APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organomet. Chem. 2004; **18**: 19–22

Electrochemically reduced tungsten-based active species as catalysts for cross-metathesis reactions: cross-metathesis of erucic acid with 2-octene

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Received 14 May 2003; Accepted 30 September 2003

The cross-metathesis of erucic acid, ($CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$), with an excess of 2-octene in the presence of an electrochemically produced tungsten-based catalyst has been studied. Cross- and self-hydrocarbon products, viz. 2-undecene (C_{11}), 6-dodecene (C_{12}) and 6-pentadecene (C_{15}), were detected. The influence of several parameters, such as the 2-octene/erucic acid and 2-octene/catalyst ratios and the reaction time, on the yield of the cross-metathesis product, 6-pentadecene, was studied. The cross-metathesis of functionalized olefins in the presence of an $Al–e^-–WCl_6–CH_2Cl_2$ system has not been reported in the literature so far. The cross-metathesis products in the presence of this catalyst system can be obtained with high yield and high specificity. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: cross-metathesis; metathesis catalyst; functionalized olefin; reduction; erucic acid

INTRODUCTION

The metathesis of functionally substituted olefins, i.e. olefins containing one or more heteroatoms, affords interesting prospects for the synthesis of valuable organic products.[1] The metathesis of functionalized olefins has been studied by a number of groups.[2–4] These reactions allow single-step syntheses of mono- and di-functional derivatives of hydrocarbons and conversion of functionalized olefins into shorter or longer homologues. The reaction products are highly useful as raw material and intermediates. The metathesis of olefins containing OH groups, such as carboxylic acids and alcohols, is difficult to perform.[5] Cross-metathesis of erucic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$, with excess 4-octene[6] and of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, with 2-hexene[7] has been studied before, but only the hydrocarbon metathesis product was observed.

Functional groups deactivate the catalyst and interfere with the metathesis in different stages of the reaction:[8] (1) by interaction with the cocatalyst, if present; (2) by competition with the C=C bond of the olefin for complexation with the metal centre; (3) by destruction of the catalyst precursor or the metal-carbenes.

Here, we report the cross-metathesis of erucic acid with excess 2-octene catalysed by an active tungsten species generated electrochemically. Electrochemical reduction of WCl_6 and $MoCl_5$ results in the formation of stable and active olefin metathesis catalysts.[9–11] A $WCl_6–Al–CH_2Cl_2$ catalyst system that has been electrochemically reduced brings about the metathesis of α- and β-olefins, as well as the cross-metathesis of non-functionalized olefins[12,13] and the ADMET polymerization of 1,9-decadiene[14,15], with good activity and selectivity. The electrochemical generation apparently stabilizes the higher oxidation state of the active species responsible for the metathesis reaction, resulting in a high selectivity.

EXPERIMENTAL

Chemicals

Dichloromethane (Merck) was washed with concentrated H_2SO_4, water, an aqueous solution of Na_2CO_3 (5 wt%) and water again. It was dried over anhydrous $CaCl_2$ and then distilled over P_2O_5 under nitrogen. 2-Octene (Aldrich) was purified by distillation over calcium hydride and kept under nitrogen. Erucic acid (Merck) was recrystallized from

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Contract/grant sponsor: The Scientific and Technical Research Council of Turkey; Contract/grant number: TBAG-2148 (102T039).

methanol and distilled under vacuum. A 0.1 M erucic acid solution was prepared in CH_2Cl_2. WCl_6 was purified by sublimation of the more volatile impurities (WO_2Cl_2 and WCl_4O) under nitrogen at about 200 °C and kept under nitrogen atmosphere.[12]

Electrochemical instrumentation

The electrochemical instrumentation consisted of an EGG-PAR Model 273 coupled with a PAR Model Universal Programmer. The measurements were carried out under a nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant-temperature bath was circulated. In the electrochemical experiments, the reference electrode consisted of AgCl coated on a silver wire in CH_2Cl_2/0.1 M tetra-*n*-butyl ammonium tetrafluoroborate ($TBABF_4$), which was separated from the electrolysis solution by a sintered glass disc. Experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm^2) and aluminium foil (2.0 cm^2) counter electrode. Electrolysis was carried out without a supporting electrode because of its deleterious effect on the catalyst system. For this reason, the distance between the platinum working electrode and aluminum counter electrode was kept constant and as small as possible (i.e. 2.0 mm) in order to keep the solution resistance to a minimum.

Activation of catalyst

Electrochemical experiments were performed under a nitrogen atmosphere. WCl_6 (0.2 g, 0.50 mmol) was introduced into the electrochemical cell containing CH_2Cl_2 (25 ml) and a red solution was observed. The electrodes were introduced into the deep red solution and reductive electrolysis at +0.9 V was applied to the solution for 3 h. The colour of the solution darkened progressively. Aliquots from this catalytic solution were used in cross-metathesis reactions.

Synthesis and analysis

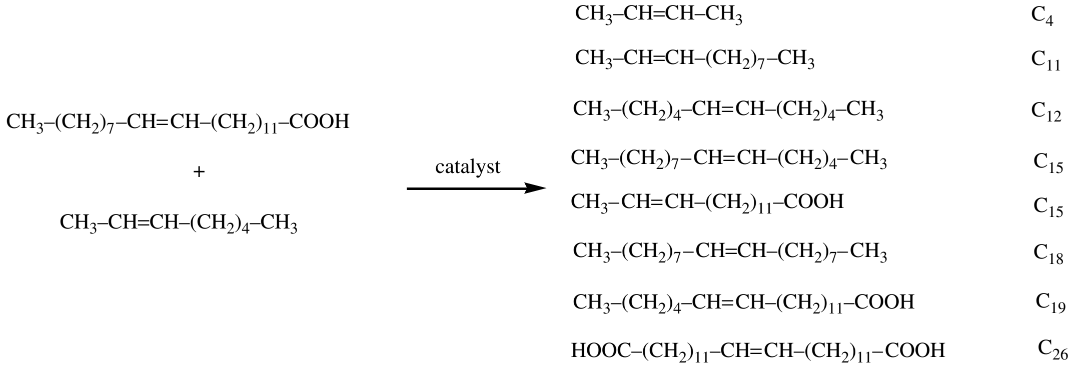
Reactions were carried out in a stirred glass reactor, using different substrate/catalyst ratios. A typical reaction as follows: 1×10^{-2} mmol erucic acid and 2.5 mmol 2-octene were first introduced into the reactor, followed by 1.25 ml (2.5 mmol WCl_6) of the catalytic solution. All additions were done at room temperature and under a nitrogen atmosphere. Metathesis reactions were performed under different 2-octene/erucic acid ratios, 2-octene/catalyst ratios and reaction times to optimize the cross-metathesis reaction of erucic acid with 2-octene. The cross-metathesis products were analysed by gas chromatography–mass spectrometry (GC–MS). GC analysis was performed with a Shimadzu GCMS-QP5050A using an Optima column, 5–1.0 μm (50 m × 0.32mm), a temperature range of 80–250 °C (20 °C min^{-1}) and the carrier gas was helium at 1 ml min^{-1}.

n-Heptadecane ($C_{17}H_{36}$) was used as internal standard for the quantitative determination of the products.

RESULTS AND DISCUSSION

The possibilities of cross-metathesis of carboxylic acids with olefins promise to open up new routes to homologues of these acids, which are often difficult to obtain by other methods. Only a few metathesis catalysts are effective with functionalized olefins. The expected products in the metathesis of unsaturated carboxylic acid (erucic acid) with 2-octene are cross-metathesis products (viz. 2-undecene (C_{11}), 6-pentadecene (C_{15}), 13-pentadecenoic acid (C_{15}) and 13-nonadecenoic acid (C_{19})), self-metathesis products of 2-octene (viz. 2-butene (C_4) and 6-dodecene (C_{12})) and self-metathesis of erucic acid (viz. 13-tridecendicarboxylic acid (C_{26}) and 9-octadecene (C_{18})), see Scheme 1.

Since carboxylic acid groups deactivate the catalyst, an excess amount of non-functionalized olefin (2-octene) was used.[6,16] Cross-metathesis of erucic acid with an excess amount of 2-octene in the presence of electrochemically generated active catalyst resulted in the formation of non-functionalized hydrocarbon products. Acid-functionalized products were not detected by GC–MS, because of their high boiling points. Here, we report the yields according to one of the main products of cross-metathesis of 2-octene with erucic acid, C_{15}. Side reactions, like isomerization, secondary



Scheme 1.

metathesis and dimerization, were not observed in these reactions.

Effect of excess olefin concentration

To study the effect of olefin concentration on the formation of the cross-metathesis product 6-pentadecene, the reactions were performed with different 2-octene/WCl_6 ratios. Changing the 2-octene concentration had a great effect on the yield of 6-pentadecene. Formation of 6-pentadecene increased with the 2-octene concentration up to a critical value, then decreased with further addition of the 2-octene. The best yield of 6-pentadecene was obtained when the molar ratio of 2-octene to WCl_6 was 100 to 1. At this critical concentration, a yield of 73% 6-pentadecene was obtained after 24 h at room temperature (Table 1).

Table 1. The yield[a] of 6-pentadecene in the cross-metathesis of erucic acid with excess amount of 2-octene catalysed by electrochemically reduced WCl_6

2-Octene/WCl_6	Cross-product, C_{15}, yield (%)
75 : 1	58
100 : 1	73
125 : 1	72
150 : 1	64
200 : 1	63
250 : 1	61
300 : 1	41

[a] Reaction conditions: [erucic acid]: 1.0×10^{-2} mmol; [WCl_6]: 2.5×10^{-2} mmol; reaction time: 24 h. Yield: ([6-C_{15}]/[erucic acid]$_i$) × 100.

Effect of erucic acid concentration

The yield of 6-pentadecene depends on the erucic acid concentration used. In order to optimize the erucic acid concentration by using two different 2-octene/WCl_6 ratios, viz. 250 and 100, some experiments were carried out in which the concentration of erucic acid was varied (Fig. 1). When the amount of erucic acid was increased to 1.0×10^{-2} mmol, the activity of the catalyst increased. When the amount of erucic acid was more than 1.0×10^{-2} mmol, the activity of the catalyst decreased. At this point, the yield of 6-pentadecene is 73% when the ratio of 2-octene/WCl_6 is 100. The maximum yield of 6-pentadecene was obtained with 8.0×10^{-3} mmol erucic acid concentration and the yield of cross-product 6-pentadecene was 61% when the ratio of 2-octene/WCl_6 was 250. Apparently, at high unsaturated acid concentrations, the acid poisoned the catalyst and the yield of products decreased.

Effect of reaction time

Table 2 summarizes the catalytic data, showing the influences of different reaction times on the yield of 6-pentadecene. The cross-metathesis reaction of erucic acid with excess amount of 2-octene reacted to an equilibrium after 24 h. The maximum yield of product was obtained after 24 h and no decrease was observed above 24 h. The time required for the establishment of equilibrium is quite long compared with other catalyst systems.

CONCLUSIONS

The catalyst system $WCl_6–e^-–Al–CH_2Cl_2$ appeared to be very active for cross-metathesis reactions of unsaturated

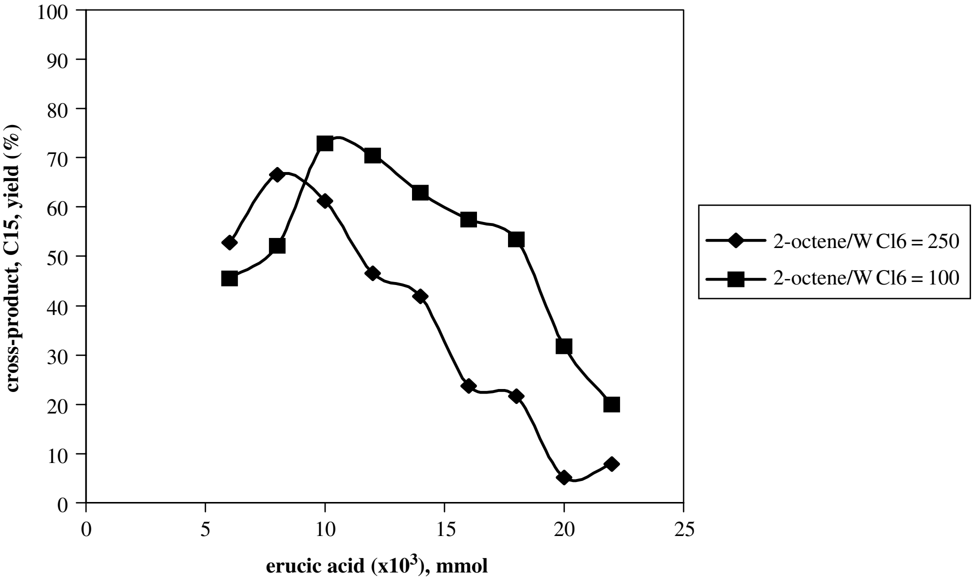


Figure 1. Effect of acid concentration on the yield of 6-pentadecene in the cross-metathesis of erucic acid with excess amount of 2-octene catalysed by electrochemically reduced WCl_6 (reaction time: 24 h).

Table 2. Effect of reaction time on the yield of the cross-product 6-pentadecene in the cross-metathesis of erucic acid with excess amount of 2-octene catalysed by electrochemically reduced WCl_6

Reaction time (h)	Cross-product, C_{15}, yield (%)
1	16
2	18
4	34
8	40
12	57
18	58
24	73
32	73

Reaction conditions: [erucic acid]: 1.0×10^{-2} mmol; [WCl_6]: 2.5×10^{-2} mmol; [2-octene]: 2.5 mmol; reaction time: 24 h. Yield: ([6-C_{15}]/[erucic acid]$_i$) × 100.

carboxylic acids with excess olefins. In comparison with other catalysts, an electrochemically generated tungsten-based catalyst has the advantage of high yield; however, a disadvantage is that it requires a higher reaction time to obtain a good yield.

Acknowledgements

We thank J. C. Mol (University of Amsterdam) for helpful discussions. This work was supported by The Scientific and Technical Research Council of Turkey project no. TBAG-2148 (102T039).

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