



Short Communication

Zwitterion enhanced performance in palladium–phosphine catalyzed ethylene methoxycarbonylation

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ABSTRACT

Zwitterions were used for the first time as promoters in ethylene methoxycarbonylation for the production of methyl propionate. They were found to improve the catalytic performance of the Pd–phosphine system. The presence of zwitterions could contribute to stabilize transition states and active catalytic Pd intermediates. The beneficial effect of the zwitterions was found to be most pronounced, when low amount of a strong acid (MeSO₃H) was used with respect to palladium (below 2 equiv.). Under these conditions, phosphine ligand alkylation and reaction vessel corrosion are also anticipated to be less severe.

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1. Introduction

The formation of new carbon–carbon bonds by the carbonylation of unsaturated substrates is of increasing interest [1]. Alkoxy carbonylation of olefins has been a well-known reaction for the production of commodity chemicals since the early 1990s [2]. Among the carbonylation reactions, the ethylene methoxycarbonylation (Scheme 1) to obtain methyl propionate (MP) is especially interesting due to the importance of MP as intermediate in the production of methyl methacrylate (MMA). MMA is a monomer for the production of poly-methylmethacrylate (PMMA) that is a highly demanded transparent thermoplastic with many useful applications. The ethylene methoxycarbonylation is efficiently carried out in methanol at moderate temperature in the presence of a catalyst system formed by a palladium salt, monodentate or bidentate phosphine and a strong acid [3]. The initial perception that monodentate phosphines were the best ligands for making MP was changed, when Shell reported that bidentate ligands with a 1,3-propanediyl bridge gave high selectivity and very fast reaction to MP [4–6]. So far, the best catalytic system for MP synthesis is developed by Lucite [4] (now Mitsubishi Rayon) and includes the rather expensive 1,2-bis(di-*tert*-butylphosphinomethyl)benzene (DTBPMB) ligand.

Commonly, the methoxycarbonylation reaction requires a protic acid with pK_a equal or lower than 4 such as, e.g. methanesulfonic acid (MSA), *p*-toluenesulfonic acid (*p*-TSA) or sulfuric acid (SA) to achieve high reaction rates [7]. The main role of the acid is to form and to prevent the deactivation of the active Pd(II) catalytic species [8,9]. An important

issue in the production of MP is to reduce the overall reaction cost. This issue could be addressed by replacing the DTBPMB ligand with the cheaper and readily available triphenylphosphine (TPP). Furthermore, a challenge in the industrial production of MP is the use of large amounts of strong acids. The acid can affect the process negatively due to corrosion of metal containers and protonation of the monophosphine which facilitate alkylation [1a], thus decreasing the stability of the catalytic system and consequently its activity.

Zwitterions (ZIs) are neutral, polar molecules which are often considered to be viable feedstocks for use in ionic liquid synthesis. Zwitterions have been employed successfully in different fields from electrochemistry to catalysis [10]. In addition, they can act as weak coordinating anions able to interact with transition metal complexes [11]. In this work, we present highly active, stable and selective catalyst systems for making MP by ethylene methoxycarbonylation comprising a Pd–TPP complex and four different ZIs in the presence of small amounts of acids. The small amount of acid makes the system less prone for corrosion and phosphine alkylation, thus affording MP in high yield and selectivity with the application of TPP.

2. Experimental

In a typical catalytic reaction, methanol (0.15 mol) was added into a 50 mL autoclave (Parr 4843) followed by the corresponding amounts of ZI and 1,4-butanediol or MSA, palladium acetate (0.05 mmol) and TPP (0.5 mmol). Afterwards, the reactor was flushed three times with the reactant gas mixture of CO/ethylene/Ar and pressurized to 20 bar. The reaction was started by heating the autoclave from RT to 80 or 100 °C. After the desired reaction time the autoclave was rapidly cooled,

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Scheme 1. Ethylene methoxycarbonylation.

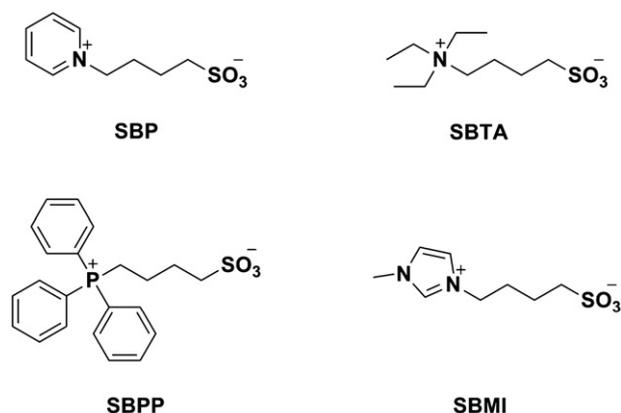


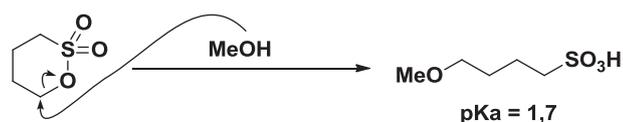
Fig. 1. The zwitterions employed in the ethylene methoxycarbonylation reaction.

depressurized and the products analyzed by GC-FID (DB-1 column, 50 m × 0.320 mm) using toluene (0.7 mL) as internal standard. The selectivity was in all reactions $\geq 99\%$ to MP thus allowing the conversion (%) to MP to be calculated as $(n_{\text{MP}}/n_{\text{substrate}}) \cdot 100$, where n_{MP} is the product amount measured by the GC analysis and $n_{\text{substrate}}$ is the initial amount of CO or ethylene in the gas mixture assuming ideal gas behavior.

3. Results and discussion

Four different ZIs were prepared using slightly modified reported procedures (Fig. 1) [12], and the purity confirmed by NMR spectroscopy and TG/DSC analysis (supporting information). The TG profiles showed a major weight loss due to ZI decomposition in the temperature range 310–370 °C with a stability order corresponding to SBPP > SBMI > SBP > SBTA. Two endothermic peaks for the ZIs SBP, SBIM and SBPP were observed in the DSC profiles; the first sharp peaks are associated to the melting points while the other peaks relate to the decomposition processes of the ZIs. In the case of SBTA, only one peak was observed related to the decomposition process, meaning that SBTA decompose immediately after melting.

The prepared ZIs were employed in the ethylene methoxycarbonylation to improve the catalytic performance of a system comprising palladium acetate, TPP and MSA or 1,4-butanedisulfone. From our knowledge this is the first time that 1,4-butanedisulfone has been employed as acid promoter in methoxycarbonylation. The conversion to MP obtained using 1,4-butanedisulfone as acid promoter was lower than what was found using the traditional strong acids MSA or SA. We speculate that the lower activity is attributed to the lower acidity (pK_a of 1.7) of the corresponding acid formed, when the 1,4-butanedisulfone ring is opened by MeOH under the reaction conditions (Scheme 2), than MSA and SA having pK_a values of -1.9 and -3 , respectively.



Scheme 2. 1,4-Butanedisulfone ring opening by methanol.

Table 1
Methoxycarbonylation of ethylene in the presence of TPP and SBTA zwitterion.^a

Entry	SBTA: Pd ratio	Sultone: Pd ratio	MSA: Pd ratio	Reaction time (min)	TPP: Pd ratio	Conversion (%)
1 ^b	60	0	0	30	10	2
2 ^b	60	5	0	30	10	98
3 ^b	60	0	5	30	10	98
4 ^b	20	5	0	30	10	94
5 ^b	10	5	0	30	10	82
6 ^b	5	5	0	30	10	69
7 ^b	0	5	0	30	10	65
8 ^c	60	0	0	90	10	<1
9 ^c	60	5	0	90	10	84
10 ^c	40	5	0	90	10	73
11 ^c	20	5	0	90	10	59
12 ^c	10	5	0	90	10	53
13 ^c	0	5	0	90	10	34
14 ^c	60	5	0	150	10	98
15 ^c	60	5	0	90	5	74
16 ^c	60	5	0	90	20	65
17 ^c	60	5	0	90	0	<1

^a Reaction conditions: MeOH (6 mL), CO:ethylene:Ar gas mixture (2:2:1) (20 bar), Pd(OAc)₂ (0.05 mmol); ^b 100 °C; ^c 80 °C.

When the ZIs were added to the catalytic system both stability and activity were increased significantly. The catalytic reactions were firstly carried out at 100 °C for 30 min with different molar ratios of the SBTA ZI (Table 1, entries 1–7). Without added ZI 65% conversion to MP was achieved, while the conversion reached 98% when the SBTA was added. For comparison, only 2% conversion was achieved in reference reactions with SBTA without 1,4-butanedisulfone addition. The effect of the ZI amount on the catalytic activity was also studied by employing different amounts of SBTA. As shown in Table 1, high conversion to MP of 98 and 94% was obtained with 60 and 20 equiv. of SBTA, respectively, while conversion decreased further to 82 and 69%, respectively, when using 10 or 5 equiv. of ZI.

After obtaining excellent results with the ZI at 100 °C and 30 min reaction time, the reaction was examined at a lower reaction temperature of 80 °C, which may contribute to save both energy and limit phosphine alkylation (Table 1, entries 8–17). At 80 °C up to 84% conversion to MP were attained after 90 min reaction and 98% after 150 min by employing 60 equiv. of the same ZI. In comparison, only 34% was obtained in the absence of SBTA after 90 min, thus clearly demonstrating the beneficial effect of the ZI on the catalytic performance also at 80 °C. When lower amounts of SBTA corresponding to 40, 20 or 10 equiv. were employed, the conversion was reduced to 73, 59 and 53%, respectively. Under these conditions the influence of the TPP ligand ratio was also studied as can be seen in Fig. 2. The optimal TPP: Pd molar ratio was found to be 10. With a ratio lower than 10 formation of Pd black

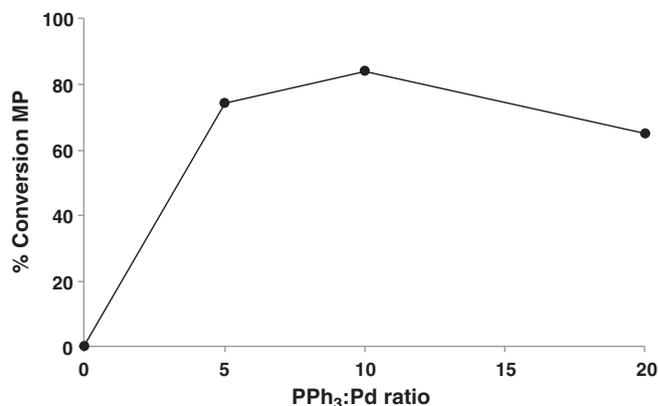
Fig. 2. Influence of the PPh₃ amounts.

Table 2
Methoxycarbonylation of ethylene in the presence of TPP and SBP, SBPP or SBMI zwitterion.^a

Entry	ZI: Pd ratio	Temperature (°C)	Sultone: Pd ratio	Conversion (%)
1	SBP (60)	80	5	83
2	SBP (40)	80	5	70
3	SBP (20)	80	5	50
4	SBPP (60)	80	5	63
5	SBPP (40)	80	5	63
6	SBPP (20)	80	5	62
7	SBMI (60)	80	5	66
8	SBMI (40)	80	5	65
9	SBMI (20)	80	5	49
10	SBP (60)	80	0	2
11	SBPP (60)	80	0	3
12	SBMI (60)	80	0	<1

^a Reaction conditions: MeOH (6 mL), CO:ethylene:Ar gas mixture (2:2:1) (20 bar), Pd(OAc)₂ (0.05 mmol); TPP (0.5 mmol); reaction time 90 min.

occurred towards the end of the reaction, i.e. the Pd–TPP complex catalyst was not stable with low concentration of ligand. At higher TPP concentration (TPP: Pd = 20) the rate of the reaction was slowed down due to competitive coordination of TPP with the reactants CO and ethylene.

Table 2 shows the catalytic results obtained for the remaining three prepared ZIs (i.e. SBP, SBPP and SBMI), when applied at 80 °C in different ratios corresponding to 20, 40 or 60 equiv. during 90 min reaction (Table 2, entries 1–9). When 60 equiv. of the ZIs were applied the best results were obtained yielding conversions to MP of SBP (83%), SBMI (66%) and SBPP (62%), respectively. At lower ZI ratios the conversion decreased for all three ZIs, however not in a gradual manner as found for SBTA. A likely explanation for this difference could be related to the solubility of the ZIs in MeOH, which was found to follow the same general order as the activity, namely SBPP < SBMI < SBP ~ SBTA. Hence, it suggests that the obtainable promoting effect of the individual ZIs to a large extent is determined by their solubility and less by their structural difference.

Since MSA is the acid the Mitsubishi Rayon company uses in the industrial production of MP, catalytic test were also performed with this acid in the presence of the SBTA ZI at 80 °C using TPP as ligand (Table 3, entries 1–8). No promoting effect on the catalytic activity was measured of the ZI when 5 equiv. of MSA were employed (98% MP formed). Assuming that the role of the ZI in the catalytic cycle could be to act as a stabilizing weak coordinating anion to the catalytically active Pd(II) species, the amount of acid was gradually reduced to facilitate the coordination of the ZI relative to the acid anion. No apparent activity difference was measured when decreasing the amount of MSA to 2 equiv. and 96–97 % MP formed in 30 min, confirming that enough weak coordinating ions (MeSO₃⁻) were available to stabilize the Pd species during the catalytic cycle. However, when using only 1 equiv. of MSA a significant activity difference and ZI effect were observed, as the conversion increased from 43% without added ZI to 60% with added ZI (60 equiv.) after 90 min reaction. Also here it was confirmed, that a high concentration of the SBTA ZI resulted in an increased reaction rate and consequently enhanced catalytic activity. In summary, the use of neutral, non-toxic ZIs can limit the use of corrosive and harmful strong acids necessary to run the catalytic reaction thus making the overall process greener.

Table 3
Methoxycarbonylation of ethylene in the presence of TPP and SBTA zwitterion.^a

Entry	SBTA: Pd ratio	MSA: Pd ratio	Reaction time (min)	Conversion (%)
1	0	5	30	98
2	60	5	30	98
3	0	2	30	97
4	40	2	30	96
5	0	1	90	43
6	5	1	90	42
7	40	1	90	55
8	60	1	90	60

^a Reaction conditions: MeOH (6 mL), CO:ethylene:Ar gas mixture (2:2:1) (20 bar), Pd(OAc)₂ (0.05 mmol); temperature 80 °C; TPP (0.5 mmol).

4. Conclusions

Zwitterions (ZIs) were found to enhance the catalytic performance of a Pd–TPP complex catalyst system in ethylene methoxycarbonylation yielding 98% of MP at 100 °C in 30 min in the presence of 1,4-butanediol or MSA. Both 1,4-butanediol and ZI were used for the first time as acid promoter and stabilizer, respectively. The use of ZI diminished considerably the amount of strong acid (MSA or others) required for the catalytic reaction, facilitated use of the cheap and readily available TPP ligand while lowering possible corrosion issues in up-scaled applications. Further investigations are currently being carried out in order to understand the role of both ZIs and 1,4-butanediol in methoxycarbonylation in more detail.

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References

- [1] P.W.N.M. van Leeuwen, *Homogeneous Catalysis - Understanding the Art*, ed. Kluwer Academic Publishers, Dordrecht, The Netherlands, 2004; Catalytic carbonylation reactions, in: M. Beller (Ed.), *Topics in Organometallic Chemistry*, Springer, Berlin, 2006.
- [2] E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663; R.A.M. Robertson, D.J. Cole-Hamilton, *Coord. Chem. Rev.* 225 (2002) 67; C. Godard, B.K. Muñoz, A. Ruiz, C. Claver, *Dalton Trans.* (2008) 853.
- [3] W.G. Reman, G.B.J. De Boer, S.A.J. Van Langen, A. Nahuijsen, *Eur. Pat. Appl.* (1989) EP 411 721 A3 (to Shell).
- [4] W. Clegg, G.R. Eastman, M.R.J. Elsegood, R.P. Tozze, X.L. Wang, K. Whiston, *Chem. Commun.* (1999) 1877.
- [5] E. Drent, E. Kragt, *Eur. Pat. Appl.* (1991) (EP 495 548 to Shell).
- [6] R.I. Pugh, E. Drent, P.G. Pringle, *Chem. Commun.* (2001) 1476.
- [7] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, C.F. Roobeek, *J. Organomet. Chem.* 430 (1992) 357.
- [8] C.J. Rodriguez, D.F. Foster, G.R. Eastham, D.J. Cole-Hamilton, *Chem. Commun.* 15 (2004) 1720.
- [9] C. Bianchini, A. Meli, *Coord. Chem. Rev.* 225 (2002) 35; M.A. Zuideveld, P.C.J. Kramer, P.W.N.M. van Leeuwen, P.A.A. Klusener, H.A. Stil, C.F. Roobeek, *J. Am. Chem. Soc.* 120 (1998) 7977.
- [10] C. Tiyapiboonchaiya, J.M. Pringle, J. Sun, N. Byrne, P.C. Howlett, D.R. MacFarlane, M. Forsyth, *Nat. Mater.* 3 (2004) 29; D. Kundu, A. Majee, A. Hajra, *Catal. Commun.* 11 (2010) 1157.
- [11] E. Drinkel, F.D. Souza, H.D. Fiedler, F. Nome, *Curr. Opin. Colloid Interface Sci.* 18 (2013) 26.
- [12] Z. Du, Z. Li, Y. Deng, *Synth. Commun.* 35 (2005) 1343; Y. Zhao, F. Deng, C. Xia, J. Peng, *Catal. Commun.* 10 (2009) 732.