# Butadiene Hydroformylation to adipaldehyde: insights into reaction pathways via temporal concentration profiles

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## Introduction

Adipaldehyde is an attractive precursor for the synthesis of valuable $C_6$ compounds, such as adipic acid, hexanediamine, and hexanediol. These compounds are industrially important monomers for the production of polyamides (e.g., Nylon-6,6), polyesters, or polyurethanes [1]. With increased availability of inexpensive natural gas liquids in the United States, the use of butadiene as a feedstock is receiving renewed interest. Although butadiene based process provides a clean and atom-economical route for aidpladehdye, the selectivity of adipaldehyde is rather low (< 50%) [2,3].

For process optimization and catalyst development, it is essential to gain reliable knowledge of reaction pathways. Rhodium-catalyzed butadiene to adipaldehyde hydroformylation requires the following two steps to occur preferentially: (i) butadiene hydroformylation to monoaldehyde (pent-4-enal); and (ii) pent-4-enal hydroformylation to adipaldehyde. Previously reported work [2-4] typically reports the total product selectivity at end of batch runs lasting several hours Hence it is not possible to discern the contribution of the two aforementioned steps toward adipaldehyde selectivity. To address this issue, we modified an existing setup to allow periodic sampling and measurement of product evolution profiles. Among several ligands tested, it was found that (i) pent-4-enal is the kinetically favored product over a Rh/DIOP catalyst, and that (ii) the 6-DPPon ligand gave the best performance for the pent-4-enal hydroformylation step yielding 91% adipaldehyde selectivity.

## Materials and Methods

The hydroformylation experiments were carried out in a 50 mL high-pressure Parr reactor equipped with a 6-port valve and 50 μL sample loop for periodic sampling of reactor contents. Butadiene or pent-4-enal, $(CO)_2Rh(acac)$ and appropriate ligand (DIOP, 6-DPPon, etc.) were dissolved in 15 mL toluene. After heating to 80 ˚C, the syngas ($CO/H_2$ = 1:1) was charged into reactor from an external reservoir to maintain a constant reactor presure. The syngas consumption was monitored by Labview. The temporal butadiene and pent-4-enal hydroformylation conversion/selectivity were determined by GC/FID with decane as an internal standard. The C balance in all the runs ranged from 90% to 98%.

## Results and Discussion

Temporal concentration profiles (Figure 1) indicate that the first hydroformylation step rapidly produces pent-4-enal with 55% selectivity. The pent-4-enal is completely transformed to adipaldehyde and other products in approximately 100 min. The adipaldehyde selectivity rises during this period reaching approximately 42% and remains fairly constant for the remaining duration of the batch run. Beyond 100 minutes, the internal isomerization of pent-3-enal was the main reaction. In separate experiments, we compared the performance of six ligands for the hydroformyations of butadiene and of pent-4-enal. As shown in Table 1, DIOP is preferred for the first hydroformyaltion step (conjugated butadiene to pent-4-enal) with a maximum selectivity of approximately 55% toward pent-4-enal, while 6-DPPon shows the best performance for the second step (pent-4-enal to adipaldehyde). These findings suggest that the two hydroformylation steps require different ligands to maximize adipaldehyde yield.

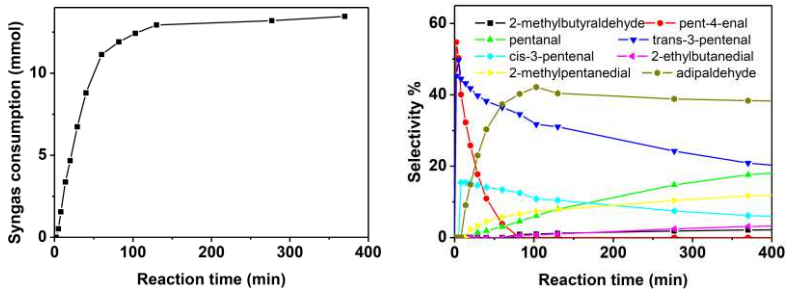


**Figure 1.** Typical experimental results by using sampling apparatus: syngas consumption and selectivity profile of butadiene hydroformylation with Rh/DIOP complex at 80 ˚C. Molar (DIOP/Rh = 2.5); 15 bar syngas ($H_2/CO$ = 1:1).

**Table 1. Ligand influences on the hydroformylation of butadiene and pent-4-enal**

| Reactant | ligand | L/Rh | time min | conversion % | maximum pent-4-enal selectivity % | adipaldehyde selectivity % | n/i |
|---|---|---|---|---|---|---|---|
| butadiene | DIOP | 2.5 | 259 | 92 | 55 | 29 | 2.1 |
| | 6-DPPon | 5.0 | 259 | 94 | 32 | 9 | 2.7 |
| pent-4-enal | DIOP | 2.5 | 79 | 100 | - | 72 | 2.5 |
| | 6-DPPon | 6.0 | 79 | 100 | - | 91 | 9.7 |

## Significance

The temporal profiles provide fresh fundamental insights into ligand effects on butadiene hydroformylation pathways and provide the first experimental evidence for using mixed ligands to maximize adipaldehyde yield, a result of fundamental and practical significance.

## References

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