



From sunflower oil toward 1,19-diester: Mechanistic elucidation

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ABSTRACT

During the last decade, an increased attention could be observed being paid on the use of renewables resources in the polymer and fine chemistry. Sunflower oil has been shown to be catalytically transformed into dimethyl 1,19-nonadecanedioate, using $\text{Pd}/o\text{-C}_6\text{H}_4(\text{CH}_2\text{P}^t\text{Bu}_2)_2$ as catalyst. This article presents a complete elucidation of the reaction mechanism and provides a detailed understanding of what makes this catalyst so active and selective for the combined transesterification/isomerization/methoxycarbonylation. Besides kinetic and density functional theory (DFT) treatment to provide evidence for the elementary steps of this reaction, we corroborate our findings by microkinetic modeling. Here, the C=C double bond was found to be isomerized kinetically favored toward the terminal position, before a CO molecule may be inserted. The insertion of a methoxy group (rate-determining step) was found to proceed via intermolecular attack of MeOH to the catalyst.

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1. Introduction

Oils and fats are becoming an increasingly significant resource for the production of polymers [1,2]. The interest in utilizing such renewables comes primarily from the desire to provide economical substitutes from fossil resources.

In fact, fats and oils are already widely used as renewable feedstock for monomers, in particular diacids and their esters, to derive valuable polymers [3]. During the last decade, many different synthesis routes to linear fatty diacids and their esters have been reviewed [4]. However, all these synthesis routes described require either unsaturated fatty acids or their esters as reactants. This implies to either saponify or transesterify vegetable oils first. In contrast, dimethyl 1,19-nonadecanedioate (1,19-diester) was recently found to be synthesized directly from sunflower oil [5–7]. Thus, 1,19-diester is an example for a novel platform chemical, from which its corresponding α,ω -functionalized C19-monomers can be synthesized and used as building blocks for the polymer industry [6].

The alkoxy carbonylation reaction is one of the most important industrial processes using homogeneous Pd catalysts leading to esters from alkenes, CO, and alcohols. Intensive studies have been performed on the methoxycarbonylation of lighter olefins and unsaturated short-chain carboxylic acids [8–15]. During the last decade, there has been an increasing interest to understand the reaction mechanism. Besides experimental studies on the meth-

oxycarbonylation of ethene and unsaturated short-chain carboxylic acids [9–14], it was also tried to elucidate a potential reaction mechanism (cf. Fig. 1) [15–19]. In those studies, the methoxycarbonylation was catalyzed using $\text{Pd}/o\text{-C}_6\text{H}_4(\text{CH}_2\text{P}^t\text{Bu}_2)_2$ (abbrev Pd_{L-Bu}) and $\text{CH}_3\text{SO}_3\text{H}$. It seems that H–Pd_{L-Bu} may be essential to generate a terminal C=C double bond followed by CO insertion prior to the addition of a methoxy species to the complex (cycle A). Another mechanism discussed follows a methoxycarbonyl route where firstly a Pd-carbonyl species and subsequently the desired product are formed (cycle B) [16,17]. However, a complete elucidation could not be given yet.

Besides the reaction mechanism needs to be understood, there is an increasing quest to optimize the reaction toward 1,19-diester. For the methoxycarbonylation of triglycerides, there are a two-stage process via methyl oleate and a direct synthesis process toward diester, as illustrated in Fig. 2. Surprisingly, a catalyst has been identified that does both *in situ*, the transesterification of the vegetable oil to methyl oleate and the subsequent combined isomerization/methoxycarbonylation toward the desired product [5,6].

This study deals with the combined transesterification, isomerization, and methoxycarbonylation of sunflower oil toward 1,19-diester. From thorough experimental data, a potential reaction mechanism is derived. According to this mechanism, the elementary steps proposed are evidenced using density functional theory (DFT) for a detailed thermodynamically treatment. To further corroborate this mechanism, we may hence develop a microkinetic model to estimate the activation barrier of this complex reaction. The comparison of the activation barrier from theoretical findings

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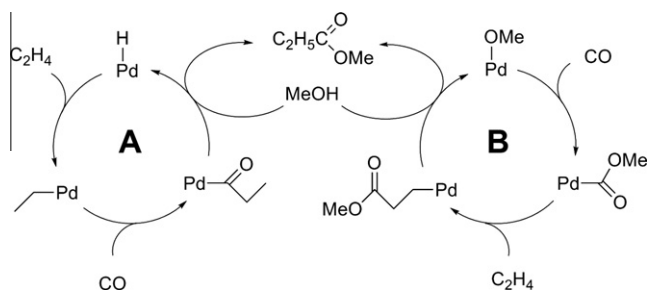


Fig. 1. Potential reaction mechanisms as discussed for the methoxycarbonylation of C_2H_4 , where cycle **A** follows a hydride and cycle **B** a methoxycarbonyl route [15–19].

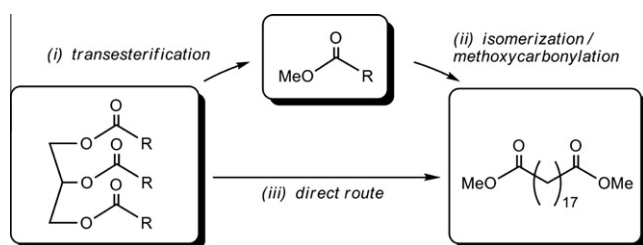


Fig. 2. Illustration of the two routes to synthesize 1,19-diester: The already known two-stage process via methyl oleate [10] (i + ii) and the novel direct synthesis process [5] (iii).

with the apparent activation energy obtained from experiments shall give an evidence of conformity and thus be a confirmation of the mechanism proposed.

2. Methods

2.1. Experimental equipment

All activity experiments were prepared and performed under inert conditions in a 300 ml stainless steel PARR autoclave. To assure identical reaction conditions for the study of combined isomerization/methoxycarbonylation toward 1,19-diester starting from different reactants, a cartridge was built for the autoclave. This aluminum cartridge is able to carry seven 4 ml vials, of which one was used for a reference temperature measurement only. The solution in these vials was stirred using a magnetic stirrer.

Reactants and reaction products were analyzed using a Shimadzu GCMS-QP2010S equipped with an HP-5MS column (30 m \times 250 μ m \times 0.25 μ m). High-oleic sunflower oil and its corresponding free acid groups were transferred *in situ* into the respective methyl esters by adding trimethylsulfoniumhydroxide (TMSH) to the sample for GC analysis.

Flash desorption spectroscopy was used to obtain the thermal stability of the catalyst. MS data were recorded on an MAT 95XP (Thermo Electron) mass spectrometer using the ionization method EI at 70 eV.

NMR spectroscopy was used to proof, whether the methoxycarbonylation does not take place at any non-terminal position of the hydrocarbon chain. NMR spectra were recorded at ambient temperature using a 300 MHz and 400 MHz Bruker NMR spectrometer (AV300 and 400, respectively). Chemical shifts δ are reported in ppm relative to TMS, and solvent signals ($CDCl_3$, $\delta_H = 7.27$ ppm, $\delta_C = 77.0$ ppm) were used as a secondary reference for 1H and ^{13}C NMR. To monitor changes in the P-ligand of the catalyst, ^{31}P NMR spectra were taken and referenced to external H_3PO_4 (85%).

Additionally, EPR measurements were performed to confirm a potential intermediate Pd^I species. All these measurements were carried out at X-band frequency ~ 9.4 GHz on an ELEXSYS 500-10/12 cw-spectrometer (Bruker) with a modulation frequency of 100 kHz, a microwave power of 6.3 mW, and a modulation amplitude up to 5 G.

2.2. Catalytic reactions

High-oleic sunflower oil 90plus from T + T Oleochemie (HOSO; oleic acid 90.4%, linoleic acid 3.4%, palmitic acid 2.6%, stearic acid 1.9%, others 1.7%) was used for the transesterification toward methyl oleate, which was then studied in terms of isomerization/methoxycarbonylation toward 1,19-diester. HOSO was also used for the direct synthesis of 1,19-diester, following a combined reaction of transesterification, isomerization, and methoxycarbonylation.

In batch reactions, 300 μ l HOSO and methyl oleate were converted into 1,19-diester, using $o-C_6H_4(CH_2P^tBu_2)_2$, abbrev PdL_{Bu} (Rhodia), as catalyst. The quantity of the catalyst used corresponds to 0.8 mol% PdL_{Bu} per fraction of oleate. The reaction conditions were kept constant at $p_{CO} = 30$ bar and a temperature $\vartheta \in \{60, 70, 80, 90, 100, 110, 120, 130\}$ $^\circ C$ in 9.6 mol% CH_3SO_3H (Aldrich) for $t = 32$ h. After separation of the catalyst, the reaction products were analyzed using a Shimadzu GCMS.

2.3. Setup for *in situ* UV–vis investigations

UV–vis measurements were performed using an AvaSpec 2048 spectrometer (Avantes B.V., Eerbeek, Netherlands) equipped with an FDP-7UV200-2-1 transmission probe and an AvaLight DHS light source. All spectra were sampled with 50 accumulations, an integration time of 10 ms and an optical path length of 2 mm. The probe was installed in a special customized autoclave manufactured by Parr Instrument Co. (Illinois, USA) [20]. For the *in situ* investigations, a mixture of 5% CO in helium (Air Liquid Crystal Mix 5.04 \pm 0.10 vol.% CO) was dosed via a high-pressure gas burette (Parr Instrument Co., Illinois, USA).

For the experiments, 54 mg $Pd(OAc)_2$ (0.24 mmol) or 39 mg $PdCl_2$ (0.24 mmol) (Aldrich) and 473.5 mg (1.20 mmol) L_{Bu} or 194 mg (0.96 mmol) tBu_3P (Strem) were dissolved in 40 ml methanol (HPLC grade, Roth) in inert atmosphere and stirred with 300 rpm. For the experiments with CO, the autoclave was flushed three times with 5 bar of the CO/He-mixture. After that the pressure was set to 10 bar.

2.4. Computational details

As a simplification, we used $o-C_6H_4(CH_2PMe_2)_2(L_{Me})$ to model the real bidentate ligand L_{Bu} , and for the long-chain oleate, we used *cis*-3-hexene as model substrate. For easy reorganizations, we abbreviated our model active catalyst as $HPdL_{Me}$ (the Pd hydride species). There are several computational studies on Pd-catalyzed Heck reactions known, and the B3LYP hybrid functional [21–23] has been tested and validated accordingly [24–29]. It was therefore reasonable to use the B3LYP method to model our reactions. At first, all structures were optimized at the B3LYP level of density functional theory in combination with the LANL2DZ basis set from the effective core potentials of Hay and Wadt (LANL2DZ) for palladium [30,31], and the 6-31G(d) [32,33] basis set for all non-metal elements (C, H, O, P), and all optimized structures have been characterized either as energy minima with only real frequencies or transition states (TS) with only one imaginary frequency by frequency calculations at the same level (B3LYP/6-31G*) and the imaginary model connects the initial and the final states. Since B3LYP might give very reasonable

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