Platinum-Catalysed Hydrosilylation of Unsaturated Fatty Acid Esters

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Abstract: Different Pt(IV), Pt(II) and Pt(0) catalysts were screened for the hydrosilylation of fatty acid esters containing terminal as well as internal double bonds. The reaction of terminally unsaturated fatty acid esters proceeded smoothly with short reaction times for nearly all examined catalysts, whereas Pt(IV) species and Pt(II) or Pt(0) species with labile ligands were sufficiently active in the reaction of internally unsaturated compounds. For methyl linoleate, a conjugation of the two internal double bonds before the hydrosilylation was observed. The reaction was carried out in substance as well as in solvent systems permitting a catalyst recycling and reuse. In these systems, however, hydrogenation and double bond isomerisation were found as side reactions.

Keywords: biphasic catalysis; homogeneous catalysis; hydrosilylation; oleochemicals; platinum

Introduction

Many hydrosilylation reactions are carried out using homogeneous transition metal catalysts, especially platinum compounds such as H_2PtCl_6 in 2-propanol solution (Speier's catalyst[1]) or the Pt(0)-divinyltetramethyldisiloxane complex (Karstedt catalyst[2]). The hydrosilylation of unsaturated fatty esters leads to a number of substances with potentially interesting physical and chemical properties, such as low surface tension, hydrophobic and antifoam behaviour.

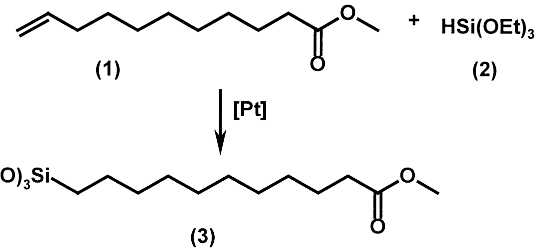
In 1974, Saghian and Gertner presented the first results of the hydrosilylation of unsaturated fatty acid esters using the Speier catalyst.[3] A publication of Delpech et al. in 2001 focused on the regioselectivity of this reaction.[4] Our group has recently reported about the hydrosilylation of unsaturated fatty acid esters using H_2PtCl_6 in single-phase and biphasic reaction systems.[5,6]

In this article, we present the results of the screening of different Pt(0), Pt(II), and Pt(IV) compounds for the hydrosilylation of fatty acid esters containing terminal as well as internal double bonds.

Results and Discussion

Hydrosilylation of Terminally Unsaturated Fatty Acid Esters

At first, we checked the hydrosilylation activity of Pt compounds for the reaction of methyl undec-10-enoate **1** with triethoxysilane **2** in a single phase to 11-triethoxysilanylundecanoic acid methyl ester **3** (Scheme 1). The results are given in Table 1.



Scheme 1.

Table 1. Hydrosilylation of methyl undec-10-enoate **1** with triethoxysilane **2** ($T = 40\,°C$, $t = 10$ min, 1 mol % catalyst, ester/silane ratio 1:1).

Catalyst	Fatty acid ester conversion [%][a]	Product yield [%][a]
H_2PtCl_6	94	88
$PtCl_4$	51	50
$PtCl_2$	93	79
Pt on carbon	38	21
K_2PtCl_4	0	0
Karstedt	78	77
$H_2Pt(OH)_6$	1	0
$H_2Pt(OH)_6$[b]	99	70
$Pt(acac)_2$[c]	10	10
$Pt(cod)Cl_2$[d]	51	50

[a] Determined by GC analysis.
[b] 4 h reaction time.
[c] (acac): 2,4-pentanedionate.
[d] (cod): 1,5-cyclooctadiene.

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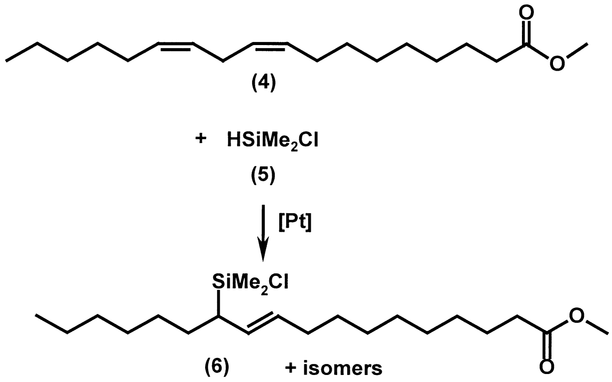
Using H_2PtCl_6, $PtCl_2$ or the Karstedt catalyst, product yields of 77 up to 88% are obtained in spite of the short reaction time of only 10 min. $PtCl_4$ as catalyst gives a lower yield due to its low solubility in the reaction system. The catalysts with oxygen-containing ligands [$H_2Pt(OH)_6$ and $Pt(acac)_2$] gave only small amounts of the product **3** under the chosen conditions. The reason for this might be a relatively long induction period that is necessary for the formation of the catalytically active compound. Prolongation of the reaction time leads to much better results [70% yield for $H_2Pt(OH)_6$ after 4 h]. The heterogeneous catalyst Pt on activated carbon showed only a moderate hydrosilylation activity. After filtration and reuse, the catalyst had no activity at all, showing that the metal catalyst was "leaching" from the carbon surface. K_2PtCl_4 was very sparingly soluble in the reaction system and showed no catalytic activity in the hydrosilylation of **1**.

Hydrosilylation of Internally Unsaturated Fatty Acid Esters

We also examined the hydrosilylation of methyl linoleate **4** (Scheme 2).

The reaction time was prolonged from 10 min (as for methyl undec-10-enoate) to 4 h to achieve acceptable ester conversions. We found that best product yields were achieved with a two-fold molar excess of the hydrosilane. As hydrosilane, we chose chlorodimethylsilane **5**, because the hydrosilylation of **4** with triethoxysilane **2** using hexachloroplatinic acid as catalyst did not proceed under our conditions. We obtained mixtures of isomers of dimethylchlorosilanyl-octadecenoic acid methyl ester **6** as products and found that the remaining double bond in **6** was in the α-position to the silanyl-substituted carbon atom, indicating a double-bond migration. Interestingly, no double bond migration was observed without addition of the silane to the reaction mixture. Our results are given in Table 2.

In all cases, oligomerisation of the fatty acid ester to high boiling products occurred. Furthermore, hydrogenation of the double bonds was observed. The hydrogen source might be the silane. The GC-mass spectra of the reaction mixtures gave hints for the occurrence of disilanes, however, attempts to isolate those compounds were not successful. With the Pt(IV) catalysts H_2PtCl_6, $PtCl_4$, and $H_2Pt(OH)_6$, as well as with $Pt(cod)Cl_2$, moderate to good yields of 60 up to 84% were obtained, where $PtCl_4$ works best. Using the Karstedt catalyst, only 46% product formation is observed. The reason for this might be a decomposition of the catalyst with the formation of platinum colloids during the reaction, which is shown by the dark brown colour of the reaction mixture. The use of $Pt(acac)_2$ led to a product formation of only 33% after 4 h, whereas further 18% of conjugated methyl linoleate were formed without subsequent hydrosilylation. In contrast to the hydrosilylation of methyl undec-10-enoate **1**, $PtCl_2$ and Pt on carbon showed no hydrosilylation activity at all for the internally unsaturated methyl linoleate **4**. Pt(IV) species or Pt(II) species with labile ligands such as (cod) or, to some extent, (acac) as well as the Karstedt catalyst can be used to perform the hydrosilylation of **4**.



Scheme 2.

The results mentioned before led us to a closer examination of the double bond conjugation during the formation of **6**. Performing the reaction again with 1 mol % H_2PtCl_6 as catalyst, we obtained the yield *versus* time plot that is given in Figure 1.

It is shown that the formation of **6** is a consecutive reaction of double bond conjugation and hydrosilylation of the conjugated double bond. Furthermore, a slight decomposition of **6** to high-boiling products is observed at reaction times above 45 min. This decomposition occurs due to the reactive Si-Cl bond in the product.

Hydrosilylation *versus* Hydrogenation in Solvent Systems

Recently, we proposed the use of temperature-dependent solvent systems for the recycling of homogeneous

Table 2. Hydrosilylation of methyl linoleate **4** with chlorodimethylsilane **5** ($T = 40\,^{\circ}C$, $t = 4$ h, 1 mol % catalyst, ester/silane ratio 1:1.8).

Catalyst	Fatty acid ester conversion [%][a]	Product yield [%][a]
H_2PtCl_6	93	70
$PtCl_4$	92	84
$PtCl_2$	11	0
Pt on carbon	17	0
K_2PtCl_4	28	0
Karstedt	98	46
$H_2Pt(OH)_6$	91	60
$Pt(acac)_2$	58	33
$Pt(cod)Cl_2$	94	67

[a] Determined by GC analysis.

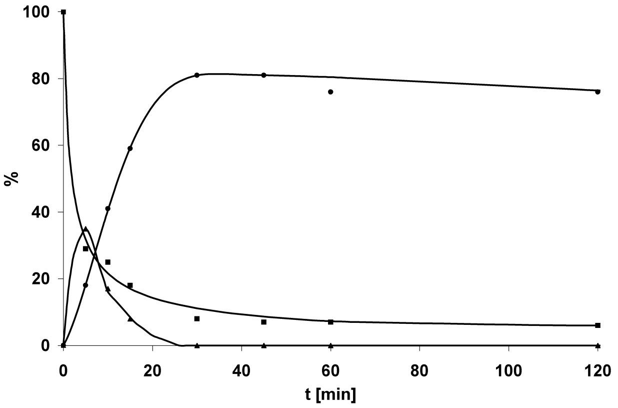


Figure 1. Yield *versus* time plot of the hydrosilylation of methyl linoleate **4** with chlorodimethylsilane **5.** ■: methyl linoleate **4**, ▲: conjugated methyl linoleate, ●: product **6**. 1 mol % H_2PtCl_6, further conditions as given in Table 2.

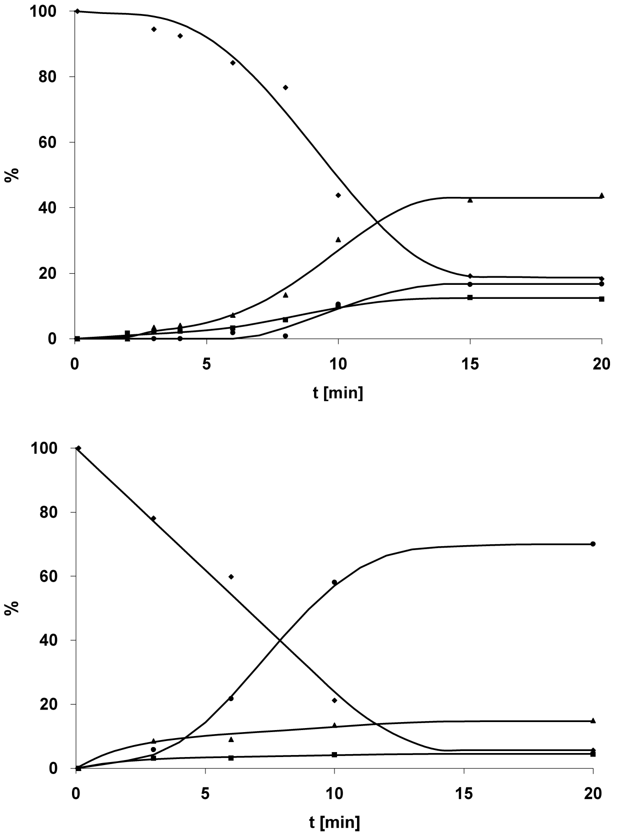


Figure 2. Yield *versus* time plot of the hydrosilylation of methyl undec-10-enoate **1** with triethoxysilane **2** in the solvent system cyclohexane/toluene/propylene carbonate. Conditions: 40 °C, equimolar amounts of **1** and **2**, 1 mol % H_2PtCl_6 (*above*: first use, *below*: second use). ◆: methyl undec-10-enoate **1**, ■: isomerised methyl undecenoates, ▲: methyl undecanoate, ●: hydrosilylation product **3**.

catalysts.[7] Special multicomponent solvent systems allow a single-phase reaction process at reaction temperature combined with an easy catalyst separation by the two-phase technique at room temperature.

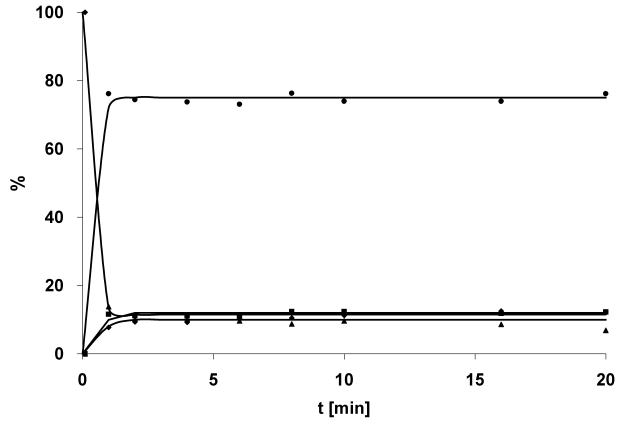


Figure 3. Yield *versus* time plot of the hydrosilylation of methyl undec-10-enoate **1** with triethoxysilane **2** in the solvent system cyclohexane/toluene/propylene carbonate. Conditions: 40 °C, equimolar amounts of **1** and **2**, 1 mol % Pt as Karstedt solution. ◆: methyl undec-10-enoate **1**, ■: isomerised methyl undecenoates, ▲: methyl undecanoate, ●: hydrosilylation product **3**.

The hydrosilylation of methyl undec-10-enoate **1** with triethoxysilane **2** was further examined in a temperature-dependent solvent system of cyclohexane, toluene and propylene carbonate in equal parts by weight (see Figure 2).

We found that the use of H_2PtCl_6 as catalyst led mainly to hydrogenation of **1** in the first run, but after separation and recycle of the catalyst phase, mainly hydrosilylation of **1** occurred. As a further side reaction, the double bond isomerisation of methyl undec-10-enoate was observed. In the first run, the catalyst showed an induction period of about 4 minutes, which was not observed in the second run.

The Karstedt catalyst solution was also examined in the same solvent system (Figure 3).

The reaction was complete even after 1 min at 40 °C, with 76% hydrosilylation product formed. This shows that the Karstedt solution already contains the catalytically active species that has to be preformed when H_2PtCl_6 is used. Unfortunately, our further investigations showed that the Karstedt solution decomposes at temperatures above 70 °C forming a dark brown solution with a significantly reduced activity. Therefore, it is only suitable for reactions at or slightly above room temperature.

Conclusion

For the hydrosilylation of the terminally unsaturated methyl undec-10-enoate, a broad range of Pt(IV), Pt(II) and Pt(0) compounds can be used under mild conditions giving moderate to good yields of up to 88% after 10 minutes. For catalysts with oxygen-containing ligands, prolonged reaction times are necessary due to an induction period for the formation of the catalytically active compound.

The hydrosilylation of methyl linoleate, a fatty acid ester with two internal double bonds, proceeded only with Pt(IV) species, Pt(II) species with labile ligands, or with the Karstedt solution with a yield of 33 up to 84% after 4 h reaction time. A conjugation of the double bonds was observed as first step of the reaction.

The activity of H_2PtCl_6 and the Karstedt solution in the hydrosilylation of methyl undec-10-enoate was also examined in solvent systems where the catalyst was separated and recycled. H_2PtCl_6 showed a significant induction period and good hydrogenation activity in the first run, whereas in the second run, the hydrosilylation predominated without a noticeable induction period. Using the Karstedt solution, mainly hydrosilylation occurred, and the reaction was completed even after only 1 min.

Our results indicate that the catalytically active species is formed by silane addition to the Pt complex, which agrees with the widely accepted Chalk–Harrod mechanism.[8]

Experimental Section

Materials

$H_2PtCl_6 \cdot 6\,H_2O$ (40% Pt), $H_2Pt(OH)_6$ (64% Pt), K_2PtCl_4 (46.65% Pt), $PtCl_4$ (57% Pt), $PtCl_2$ (73% Pt), $Pt(acac)_2$ (49.6% Pt), $Pt(cod)Cl_2$ (52% Pt), Karstedt solution [Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 19.2% Pt] and Pt on carbon (5% Pt) were obtained from Degussa Metals Catalysts Cerdec (now a division of OMG group). $H_2PtCl_6 \cdot 6\,H_2O$ was dried under vacuum (2 h, 200 °C) before use. Methyl linoleate was obtained from Cognis Deutschland GmbH (Edenor SbO5 ME, methyl linoleate content 62%). Undec-10-enoic acid was purchased from Acros and quantitatively esterified using catalytic amounts of thionyl chloride. Triethoxysilane (99%) and chlorodimethylsilane (99%) were obtained from Wacker Chemie. Cyclohexane, toluene and propylene carbonate were purchased from Fluka and Acros and dried over molecular sieve. All reactions were carried out under an inert argon atmosphere.

Hydrosilylations without Solvent

Hydrosilylation of methyl undec-10-enoate **1**: 1.98 g (10.0 mmol) methyl undec-10-enoate and 1.64 g (10.0 mmol) triethoxysilane were heated to 40 °C under argon. After addition of 0.1 mmol of the catalyst, the reaction mixture was stirred for 10 min at 40 °C. To stop the reaction, 8 mL cyclohexane and 8 mL propylene carbonate were added. A biphasic mixture formed, and the upper cyclohexane phase was analysed by GC as already reported in ref.[5]

Hydrosilylation of methyl linoleate **4**: 4.74 g (10.0 mmol) methyl linoleate and 1.70 g (18.0 mmol) chlorodimethylsilane were combined under argon and heated to 40 °C. After addition of 0.1 mmol of the catalyst, the reaction mixture was stirred 4 h at 40 °C. The work-up procedure was the same as described for the hydrosilylation of **1**.

The products were characterised by NMR and GC/MS methods as already described.[5].

Hydrosilylation in Solvent Systems

1.98 g (10.0 mmol) methyl undec-10-enoate and 1.64 g (10.0 mmol) triethoxysilane were dissolved in 10 mL cyclohexane and 10 mL toluene. To this mixture, a solution of 0.01 mmol catalyst in 20 mL propylene carbonate was added under argon. The mixture was stirred for 1 h at 40 °C. Samples were taken from the reaction mixture using a syringe. After cooling down to room temperature and phase separation, the upper phase was analysed by GC.

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