

# 1 INTRODUCTION

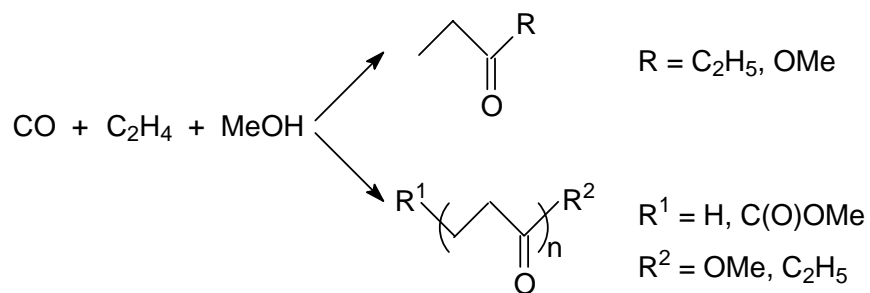
## 1.1. INTRODUCTION

A very attractive route to produce methyl propionate (MePr) is *via* the palladium catalyzed methoxycarbonylation of ethylene ( $C_2H_4$ ).<sup>1</sup> Various articles have been published on the subject of methoxycarbonylation and various alkenes, e.g. propene,<sup>2</sup> styrene,<sup>3</sup> cyclohexene,<sup>4</sup> *etc.*, have also been studied. The methoxycarbonylation process involves the use of a cationic Pd phosphine system, which comprise of a Pd<sup>II</sup> salt, usually palladium acetate ( $Pd(OAc)_2$ ), a phosphine ligand and a strong acid that has a weakly or non-coordinating anion. Various mono- and bidentate phosphines can be employed in this reaction. However, the use of triphenylphosphine ( $PPh_3$ ) as ligand is very attractive from a commercial point of view due to its low cost. For this reason, as well as its ready availability, it was the ligand of choice in this study.

A wide variety of acid promoters can be used in the reaction, although strong acids (with  $pK_a$  less than 2) give higher activity. Examples include *p*-toluenesulfonic acid (TsOH) and methanesulfonic acid (MsOH). The use of these acids does, however, have an inherent drawback, since it is known that monodentate phosphine ligands, most notably  $PPh_3$  are quarternized in the presence of strong acids and methanol (MeOH), The result is that a large amount of the phosphorous ligand is removed from the reaction mixture due to the quaternization of the ligand. A significant role of the ligand is that it stabilizes the Pd catalyst and removal of the phosphorous ligand ultimately leads to catalyst decomposition. The goal was, therefore, to find an alternative acid promoter that would inhibit the quaternization of the phosphine ligand, but that would still provide the right acidity and type of counterion. One such acid is borosalicylic acid ( $HB(Sal)_2$ ),<sup>5</sup> an acid prepared from boric acid ( $B(OH)_3$ ) and salicylic acid ( $SalH_2$ ) and it was first employed by in a polyketone reaction.<sup>6</sup> It was, however, found that the acid can also be used in the esterification of  $C_2H_4$ .

Two mechanisms, namely the hydride and the carbomethoxy mechanisms, have been proposed for the formation of MePr from  $C_2H_4$  and CO in MeOH. Evidence for both

cycles has been found and described in literature.<sup>1</sup> There are a range of products that can possibly form from the reaction of C<sub>2</sub>H<sub>4</sub> and CO in MeOH, from high molecular weight C<sub>2</sub>H<sub>4</sub>/CO copolymers, to oligomeric keto-esters/di-esters/diketones (via multiple alternating insertions of CO and C<sub>2</sub>H<sub>4</sub>), to the mono-carbonylated products diethyl ketone (DEK) and methyl propionate (MePr) (1:1:1 insertion of CO, C<sub>2</sub>H<sub>4</sub> and MeOH), as is presented in Scheme 1.1.<sup>1f</sup>



**Scheme 1.1. Possible products that can form between C<sub>2</sub>H<sub>4</sub> and CO in MeOH.**

## 1.2. AIM OF THE STUDY

The aim of this study was to investigate and compare the solution behaviour for the Pd(OAc)<sub>2</sub> and PPh<sub>3</sub> system using MsOH and HB(Sal)<sub>2</sub> as acid promoter, respectively. The stability and the species distribution of the respective systems were studied and evaluated in solution in the absence as well as in the presence of C<sub>2</sub>H<sub>4</sub> and CO. The two acids were also evaluated in terms of catalysis.

The contents of the thesis are the following:

A literature survey, covering various aspects of the methoxycarbonylation process, is reported in Chapter 2.

In Chapter 3 the solution behaviour of the Pd(OAc)<sub>2</sub>-PPh<sub>3</sub>-MsOH system was investigated by using <sup>31</sup>P NMR and UV-Vis techniques. The dynamic behaviour of the system is described and reaction rates are presented. A reaction scheme is also proposed.

In Chapter 4 the  $^{31}\text{P}$  NMR results of the  $\text{Pd}(\text{OAc})_2\text{-PPh}_3$  system with the alternative acid promoter,  $\text{HB}(\text{Sal})_2$ , are discussed. The system is very stable as was confirmed with UV-Vis spectrophotometry.

In Chapter 5 the properties of  $\text{HB}(\text{Sal})_2$  were investigated. It was confirmed with  $^{11}\text{B}$  NMR spectroscopy that  $[\text{B}(\text{Sal})_2]^-$  does form in aqueous solutions. The acidity of solutions of  $\text{B}(\text{OH})_3$  and  $\text{SalH}_2$  in various ratios were determined by using UV-Vis spectrophotometry,  $^{31}\text{P}$  NMR spectroscopy, as well as potentiometry.

In Chapter 6 the solution behaviour of neutral Pd phosphine complexes is investigated and crystal structures are presented.

The catalytic reactions for  $\text{Pd}(\text{OAc})_2$  and  $\text{PPh}_3$ , with  $\text{MsOH}$  and  $\text{HB}(\text{Sal})_2$ , respectively is presented in Chapter 7 and the rates and stabilities are compared. The methoxycarbonylation rates of various phosphine ligands and acid promoters were also investigated.

An evaluation and summary of the disadvantages and advantages of the respective systems are presented in Chapter 8.

- 
- <sup>1</sup> a) J. Liu, B. T. Heaton, J. A. Iggo, R. Whyman, *Angew. Chem. Int. Ed.* 2004, 43, 90.  
b) G. R. Eastham, R. P. Tooze, M. Kilner, D. F. Foster, D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* 2002, 1613. c) G. R. Eastham, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman, S. Zacchini, *Chem. Commun.* 2000, 609. d) P. W. N. M. van Leeuwen, M. A. Zuideveld, B. H. Swennenhuis, Z. Freixa, P. C. J. Kramer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, *J. Am. Chem. Soc.* 2003, 5523. e) A. Vavasori, G. Cavinato, L. Toniolo, *J. Mol. Catal. A.: Chem.* 2001, 176, 11. f) R. Robertson, D. Cole-Hamilton, *Coord. Chem. Rev.* 225, 2002, 67 and references therein.
- <sup>2</sup> C. Bianchini, A. Meli, *Coord. Chem. Rev.* 2002, 225, 35.
- <sup>3</sup> A. Vavasori, G. Cavinato, L. Toniolo, *J. Mol. Catal. A.: Chem.* 2000, 1, 3241.
- <sup>4</sup> A. Vavasori, G. Cavinato, L. Toniolo, *J. Mol. Catal. A.: Chem.* 2003, 191, 9.

---

<sup>5</sup> R. Crous, M. Green, World Pat. Appl. 2004089865, Sasol Technology Pty. Ltd., 2004.

<sup>6</sup> a) K. G. Smith, Eur. Pat. Appl. 0396268, British Petroleum Co. PLC, 1991. b) S. L. Brown, A. R. Lucy, Eur. Pat. Appl. British Petroleum Co. PLC, 1990.