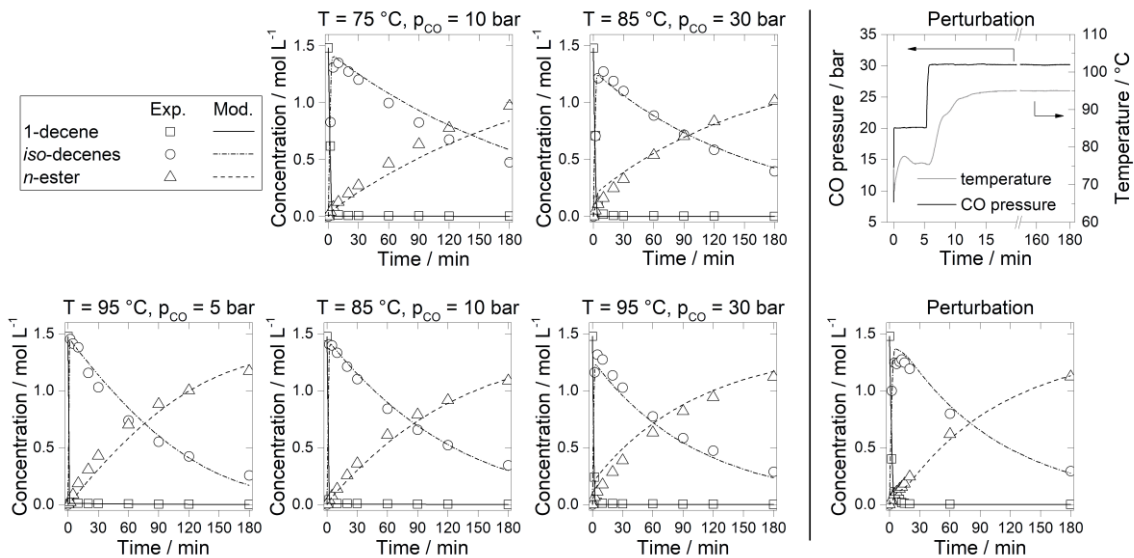


Figure 2. Experimental (symbols) and simulation results (lines). For reasons of clarity results for iso-esters are not shown.

The simulations using the derived kinetic models including essential parameters that account for the inhibitions by 1-decene and CO described the experimental data well for the covered experimental conditions. Significant deviations between experiment and simulation are related to the fast isomerization at the beginning. The calculated 95 % confidence intervals (CI) were found to be 5 % or less which emphasizes the statistical significance of the estimated parameters. The activation energies which correspond to the estimates B_j were found to be 72.2 kJ mol⁻¹ and 37.3 kJ mol⁻¹ for the methoxycarbonylation and isomerization, respectively. Roesle et al. [8] investigated the Pd/DTBPMB-catalyzed methoxycarbonylation of methyl 4-heptenoate theoretically. Thus, using density function theory (DFT) calculations activation energies of 121.8 kJ mol⁻¹ and 25.1...50.2 kJ mol⁻¹ were calculated for the methoxycarbonylation and all isomerization sequences, respectively. Walther et al. studied the two-stage methoxycarbonylation of sunflower oil via methyl oleate experimentally using the same catalyst [9]. For the methoxycarbonylation an activation energy of 75.0 kJ mol⁻¹ was determined. In comparison, a higher activation energy would be expected for methyl oleate with respect to methyl 4-heptenoate because of the longer aliphatic chain length that increases the steric demand [8]. Main difference of both contributions to this work is the usage of short chain unsaturated esters. DFT calculations for 1-decene will follow in future work.

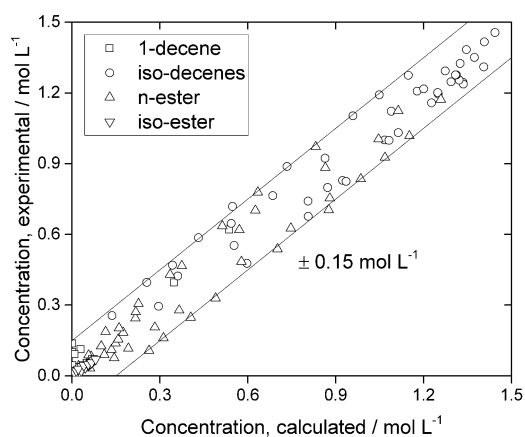


Figure 4. Parity plot of all fitted experiments.

Table 3. Initial values, estimated values and 95 % CI for estimated parameters. Corresponding parameters k_j^∞ and E_j^A were calculated according to Eq. 4b - 4c.

Parameter	Initial values	Estimated values	95 % CI [%]
$A_{MC,I}$ [-]	23.82	29.23	< 1
$B_{MC,I}$ [-]	26.87	24.26	4
$k_{MC,I}^\infty$ [L ³ mol ⁻³ min ⁻¹]	1.034 x 10 ²²	1.696 x 10 ²³	-
$E_{MC,I}^A$ [kJ mol ⁻¹]	80.0	72.2	-
A_{ISO} [-]	13.53	18.40	< 1
B_{ISO} [-]	13.43	12.54	5
k_{ISO}^∞ [L mol ⁻¹ min ⁻¹]	5.122 x 10 ¹¹	2.740 x 10 ¹³	-
E_{ISO}^A [kJ mol ⁻¹]	40.0	37.3	-
K_1^{inh} [L mol ⁻¹]	1000	138000	< 1
K_2^{inh} [L mol ⁻¹]	10000	891300	< 1

The inhibiting effect of CO on the isomerization as well as the inhibiting effect of 1-decene on both reactions could be confirmed by the fitting results. Fuentes et al. [20] observed the same negative effect of CO on the isomerization of *N*-toysl-pyrroline experimentally and theoretically. In the latter, DFT calculations revealed evidence for a catalyst pre-equilibrium with CO where the Pd-catalyst is kept in a stable resting state with CO. This increases the energy barrier for the coordination of the double bond of *N*-toysl-pyrroline and the dissociation of CO thus inhibiting the catalyst in a competitive manner. Regarding the constants related to 1-decene inhibition of the methoxycarbonylation and isomerization rates similar values were estimated. These findings suggest that both reactions share a common path in the catalytic cycle.

6. Conclusion

The Pd/DTBPMB-catalyzed isomerizing methoxycarbonylation of 1-decene was investigated in the TMS 1-decene/dodecane/MeOH. Semi-batch and dynamic perturbation experiments were conducted in a broad range of temperature and CO partial pressure. The complex reaction network was condensed to three main reactions for a model based kinetic description. Semi-empirical kinetic models for the *n*- and *iso*-selective methoxycarbonylation and the side reaction isomerization were derived and successfully parameterized with statistical significance.

The experimental and model based results indicate an inhibiting effect of 1-decene on the methoxycarbonylation and isomerization reaction rates catalyzed by Pd/DTBPMB. In addition, the isomerization rate is significantly inhibited by CO. Thus, the isomerizing methoxycarbonylation of long chain olefins should be performed at low CO partial pressures and elevated temperatures to achieve high yields of *n*-methyl ester.

In future work, more general mechanistic kinetic models should be derived by implementing elementary reaction steps of a catalytic cycle. Complex interactions of multiple catalytic cycles competing for the catalyst material will describe the complex interaction of dynamic catalyst distribution in the methoxycarbonylation and isomerization cycles. Furthermore, an extension of the experimental basis by variations of MeOH and catalyst concentrations will be useful in order to describe the influences mathematically.

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Symbols used

Symbols

A, B	[-]	parameter of reparametrized Arrhenius equation
c	[mol L ⁻¹]	concentration
E^A	[kJ mol ⁻¹]	activation energy
H_{CO}	[bar L mol ⁻¹]	Henry coefficient for carbon monoxide
j_{CO}	[bar min ⁻¹]	flux of carbon monoxide partial pressure
k	[L ⁿ mol ⁻ⁿ min ⁻¹]	reaction rate constant (isomerization $n = 0$, methoxycarbonylation $n = 2$)
K	[-]	equilibrium or inhibition constant
k_j^∞	[L ⁿ mol ⁻ⁿ min ⁻¹]	collision factor of reaction j
l/b	[-]	ratio of linear to branched methyl ester

N_C	[-]	number of components
N_{exp}	[-]	number of experiments
N_R	[-]	number of reactions
N_{sp}	[-]	number of sample points
$NRSS$	[-]	normalized residual sum of squares
p_{CO}	[bar]	partial pressure carbon monoxide
r	[mol L ⁻¹ min ⁻¹]	reaction rate
STY	[kg m ⁻³ h ⁻¹]	space-time yield
t	[min]	time
TOF	[h ⁻¹]	turnover frequency
TON	[-]	turnover number
T	[°C]	temperature
V_{liq}	[mL]	liquid volume

Greek symbols

β_{eff}	[min ⁻¹]	effective mass transfer coefficient
ν	[-]	stoichiometric coefficient
$\bar{\theta}$	[-]	parameter vector

Sub- and Superscripts

cat	catalyst
eq	equilibrium
i	component indicator
inh	inhibition
ISO	isomerization
j	reaction indicator
m	experiments indicator
MC,b	methoxycarbonylation, branched, <i>iso</i> -selective
MC,l	methoxycarbonylation, linear, <i>n</i> -selective
n	sample point indicator
ref	reference
*	equilibrium

Abbreviations

CI	95 % confidence interval
CO	carbon monoxide
DTBPMB	1,2-Bis(di- <i>tert</i> -butylphosphinomethyl)benzene
MeOH	methanol
MMA	methyl methacrylate
MSA	methane sulfonic acid
UME	methyl 10-undecenoate
TMS	thermomorphic solvent system

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