
Eötvös Univeristy
Faculty of Sciences

Theses of the Ph.D. dissertation entitled

**IN SITU MECHANISTIC STUDIES ON METHOXYCARBONYLATION OF
1,3-BUTADIENE AND SYNTHESIS OF WATER SOLUBLE
PHOSPHINE LIGANDS**

submitted by

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- [5] Reaction Monitoring in Conventional and Green Solvents by ReactIR™ Csihony, Sz.; Mehdi, H.; Tuba, R.; Mika, L.T.; Horváth, I. T. *International Conference on Green Solvents for Catalysis*, October 13-16, **2002**, Bruchsal, Germany. Book of Abstracts p. 50.

1 INTRODUCTION, OBJECTIVES

The cyclohexane oxidation based production of the C₆-feedstocks of plastic industry emits environmentally hazardous nitrogen oxides (NO_x, N₂O).¹ The hydromethoxycarbonylation of 1,3-butadiene (**1**) to methyl 3-pentenoate (M3P, **2**) could be the first step in the green production of adipic acid or ε-caprolactam (Figure 1.), which are key intermediates in nylon manufacture. Co₂(CO)₈ in the presence of N-heterocycles represents one of the few catalytic systems which is suitable for this transformation.² Although several different mechanisms have been proposed for this system,³ no intermediates have been isolated and characterized under reaction conditions. The catalytic reaction and the mechanism of the pyridine modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene was investigated.

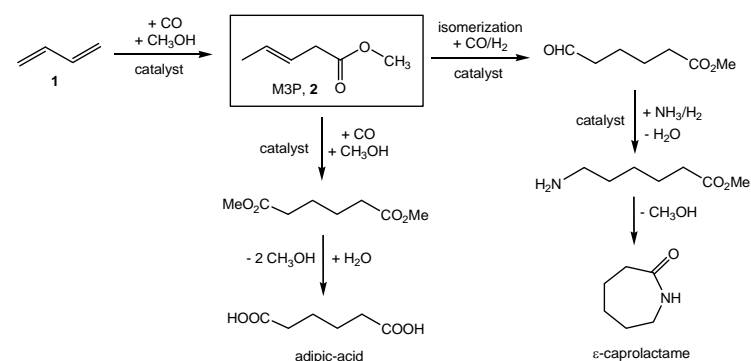


Figure 1. Butadiene based production of adipic-acid and ε-caprolactam

The importance of organometallic catalysis combined with facile catalyst/product separation has been increasing due to potential applications in greener processes,

¹ Bertleff, W.; Roeper, M.; Sava, X., Carbonylation. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th. ed.; John Wiley & Sons: New York, **2009**.

² (a) Matsuda, A., *Bull. Chem. Soc. Jpn.* **1973**, *46*, 524. (b) Bertleff, W.; Maerk, R.; Gerhard, K.; Panitz, P.; Kummer, R. BASF. EP0267497 (1987).

³ (a) Forster, D.; Hersman, A.; Morris, D. E., *Catal. Rev. Sci. Eng.* **1981**, *23*, 89. (b) Milstein, D.; Huckaby, J. L., *J. Am. Chem. Soc.* **1982**, *104*, 6150.

providing value added chemicals at the laboratory and industrial scale. Water, fluorosolvents, ionic liquids, and supercritical carbon dioxide have been tested successfully as alternative reaction media replacing conventional organic solvents in homogeneous catalysis. The combination of the alternative solvents with appropriately designed ligands, for instance, phosphines, could result in higher atom economy and facile catalyst recycling.⁴ In aqueous biphasic catalysis, one of the important goals concerning the effective use of aqueous phosphine-modified transition metal catalysts is to keep metal leaching at the lowest possible level. In the cobalt based biphasic hydroformylation process, the basicity of the trisulfonated-triphenylphosphine (TPPTS) is not enough to keep the catalyst in aqueous phase. The application of more basic phosphines increases the strength of the metal-phosphorus bonds and thus results in lower metal leaching. The synthesis of more basic water soluble phosphines containing sulfonated phenyl ring(s) and easily variable alkyl group(s) was developed.

2 DEVICES AND METHODS

The catalytic carbonylation of 1,3-butadiene (**1**) was performed in an automated Parr-4500 (Honeywell HC-900, PARR PID-A462EE) PASCAR* system containing six HC reactors (p_{\max} : 350 bar, t_{\max} :350°C). The deuterium labelled compounds were prepared in HC Parr 4742 (25 mL) reactor using CD₃OD. The NMR spectra were collected on Bruker Avance 250 and Bruker DRX-500 spectrometers. The high pressure NMR measurements were performed in 10 mm single crystal sapphire NMR tubes with titanium head. The *in situ* IR spectra were collected with ReactIR 1000™ (Mettler-Toledo AutoChem Inc., USA) reaction analysis system equipped with atmospheric or high pressure SiComp™ probe head.

⁴ Cornils, B.; Herrmann, W. A.; Horváth, I. T.; Leitner, W.; Mecking, S.; Oliver-Bourbigou, H.; Vogt, D., *Multiphase Homogeneous Catalysis*. Wiley-VCH:Weinheim: 2005.

* PASCAR: Parallel Screening of Catalytic Reactions

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- [3] **Mika L. T.** Industrial Processes. In *CHEMISTRY* (Ed.. Gábor Náray-Szabó), Academic Press, Budapest, **2006**.
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Patent

- [1] Igniting liquid comprising gamma-valerolactone and its use Horváth, I. T.; Fábos, V.; Mika, L. T. WO2009136213 A1 **2009**

Presentation

- [1] **László T. Mika**, Róbert Tuba, Andrea Bodor, Imre Tóth, I. T. Horváth: HCo(CO)₄ in methanol: acid or hydride? *Centenárium Vegyészkonferencia*, May 29. – June 1. 2007. Sopron, Hungary ISBN 978-963-9319-68-4, p. 419.

Selected Posters

- [1] HCo(CO)₄ in methanol - an acid or a hydride? L. T. Mika, A. Bodor, R. Tuba, I. Tóth and I. T. Horváth. *XVI. International Symposium on Homogeneous Catalysis, July 6-11, 2008*, Florence, Italy. Book of Abstracts p. P393.
- [2] Controlled Synthesis and Applications of Water Soluble Alkyldiaryl- and Dialkylarylphosphanes. L. Orha., L. T. Mika., H. Mehdi, N. Farkas and I. T. Horváth *XVI. International Symposium on Homogeneous Catalysis, July 6-11, 2008*, Florence, Italy. Book of Abstracts p. P393.
- [3] Mechanistic Insight To Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene L. T. Mika; R. Tuba; A. Bodor; I. Tóth; I. T. Horváth, *XVI. FEChem Conference on Organometallic Chemistry, 2005*. September 3-8, Budapest, Hungary. ISBN: 963-9319-48-1 p. 202.
- [4] Application of *in situ* High Pressure NMR Spectroscopy in the Characterization of Key Intermediates of the Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene. Bodor, A.; Tuba, R.; Mika, L. T.; I. Tóth; H.; Horváth, I. T. *XVI. International Conference on NMR Spectroscopy*, June 29 – July 3, **2003**, Cambridge, UK. Book of Abstracts P 8.6

4 PUBLICATIONS

- [1] Tuba, R.; **Mika, L. T.**; Bodor, A.; Pusztai, Z.; Tóth, I.; Horváth, I. T. The Mechanism of the Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene. *Organometallics*, **2003**, 22, 1582.
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- [7] **Mika, L. T.**; L., Sümegi L.; Tüdös, F. Kinetic investigation of hydrogen peroxide decomposition in sec-butyl alcohol and in sec-butyl alcohol in the presence of 1,3-butadiene. *Oxidation Communications*, **2006**, 29, 828.
- [8] **Mika, L. T.**; Sümegi, L.; László-Hedvig, Zs.; Tüdös, F. Kinetic Investigation of Hydrogen Peroxide Decomposition in sec-Butanol and in sec-Butanol in the Presence of 1,3-Butadiene (in Hungarian) *Hung. Chem. J.* **2001**, 107, 260.

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3 RESULTS

3.1 The mechanism of the pyridine modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene

I have investigated the catalytic reaction and the mechanism of the pyridine modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene. The investigation of the influence of different reaction conditions (catalyst's concentration, initial carbon-monoxide pressure, ration of pyridine and methanol, ratio of methanol and butadiene) showed that:

- The formation of M3P shows first order dependence on both initial carbon-monoxide pressure and cobalt concentration.
- The investigation of the different N-containing heterocycles has revealed that the maximum conversion could be achieved by pyridine, and the substituents in *orto* position decrease the product formation significantly.
- The conversion curve shows a maximum in the function of the ratio of pyridine/methanol and methanol/butadiene respectively.
- The catalyst's concentration and the carbon-monoxide pressure have no influence on the isomerization of *trans*-M3P to *cis*-M3P and methyl-2-pentenoate. It occurs in the presence of methanol and pyridine

In situ IR and NMR studies have shown, that at the beginning of the reaction $\text{Co}_2(\text{CO})_8$ undergoes a disproportionation followed by the establishment of the equilibrium mixture of $[\text{Co}(\text{Py})_6]^{2+}[\text{Co}(\text{CO})_4]_2^-$, $[\text{Co}(\text{Py})_6]^{2+}[\text{MeO}]\text{Co}(\text{CO})_4^-$, $[\text{PyH}]^+[\text{Co}(\text{CO})_4]^-$, $[\text{MeOH}_2]^+[\text{Co}(\text{CO})_4]^-$, and $\text{HCo}(\text{CO})_4$ (**3**). Since the equilibrium between $\text{HCo}(\text{CO})_4$ (**3**) and $[\text{MeOH}_2]^+[\text{Co}(\text{CO})_4]^-$ in methanol is shifted to $[\text{MeOH}_2]^+[\text{Co}(\text{CO})_4]^-$, the reaction of protonated butadiene with $[\text{Co}(\text{CO})_4]^-$ leads to the formation of the alkenyl complex $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Co}(\text{CO})_4$ (**4**). This species, depending on the conditions, can undergo facile CO-insertion to yield $\text{CH}_3\text{CH}=\text{CHCH}_2(\text{CO})\text{Co}(\text{CO})_4$ (**5**) or reversible decarbonylation to form $(\eta^3\text{-C}_4\text{H}_7)\text{Co}(\text{CO})_3$ (**7**). The methanolysis of the acyl-cobalt intermediate is taken place by the nucleophilic attack of the $[\text{MeO}]^-$ to yield M3P (?)

and regenerate the cobalt catalyst (Figure 2.). Although, the reaction takes place in the absence of pyridine, the product formation is about five times faster in the presence of N-containing (e.g. pyridine) heterocycles due to the increased concentration of the methoxy-anion.

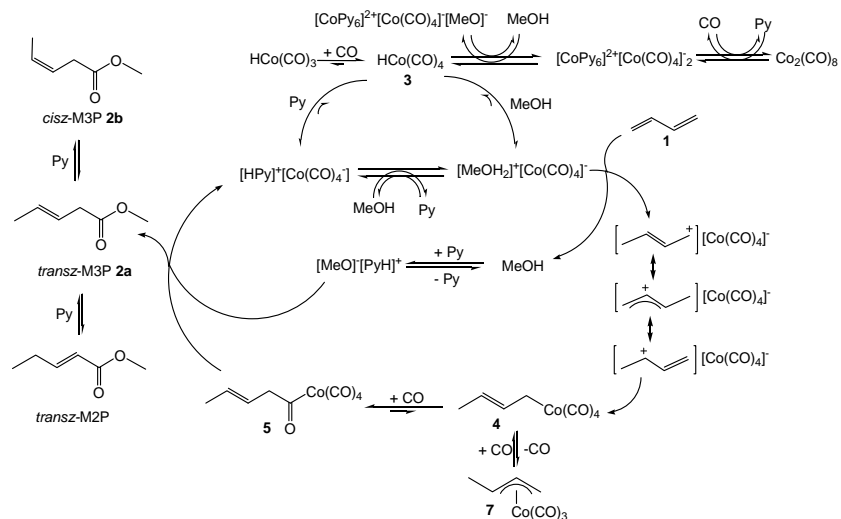


Figure 2. Mechanism of the pyridin-modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene

3.2 Synthesis of alkyl-bis-(*m*-sulfonated-phenyl)- and dialkyl-(*m*-sulfonated-phenyl)-phosphines with pH-controlled phase separation

The combined application of ^{31}P -NMR and pH measurements (Table 1.) during the tri-isooctylamine-assisted aqueous/organic separation and purification steps after the sulfonation of diphenyl-alkyl-phosphines (Ph_2PR ; R: Me, *n*-Bu, Cp) and phenyl-dialkyl-phosphines (PhPR_2 ; R: Me, *n*-Bu, Cp) resulted in the preparation of water-soluble alkyl-bis(*m*-sulfonated-phenyl)-, ($(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_2\text{PR}$; R: Me, *n*-Bu, Cp Figure 3.) and dialkyl-(*m*-sulfonated-phenyl)- ($(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})\text{PR}_2$; R: Me, *n*-Bu, Cp, Figure 4.) phosphines in the presence of less than 0.5% phosphine oxides. The fine tuning of these ligands could be achieved by the variation of steric and electronic properties of the alkyl group(s).

Table 1. pH values of the separation and purification steps

Komponenten	pH ₁	pH ₂	pH ₃
Me-P(<i>m</i> -C ₆ H ₄ -SO ₃ Na) ₂ (6a)	2.1	5.2	7.2
Bu-P(<i>m</i> -C ₆ H ₄ -SO ₃ Na) ₂ (6b)	3.0	5.2	7.5
Cp-P(<i>m</i> -C ₆ H ₄ -SO ₃ Na) ₂ (6c)	3.0	5.0	6.9
Me ₂ -P(<i>m</i> -C ₆ H ₄ -SO ₃ Na) (12a)	3.7	5.7	7.5
Bu ₂ -P(<i>m</i> -C ₆ H ₄ -SO ₃ Na) (12b)	3.5	6.0	9.3
Cp ₂ -P(<i>m</i> -C ₆ H ₄ -SO ₃ Na) (12c)	3.0	5.5	9.5

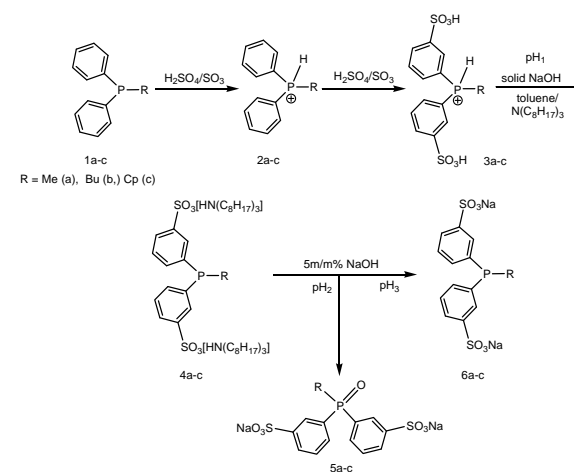


Figure 3. Preparation of water soluble diphenyl-monoalkyl phosphines

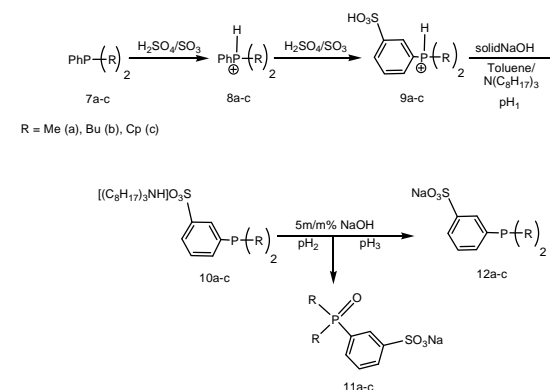


Figure 4. Preparation of monoaryl-dialkyl water soluble phosphines