

# CATALYTIC DIMERIZATION OF METHYL ACRYLATE UNDER SUPERCRITICAL CARBON DIOXIDE-IONIC LIQUID BIPHASIC MEDIUM

**D. Ballivet-Tkatchenko,<sup>a,\*</sup> M. Picquet,<sup>a</sup> M. Solinas,<sup>b,c</sup> G. Franciò,<sup>b,c</sup> P. Wasserscheid<sup>c</sup> and W. Leitner<sup>b,c</sup>**

<sup>a</sup> Laboratoire de Synthèse et Electrosynthèse Organométalliques, FRE 2595 CNRS-Université de Bourgogne, BP 47870, F-21078 Dijon cedex, France.

Fax: +33 3 80 39 37 72; E-mail: [ballivet@u-bourgogne.fr](mailto:ballivet@u-bourgogne.fr)

<sup>b</sup> Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

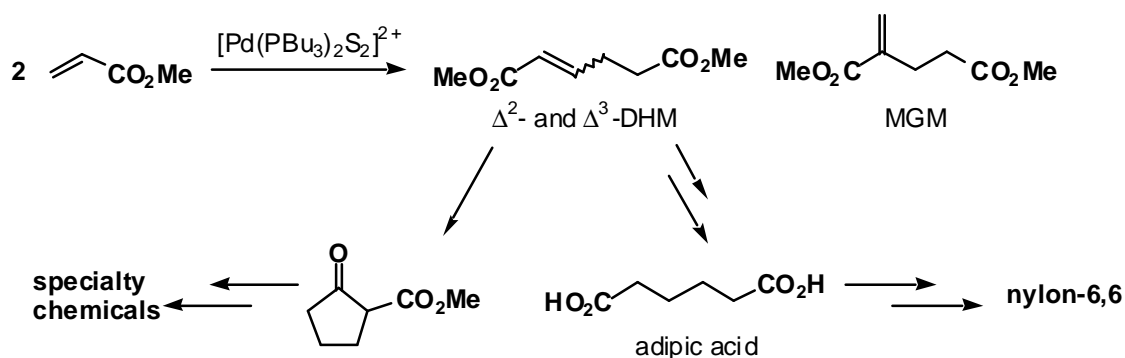
<sup>c</sup> Institut für Technische und Makromolekulare Chemie, RWTH, Worringerweg 1, D-52074 Aachen, Germany

The palladium-catalyzed dimerization of methyl acrylate was conducted under biphasic conditions composed of the ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate and of supercritical CO<sub>2</sub>. The selectivity obtained for the tail-to-tail dimers is very high (>98%) as under monophasic conditions, i.e. in the absence of dense CO<sub>2</sub>. The activity of the catalyst is also equivalent. Solubility determination of methyl acrylate and the dimers shows that they are highly soluble in the CO<sub>2</sub> phase. These results open up the possibility to run the reaction continuously with the concomitant removal of the products by employing two "greener" solvents.

## INTRODUCTION

The catalyzed dimerization of methyl acrylate to dimethyl  $\Delta^2$ - and  $\Delta^3$ -dihydromuconates (tail-to-tail dimers) presents an interesting route to highly valuable intermediates which can be further transformed to speciality chemicals such as cyclopentenone and adipic acid (Scheme 1).

**Scheme 1**



In addition, the production of adipic acid by this route is of interest since it involves propene instead of benzene [1].

It has been recently found that cationic palladium complexes such as  $[\text{Pd}(\text{PBU}_3)_2\text{S}_2]^{2+}$  efficiently induce methyl acrylate dimerization. The complex  $[\text{Pd}(\text{PBU}_3)_2\text{S}_2]^{2+}$  is selectively readily formed *in situ* by reacting  $\text{Pd}(\text{acac})_2$  with  $\text{HBF}_4$  in the presence of the phosphane *n*- $\text{PBu}_3$  [2]. Performing the reaction without any solvent, a selectivity up to 96 % in the linear dimers is obtained, thus minimizing the amount of unwanted dimethylmethylene glutarate (MGM). A further improvement of catalyst activity was achieved by immobilizing the palladium in an ionic liquid such as 1-*n*-butyl-3-methylimidazolium tetrafluoroborate,  $[\text{BMIM}][\text{BF}_4]$ , [3]. It was also observed that addition of toluene leads to a biphasic system and to suitable extraction conditions of the organics while the catalyst is immobilized in the ionic liquid. Interestingly, the activity is even higher due to the continuous elimination of the dimers which cause catalyst inhibition in the monophasic mode [3]. In continuation of this work, we focus our attention on the replacement of toluene by a greener solvent such as supercritical  $\text{CO}_2$  (*scCO}\_2*). It has been reported that  $\text{CO}_2$  is soluble in an ionic liquid, whereas the same ionic liquid has no detectable solubility in *scCO}\_2* [4]. These properties have already been exploited for the immobilization of organometallic catalysts in ionic liquids, while the organic products are extracted by a  $\text{CO}_2$ -dense phase [5–8]. We here report our results on methyl acrylate dimerization catalyzed by cationic palladium species.

## I-MATERIALS AND METHODS

All reactions and synthetic mixtures were prepared in Schlenk glassware under argon, then transferred into a stainless steel reactor, pressurised with  $\text{CO}_2$ , and heated.  $\text{Pd}(\text{acac})_2$ ,  $[\text{BMIM}][\text{BF}_4]$ , and  $[n\text{-Bu}_3\text{PH}][\text{BF}_4]$  were prepared according to ref. [10–12], respectively. The extent of the reaction was determined by gas chromatography with a Shimadzu GC14-A equipped with a 15 m Megabore Carbowax/BTR column and FID detector. The  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 300 spectrometer.

A typical catalytic run under biphasic conditions was performed as follows. In a Schlenk tube were successively added under argon  $[n\text{-Bu}_3\text{PH}][\text{BF}_4]$  (0.681 g),  $[\text{BMIM}][\text{BF}_4]$  (3.14 g),  $[\text{HOEt}_2][\text{BF}_4]$  (54 wt%, 0.254  $\text{cm}^3$ ), methyl acrylate (6.245 g),  $\text{Pd}(\text{acac})_2$  (0.071 g). The mixture was stirred for 0.25 h at room temperature, then the solution was transferred into a stainless steel reactor (53  $\text{cm}^3$ ). A known amount of  $\text{CO}_2$  was admitted to reach 200 bar at 83 °C. Finally, the reactor was placed on a pre-heated magnetic stirrer to obtain 83 °C as the internal temperature. Sampling of the ionic liquid or  $\text{CO}_2$ -rich phase was realized under pressure through a two valve system followed by depressurisation by bubbling either in acetone-*d*<sub>6</sub> for  $^1\text{H}$  NMR analysis (ionic liquid phase) or in xylene for GC analysis ( $\text{CO}_2$  phase). At the end of a run, the reactor was cooled down to room temperature, depressurised, and the remaining dimers extracted with toluene (3x30  $\text{cm}^3$ ) for final turnover numbers (TON) determination. The biphasic character of the reaction in the conditions used was checked by prior experiments with synthetic mixtures of  $[\text{BMIM}][\text{BF}_4]$ , methyl acrylate, dimers and  $\text{CO}_2$  in a 35  $\text{cm}^3$  stainless steel reactor equipped with sapphire windows [13].

## II-RESULTS AND DISCUSSION

Experiments in the ionic liquid under monophasic conditions were first run for comparison with the biphasic system in keeping the same amounts of ionic liquid, palladium, and methyl acrylate-palladium molar ratio of 300. The reaction temperature was set to 80 °C. A conversion of 55% of methyl acrylate was reached within 2 h, with TOF = 100 h<sup>-1</sup> in the first hour. After 15 h, the conversion had reached an upper limit of 60% providing a TON of 180. The dimers selectivity was >98%, independent of conversion.

Under biphasic ionic liquid-scCO<sub>2</sub> conditions, the reaction was performed under 200 bar of CO<sub>2</sub>. The activity and selectivity were determined at 83 °C. The TOF were obtained from samples collected in the CO<sub>2</sub>-rich phase at  $t = 2$  h (linear part of conversion vs. time). Conversion higher than 50% was generally obtained within 3 h. Calculation of the TON was based on the isolated dimers after the catalytic run. In addition, successive samplings of ionic liquid and CO<sub>2</sub>-rich phases at the end of a run were consistent with the mass balance. Typically, methyl acrylate and the dimers in the ionic phase accounted for less than 10% [13].

The calculated TOF value after 1 h run was equal to 95 h<sup>-1</sup>, a value similar to the monophasic regime (*vide supra*). The same trend was observed after 3 h with a conversion of 57%, the selectivity being also higher than 98%. Sampling the ionic and CO<sub>2</sub> phases after 6 h provided a TON value of 220.

It was also of interest to check the catalyst stability. For this purpose, the reactor was cooled down to room temperature after a 6 h run, then, after standing for 60 h, the temperature was raised to 83 °C, and fresh methyl acrylate was introduced into the reactor (methyl acrylate : palladium = 250). The catalyst was still active with the same selectivity, providing a cumulative TON of 450 after 31.5 h of reaction. As it was previously observed that TON increases with methyl acrylate loading, we studied the reaction with a higher initial methyl acrylate: Pd molar ratio (1000). Better performance could even be obtained with TON = 560 and TOF = 195 h<sup>-1</sup> with the same selectivity. On the basis of these results, we performed extraction experiments at the end of a catalytic run. It seemed more appropriate to realize the study at the reaction temperature (83 °C) in view of a continuous reaction-extraction process.

Step by step depressurisation of the reactor was performed while collecting the extracts for quantification. The temperature of the collecting vessel was maintained at room temperature while its pressure was fixed at atmospheric pressure. A maximum efficiency was found for reactor depressurization between 200-150 bar (CO<sub>2</sub> density >0.4 g cm<sup>-3</sup>). This observation corroborates the solubility data described in [13].

## CONCLUSION

The palladium-catalyzed dimerization of methyl acrylate into dimethyl dihydromuconates is also operative under ionic liquid-scCO<sub>2</sub> biphasic conditions and compares well with the ionic liquid monophasic system. Interestingly, lower substrate to palladium ratios in the ionic liquid phase provided TON and TOF values identical to those under monophasic conditions, with the same high selectivity for tail-to-tail dimers (>98%). One could have expected a detrimental effect on kinetics in immobilizing palladium in one phase and solubilizing most of the substrate in the

other, leading to an effective methyl acrylate:palladium molar ratio in the range 5–20. The CO<sub>2</sub>-rich phase acts as a substrate and product reservoir. The high solubility of the dimers in *sc*CO<sub>2</sub> allows further developments of this reaction under continuous feed and extraction conditions with greener solvents.

## ACKNOWLEDGEMENTS

Financial supports from the CNRS (D. B-T. and M. P.) and BMBF through the ConNeCat lighthouse project "Smart Solvents, Smart Ligands" (W. L. and P. W.) are greatly acknowledged. We also wish to thank Dr Igor Tkatchenko for his expertise in Pd-catalyzed coupling reactions.

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