Enantioselective nickel catalyzed butadiene hydroalkoxylation with ethanol: from experimental results to kinetics parameters

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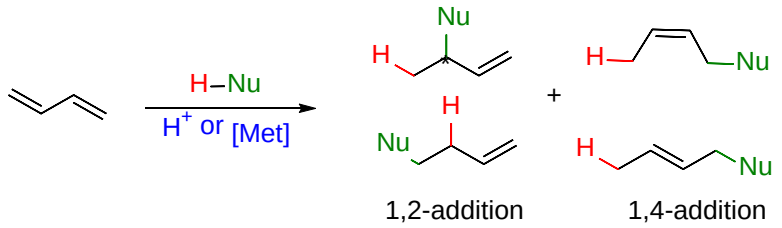
Dedicated to Prof. Alan Welch on the occasion of his retirement from Heriot-Watt University

Abstract

The enantioselective hydroalkoxylation of butadiene with ethanol has been performed in the presence of nickel-based catalysts and chiral diphosphine ligands. Ee's up to 77 % could be obtained from the use of atropoisomeric chiral ligands such as Segphos. The kinetics parameters of the reaction were determined using a qualitative kinetic model to better explain the l/b isomerization and racemization processes observed for long reaction times.

1 Introduction

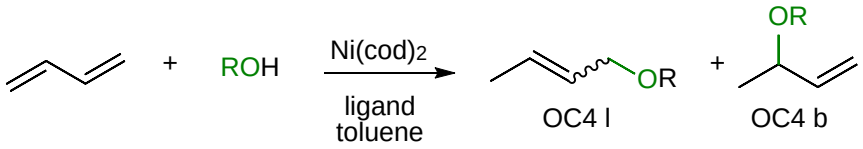
Double bond hydrofunctionalization is one of the most fundamental reactions in organic synthesis leading to a large variety of compounds [1]. This reaction corresponds to the addition of hydrogen and another fragment across a carbon-carbon or carbon-heteroatom multiple bond and is generally promoted by a Brønsted acid or a transition metal catalyst [2-10]. From an atom-economy standpoint, this transformation is ideal with no production of wastes. With butadiene, the hydrofunctionalization reaction leads to the formation of various functionalized alkenes according to the nucleophile (Scheme 1) [11-21]. Butenyl products issued from the 1,2- or 1,4-addition are thus obtained as a mixture of several isomers: the two 1,2-addition products with the Markovnikov and anti-Markovnikov compounds and the two 1,4-aducts that differ from the (*Z*) and (*E*) configurations of the internal C=C double bond.



Scheme 1. Hydrofunctionalization of butadiene

Among these examples, the hydroalkoxylation is particularly attractive since this transformation using readily accessible alcohols as nucleophiles leads to the formation of allylethers via a catalytic and environmentally friendly process. This approach is on this point of view advantageous in comparison to the classical Williamson reaction (SN reaction on an allylic halide derivative) which produces high quantity of inorganic salts as co-products [22]. Nevertheless, this transformation has been relatively rarely described in the literature, unlike considering the telomerization reaction which corresponds to the dimerization of butadiene with addition of a nucleophile [23]. Various metals as rhodium [24-26], palladium [28,29], nickel [30-33] as well as aluminum [34-36] or gold [37] have been used to design suitable catalysts. In our hands,

the hydroalkoxylation of dienes with simple and bio-sourced alcohols has been performed in the presence of nickel precatalysts associated with chelating diphosphine ligands (Scheme 2) [14-16]. With this catalytic system, high butadiene conversions and selectivities in alkylbutenyl ethers were obtained with low catalyst loadings. The major products are the branched butenylether (OC4 b) together with the linear isomer (OC4 l). The allylic structures of the branched or linear ethers formed and the absence of product issuing from the 1,2 anti-Markovnikov addition strongly support the involvement of π-allylnickel intermediates rather than a direct nucleophilic attack on the diene. [38]



Scheme 2. Nickel catalyzed butadiene hydroalkoxylation

As the branched ether bearing a stereogenic center is obtained as major isomer of the reaction, we were interested in the enantioselective version of the nickel catalyzed hydroalkoxylation reaction. This asymmetric version is relevant as it offers an access to enantiomerically enriched small building blocks. Chiral allylethers are commonly found in bioactive molecules and industrially important pharmaceutical intermediates [39]. To our knowledge, the enantioselective hydrofunctionalization of dienes with alcohols is rare with only one recent example reported in the literature [40]. Herein we report our recent progress in the enantioselective butadiene hydroalkoxylation with ethanol as model substrate.

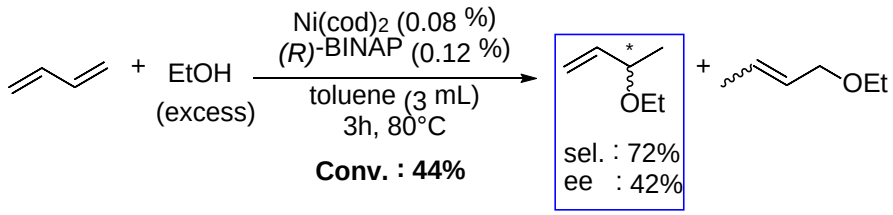
2 Experimental

Chemicals were purchased from Aldrich, Alfa Aesar, Acros, Linde Gas France (butadiene) and Strem. Ethanol was distilled over magnesium turnings. Toluene was obtained from a solvent purification system MBraun SPS-800. Conversions and selectivities were determined by gas chromatography on a Shimadzu 2010 apparatus equipped with an Equity-5 column (30 m, i.d. = 0.32 mm). Ee's were determined by chiral GC using a Chiraldex column with H_2 as gas vector.

Catalytic test: The catalytic solution is prepared in a glovebox by mixing $Ni(cod)_2$ (3.8 mg, 0.014 mmol) and the ligand (0.021 mmol) in 3 mL toluene in a glass reactor closed by a Rotaflo® stopcock. Under nitrogen atmosphere, the tube was cooled at -15 °C and dry and degassed EtOH was added (10 mL). A precise amount of butadiene (1.5 mL, 17.2 mmol) was then condensed at low temperature and transferred in the reaction mixture via a cannula. The glass reactor was closed and heated to 80°C for 30 hours. After reaction, the mixture was cooled and vented before GC analyses with heptane as internal standard. Branched vs linear products could be differentiated.

3 Results and discussion

Our group has recently reported that the hydroalkoxylation reaction can be achieved with both high butadiene conversions and high selectivites when using a catalytic system featuring zerovalent nickel in the presence of particular chelating diphosphines with two phosphorous atoms bridged with four carbons [14-16]. Among the commercially available and optically pure C4 diphosphines, BINAP is one of the most representative ligands with an axial chirality. BINAP is elsewhere used in asymmetric catalytic hydrogenations on an industrial scale, particularly for the synthesis of (-)-menthol [41]. An explorative trial for butadiene hydroalkoxylation reaction with (*R*)-BINAP has been conducted and displayed a moderate conversion (44%). Nevertheless, the regioselectivity for the branched product was important (72%) and a promising enantiomeric excess has been obtained (42%) with a low catalyst loading (0.08 mol %) (Scheme 3).



Scheme 3. Nickel based butadiene asymmetric hydroalkoxylation with ethanol using *(R)*-BINAP ligand

Thanks to this encouraging result, we screened a series of chiral ligands (***Figure 1***) for the butadiene hydroalkoxylation with ethanol using $Ni(cod)_2$ as source of zerovalent nickel, according the standard conditions reported for the evaluation of this catalytic system [15]. The previous procedure used with BINAP has been reproduced: toluene was used as co-solvent to insure a good solubility of the catalyst in the reaction media and the reactions were conducted at 80 °C. A first series of catalytic results is reported in Table 1.

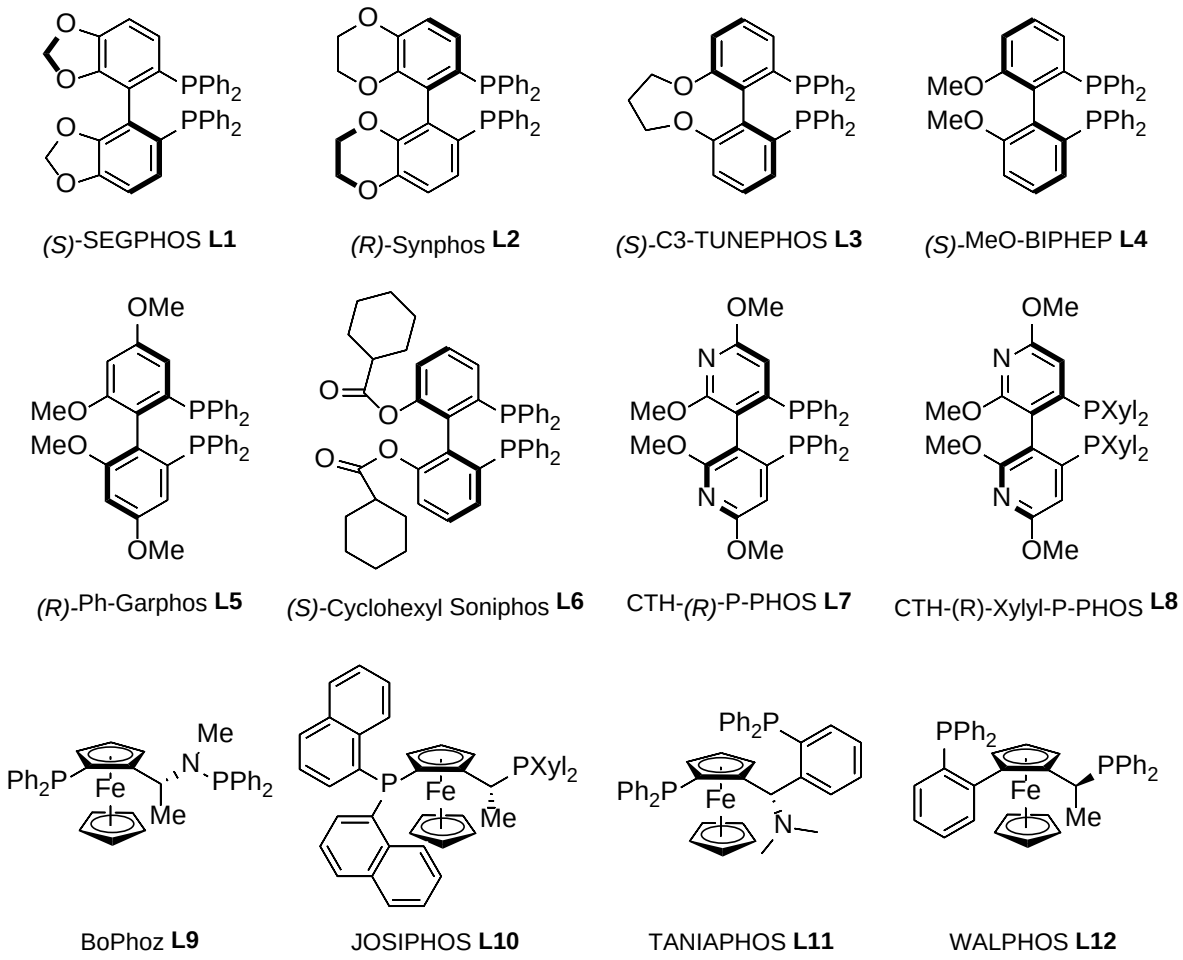
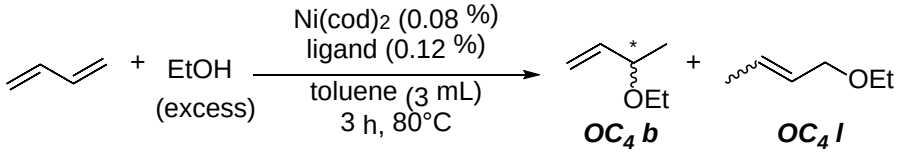


Figure 1. First series of chiral ligands used for the nickel catalyzed asymmetric hydroalkoxylation of butadiene with ethanol

Table 1. Variation of the chiral ligand for butadiene hydroalkoxylation[a]



Entry		Ligand	Conversion[b] (%)	Selectivity OC_4 *b*[b] (%)	Ee[c] (%)
1	**L1**	*(S)*-Segphos	66	71	68
2[d]	**L1**	*(S)*-Segphos	31	75	77
3	**L2**	*(*R*)*-Synphos	97	64	15
4	**L3**	(*S)*-C3-TUNEPHOS	17	70	69
5	**L4**	*(S)*-MeO-BIPHEP	67	72	58
6	**L5**	*(*R*)*-Ph-Garphos	88	69	27
7	**L6**	*(S)*-cyclohexyl Soniphos[e]	33	68	63
8	**L7**	CTH-*(R)*-P-Phos	17	74	64
9	**L8**	CTH-*(*R*)*-Xylyl-P-Phos[e]	87	68	45
10	**L9**	BoPhoz	94	85	13
11	**L10**	JOSIPHOS	94	87	13
12	**L11**	TANIAPHOS	18	91	16
13	**L12**	WALPHOS	32	92	53

[a] Butadiene : 17.2 mmoL, $Ni(cod)_2$ /ligand /butadiene (0,08% : 0,12% : 1), EtOH : 10 mL, toluene : 3 mL, ; T : 80°C, t : 3 hours.
[b] Calculated by GC analysis, from the amount of butenyl ethers, using n-heptane as internal standard.
[c] Calculated by GC analysis using a Chiraldex column
[d] Reaction conducted at 60°C
[e] t : 4 hours

We initially applied ligands with an atropoisomeric C_2-symmetric biaryl backbone as BINAP: *(S)*-Segphos **L1**, *(R)*-Synphos **L2**, *(S)*-C3-Tunephos **L3**, *(S)*-MeO-Biphep **L4**, *(R)*-Ph-Garphos **L5**, *(S)*-Cyclohexyl

Soniphos **L6**, CTH-*(R)*-P-Phos **L7** and CTH-*(R)*-Xylyl-P-Phos **L8** (entries 1-9). Yields in butenyl ethers were measured in the 17-97 % range and selectivities for the branched chiral ether varied from 64 % to 75 %. Butadiene dimers and telomers are occasionally observed as traces (up to 5%).The best combinations between yields and enantioselectivities were obtained with **L1** and **L4** (entries 1 and 5) with respectively 66% yield and 68% ee for **L1** and 67% yield and 58% ee for **L4**. When the experiment was performed at lower temperature with **L1** (entry 2), 60°C instead 80°C, the yield decreased to 31% while the selectivity into the branched isomer increased as well as the enantioselectivity (75% and 77% *vs* 71% and 68%, respectively). Among these atropisomeric ligands, **L2** and **L5** led to the highest OC_4 yields, but provided low enantiomeric excesses with 15% and 27% ee respectively (Entries 3 and 6). The highest enantiomeric excess was obtained with the ligand **L3** (69% ee) along with a very low yield (17%) (Entry 4).

We next considered chiral ligands with ferrocenyl structures (**L9**-**L12**). A nickel catalyst bearing Bophoz **L9** or Josiphos **L10** provides high yields in butenyl ethers but with low enantiomeric excesses (94 % yield and 13 % ee) (Entries 10 and 11). A low conversion as well as a low ee are obtained with Taniaphos **L11** (Entry 12). In this series of ligands, the most interesting enantiomeric excess obtained with ferrocenyl based ligand is with Walphos **L12** with 53 % ee but with a rather low conversion (Entry 13).

As ligands **L1** and **L4** gave the best compromise in terms of butadiene conversions and enantiomeric excesses, variation of **L1** and **L4** structures either on their phosphorous atoms or on their backbones was considered (Figure 2). Results are reported in Table 2. The change of the phenyl substituents on phosphorous of the Segphos by electro-donating xylyl groups (*(S)*-DM-Segphos **L1.1**) (Entry 2 *vs* 1) improves the conversion of butadiene into butenylether to 89 % along with a rather similar enantiomeric excess (compare entries 1 and 2). On the other side, the use of *(R)*-Difluorphos **L1.2** bearing fluorine atoms in position 2 of the dioxole moieties decreases drastically both the yield in OC_4 as well as the enantiomeric excess (entry 3). Reaction with *(S)*-Cl-MeO-Biphep **L4.1** which bears chloro groups on 5 and 5' position displays lower yield and enantiomeric excess than **L4** (entry 5) and electron rich aryl group on the phosphorous atom such as 3,4,5-trimethoxyphenyl **L4.2** leads to similar results (compare entry 6 and entry

5). The use of the ligand **L4.3** with an electron-donating methoxy group and bulky *t*ertiobutyl substituents on the phenyl rings increases surprisingly the conversion of butadiene into butenylether with a high selectivity for the branched isomer (95 %). Unfortunately, a moderate enantiomeric excess was obtained (21 % ee) (compare entries 4, 5 and 7). Electron poor releasing substituents at phosphorous (**L4.4**) did not allow any conversion of the diene.

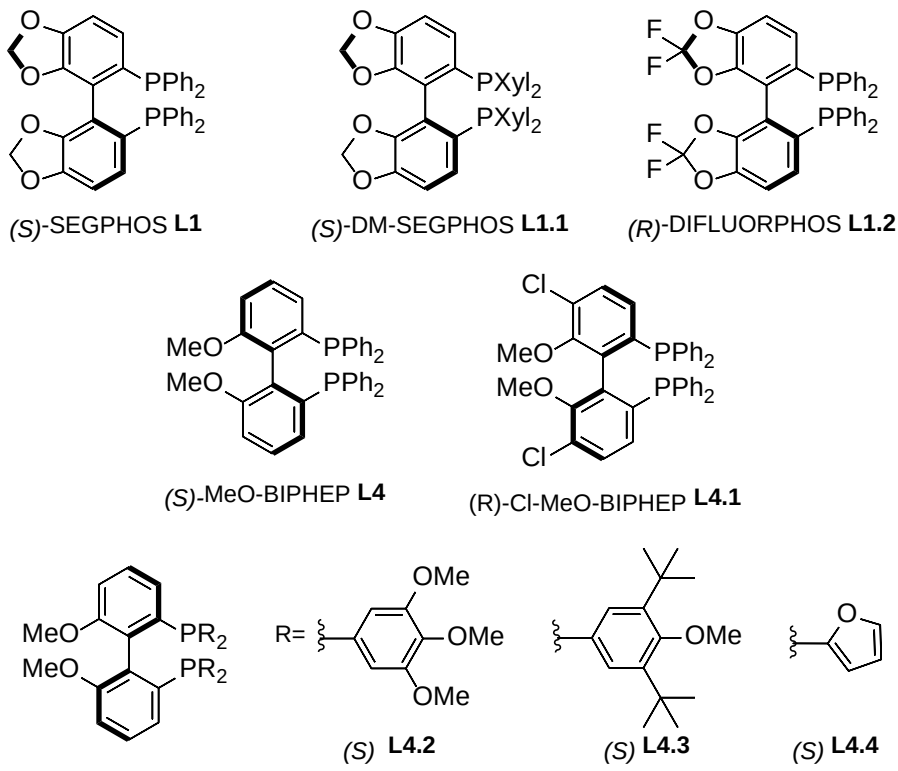
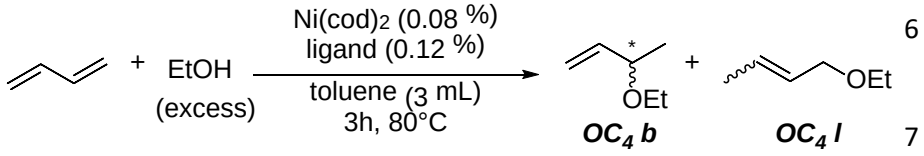


Figure 2. Atropoisomeric diphosphine ligands

Table 2. Effect of Segphos and MeO-BIPHEP derivative ligands on the enantioselective butadiene hydroalkoxylation



OC4 b ***OC4 l***

Entry		Ligand	Conversion[b] (%)	Selectivity OC_4 *b*[b] (%)	Ee[c] (%)
1	**L1**	*(S)*-Segphos	66	71	68
2	**L1.1**	*(S)*-DM-Segphos	89	74	64
3	**L1.2**	(*S)*-difluorphos	7	66	48
4	**L4**	*(S)*-MeO-Biphep	67	72	58
5	**L4.1**	*(R)*-Cl-MeO-Biphep	40	71	49
6	**L4.2**	*(S)*-**L4.2**	42	64	50
7	**L4.3**	*(S)*-**L4.3**	99	95	21
8	**L4.4**	*(S)*-**L4.4**	0	-	-

[a] butadiene : 17.2 mmoL, $Ni(cod)_2$/ligand/butadiene (0,08% : 0,12% : 1), EtOH : 10 mL, toluene : 3 mL, T : 80°C, t : 3 hours.
[b] Calculated by GC analysis, from the amount of butenyl ethers determined using n-heptane as internal standard
[c] Calculated by GC analysis using a Chiraldex column

Among the different catalysts used in this study, several of them displayed a high catalytic activity but led to a low enantioselectivity. This behavior suggested that undesired processes of isomerization / racemization of the different isomeric allylic ethers formed during the reaction could occur. We thus considered studying the evolution of the enantiomeric excess *vs* conversion on a selected example. The combination of CTH-*(R)*-Xylyl-P-Phos **L8** with $Ni(cod)_2$ was chosen for this study as a high yield and a moderate enantiomeric excess were obtained with this catalytic system. Standard reaction conditions were

used and aliquot samples of the reaction mixture were taken and analyzed by GC at regular time intervals (Figure 3). As expected, the global yield in ethers increases rapidly at the beginning of the reaction, then the reaction rate decreases, and the full conversion is reached after 28 hours. Besides, the butenylethers selectivities are moving towards a thermodynamic equilibrium via an isomerization along with an epimerization process. Firstly, the yield into the branched ether decreased regularly to the benefit of the linear one. This phenomenon of isomerization of the branched compounds (including both enantiomers) into the linear isomer follows a decreasing profile from 70 % to 54 %. Similarly, the major enantiomer within the branched ethers decreases from 77 % after 30 h. Noteworthy are the values observed at 46 h, which are respectively 53% of branched butenylethers and 54% of the major enantiomer. As expected, the enantiomeric excess is decreasing faster.

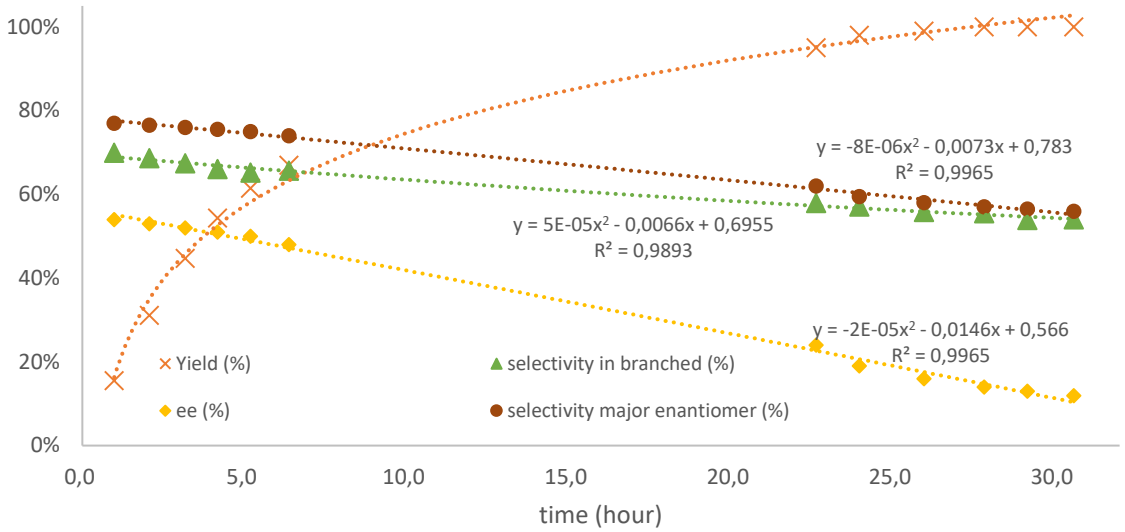


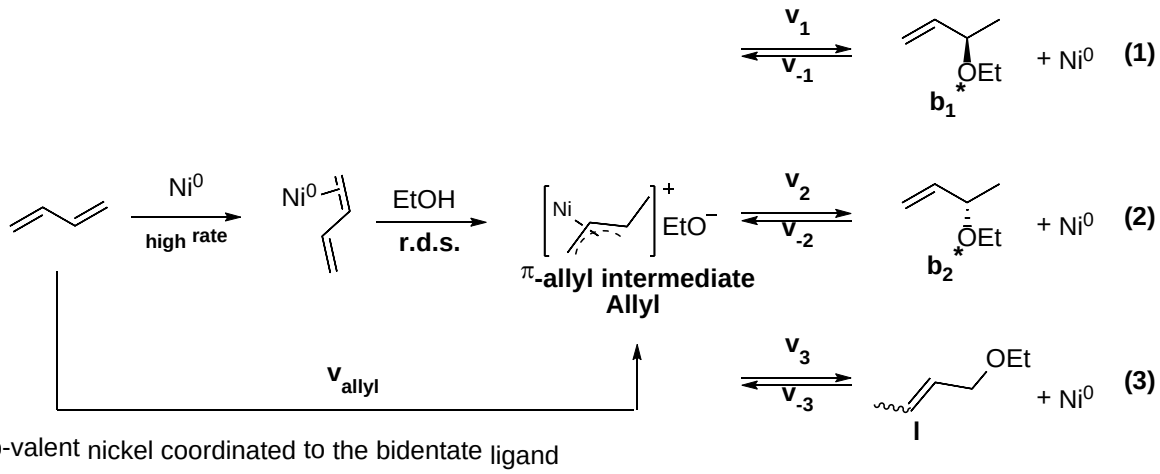
Figure 3. *Ethers yields, OC4 b selectivities, major enantiomer selectivities and OC4 b enantiomeric excesses as function of time*

(Conditions : Butadiene = 17.2 mmoL, $Ni(cod)_2$/ligand/butadiene (0,08 mol % : 0,12 mol % : 1), EtOH = 10 mL, toluene = 3 mL, T = 80°C.)

This important evolution in the products ratio implies both isomerization and racemization processes with time. A cationic Ni-allyl complex has been proposed by our group to be the key intermediate during the formation of butenyl ethers [38]. The computed barriers, in the case of the non-chiral ligand

dppb, indicated an initial kinetic preference for the formation of the branched butenyl ether product but the low calculated energy barrier for the C-O bond formation from the nickel π-allyl intermediate allows considering the reversibility of this step and the observed isomerization.

Herein, we propose a qualitative kinetic model based on the reactions described in Scheme 4 in order to extract the kinetic parameters. Previous DFT calculations showed that the formation of this cationic π-allyl nickel is accessible by direct protonation by ethanol of the initially formed butadiene-Ni(0) complex leading to an ion-pair featuring a Ni-allyl cation along with free ethoxide as counteranion [38]. Based on these previous calculations, this step corresponds to the highest activation energy value of the overall reaction. Moreover, the difficulties encountered monitoring the concentration of nickel species lead up to simplify the kinetic model. As a consequence, the initial elementary steps: nickel-diene coordination and π-allyl formation are considered as one simplified step with a rate corresponding to the RDS of this reaction, the π-allyl formation. Because the ethanol is both the nucleophile of this reaction and the solvent (so used in large excess), we applied an order degeneration simplification and thus the apparent rate constant k_{allyl} corresponds to k[EtOH]. The next elementary steps leading to the formation of the products from this intermediate are supposed to be reversible (steps **(1)**, **(2)** and **(3)**) as suggested by the experimental results (Figure 3, epimerization and isomerization of the butenyl ethers).



Ni^0: zero-valent nickel coordinated to the bidentate ligand

Scheme 4 π-allyl nickel intermediate and products formed during hydroalkoxylation of butadiene

$$
\begin{aligned}
&v_{allyl} = k_{allyl}[but][Ni^0] \\
&v_1 = k_1[Allyl] \\
&v_{-1} = k_{-1}[b_1^*][Ni^0] \\
&v_2 = k_2[Allyl] \\
&v_{-2} = k_{-2}[b_2^*][Ni^0] \\
&v_3 = k_3[Allyl] \\
&v_{-3} = k_{-3}[l][Ni^0]
\end{aligned}
\qquad (4)
$$

$$
\begin{aligned}
&\frac{d[But]}{dt} = -v_{allyl} \\
&\frac{d[Ni^0]}{dt} = -v_{allyl} + v_1 - v_{-1} + v_2 - v_{-2} + v_3 - v_{-3} \\
&\frac{d[Allyl]}{dt} = v_{allyl} - v_1 + v_{-1} - v_2 + v_{-2} - v_3 + v_{-3} \\
&\frac{d[b_1^*]}{dt} = v_1 - v_{-1} \\
&\frac{d[b_2^*]}{dt} = v_2 - v_{-2} \\
&\frac{d[l]}{dt} = v_3 - v_{-3}
\end{aligned}
\qquad \textbf{(5)}
$$

Figure 4 : Proposed kinetic model

Next, the kinetic constants for the other elementary steps were estimated at 353 K by minimizing the least squares with the solver displays by Microsoft Excel® and the GRG (Generalized Reduced Gradient) non-linear solving method. A multistart with 100 samples sized population was preferred to limit local minima in our estimation.

Values of the kinetic parameters are reported in Table 3. Rate constants k_1, k_2 and k_3 display values between 5.9 and 18.8 min^{-1} with $k_1 > k_3 > k_2$. Contrariwise, the rate constants for the reverse ways are in different orders of magnitude, with values included between 10^{-5} and 10^{-1} $L.mol^{-1}.min^{-1}$ following the same order than the direct way. The significant differences between the values obtained for the direct and indirect ways show that the formation of the butenylethers are fostered vs the formation of the allylic intermediate. The model accuracy is very good as illustrated by the parity plot of Figure 4.

Table 3 Optimal parameters of the kinetic model[a]

$\mathbf{k^b_{allyl}}$ ($L.mol^{-1}.min^{-1}$)	$\mathbf{k_1}$ (min^{-1})	$\mathbf{k_{-1}}$ ($L.mol^{-1}.min^{-1}$)	$\mathbf{k_2}$ (min^{-1})	$\mathbf{k_{-2}}$ ($L.mol^{-1}.min^{-1}$)	$\mathbf{k_3}$ (min^{-1})	$\mathbf{k_{-3}}$ ($L.mol^{-1}.min^{-1}$)
3.3	18.8	$7.7\ 10^{-1}$	5.9	$6.0\ 10^{-5}$	11.2	$4.0\ 10^{-4}$

	K_1 = 24 [c]	K_2 = 97550 [c]	K_3 = 27351 [c]

[a] estimated at 353 K
[b] $k_{allyl} = k_{app} = k[EtOH]$
[c] $K_x = k_x / k_{-x}$

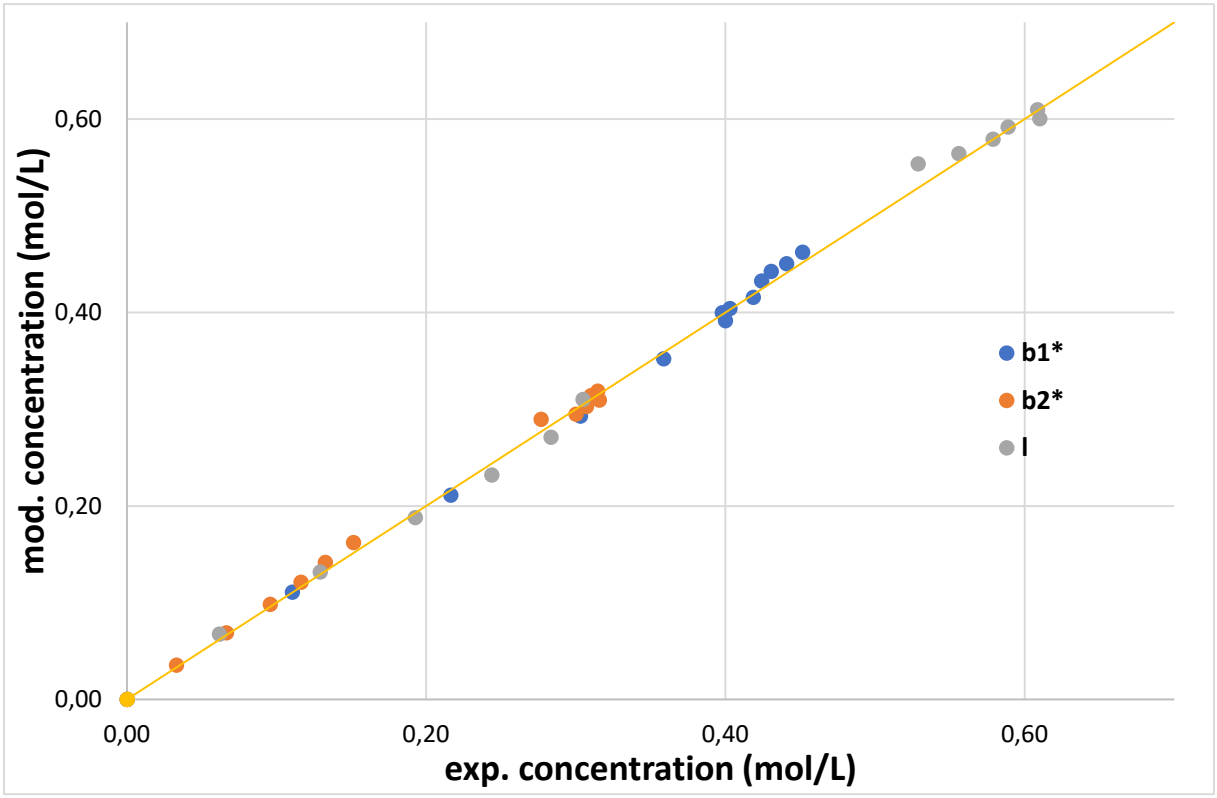


Figure 4 Parity plot of model concentration *vs* experimental concentration

Analysis of the experimental data at the early stage, before that the isomerization and racemization processes get a significant impact on the rate law of the reaction, may help in validating this computational approach. As an apparent zero order applies until a c.a. 30 % conversion, an average rate corresponding to the initial rate determining step allyl complex formation is obtained. This experimental value $v_0 = k_{app}$ is found to be 3.3 $L.mol^{-1}.min^{-1}$ with k_{app} including the ethanol concentration. Both values, obtained from computational approach and experimentally are concurring exactly.

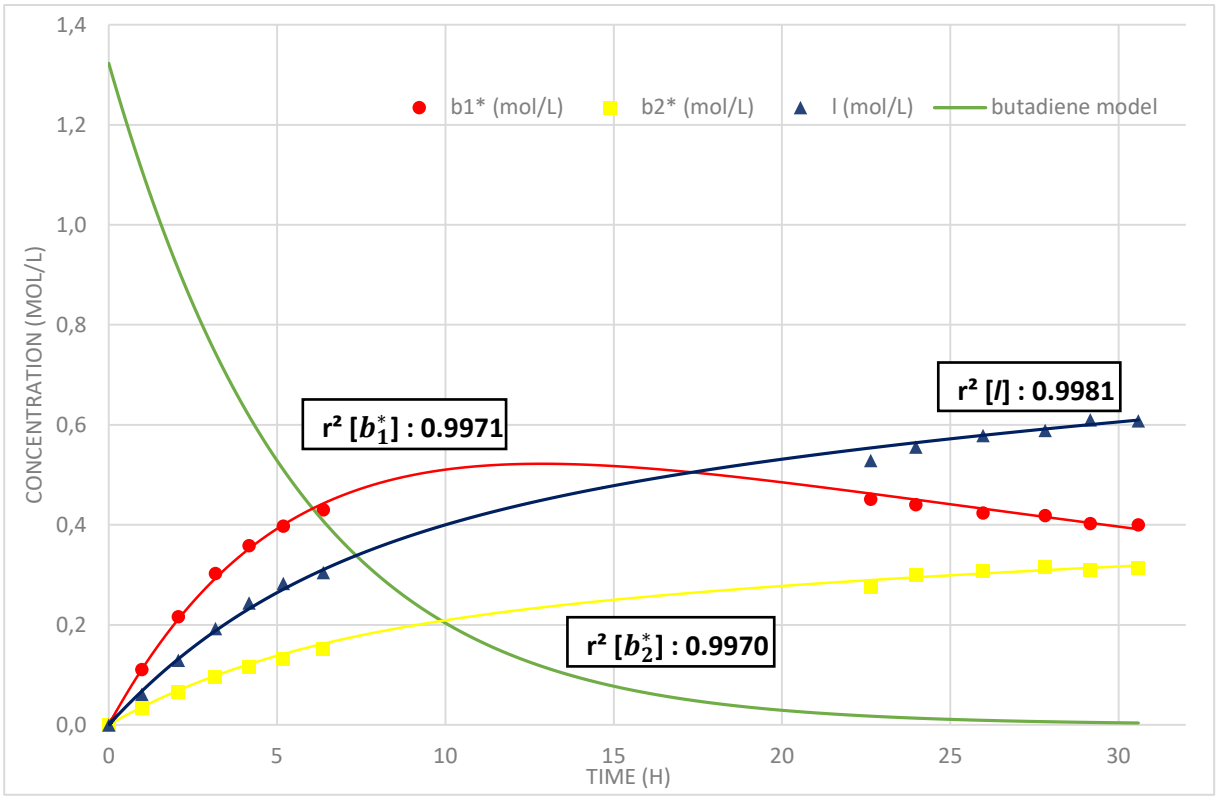


Figure 6 Experimental and simulated concentrations of products with time.

Experimental and simulated concentrations of products with time are reported in Figure 6. It appears that b_1^* as kinetic product is preferentially formed at the beginning of the reaction while the rates of formation of b_2^* and *l* are lower, but their selectivities increase regularly vs conversion. As the butadiene concentration decreases, the π-allyl complex intermediate resulting from the oxidative addition of the butenylethers on a low valent Ni(0) species (k_{-1}, k_{-2}, k_{-3}) still remains the key species of the isomerization and epimerization processes. The affinity of the products with the chiral nickel complex illustrates the differences observed between the kinetic parameters. One can expect that the spatial configuration of the enantiomer b1* allows for its preferable interaction with the chiral catalyst according to a "lock and key" molecular recognition as opposed to the other enantiomer b2* and the linear ether l [42]. As a result, the rate of the reverse way for the elementary step **(1)** is much higher than the ones for **(2)** and **(3)**. This way back of b_1^* to produce the allylic nickel intermediate tends this major enantiomer to be gradually consumed while its opposite enantiomer b_2^* and the linear isomer *l* accumulate in the reaction mixture.

Equilibrium constants determined for the elementary steps of products formation from the allylic intermediate are superior to 1 and confirm the predominance of the direct ways against the reverse reactions. As expected from the higher decreasing rate of the ee *vs the* isomerization, K_1 is the lowest equilibrium constant among these steps for the butenylethers formation and equilibration. K_2 and K_3 are respectively 4000 and 1100 times higher.

Conclusion

In conclusion, nickel catalyzed asymmetric hydroalkoxylation of butadiene with ethanol has been successfully performed in the presence of chiral diphosphine ligands. Enantiomeric excesses up to 77 % have been obtained with high yields. Nonetheless, the chemo- and enantioselectivity of the reaction are governed by the kinetic of the reaction: at the initial stage, the kinetic enantiomer is observed as the major isomer leading to high chemo- and enantioselectivities. Then, the enantiomeric excess and the selectivity into the branched isomer decrease with time due to racemization and isomerization reactions. Although higher enantiomeric excesses are obtained for short reaction time and are decreasing gradually, this catalytic system is very easy to carry out and can be considered as an interesting tool for the asymmetric synthesis of chiral allylic ethers. Further investigations are carried out in order to further increase the ee and to apply this new methodology to the synthesis of other chiral allylic ethers.

Acknowledgments

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