Molecular Catalysis xxx (xxxx) xxxx

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Butadiene hydroformylation to adipaldehyde with Rh-based catalysts: Insights into ligand effects

Si-min Yu[a], William K. Snavely[a], Raghunath V. Chaudhari[a,b], Bala Subramaniam[a,b,*]

[a] Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS, 66047, United States
[b] Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045, United States

ARTICLE INFO

Keywords:
Butadiene
Hydroformylation
Rh complexes
Temporal concentration profiles
ReactIR

ABSTRACT

Rh-catalyzed hydroformylation of butadiene to adipaldehyde is a promising alternative route for producing valuable C_6 compounds such as adipic acid and hexamethylenediamine. Fundamental insights into reaction pathways, aimed at enhancing adipaldehyde yield, were obtained from temporal concentration profiles and *in situ* ReactIR studies of butadiene hydroformylation on Rh complexes at 80 °C and 14 bar syngas (molar $CO/H_2 = 1$) pressure in a batch reactor. Specifically, the effects of operating conditions and eight commercially available ligands on activity and selectivity were systematically investigated. It was found that the adipaldehyde selectivity is independent of the ligand/Rh ratio, rhodium concentration, butadiene concentration and syngas pressure, but significantly dependent on the type of ligand used. For example, while the DIOP ligand provided an adipaldehyde yield of ~40% with butadiene as a substrate, the 6-DPPon ligand gave a maximum adipaldehyde yield of ~93% with 4-pentenal as substrate. Furthermore, the adipaldehyde selectivity correlates well with the natural bite angle of the various ligands. ReactIR studies suggest that the preferential formation of the stable rhodium η^3-crotyl complex with the various Rh complexes may be the main reason for the low adipaldehyde selectivity.

1. Introduction

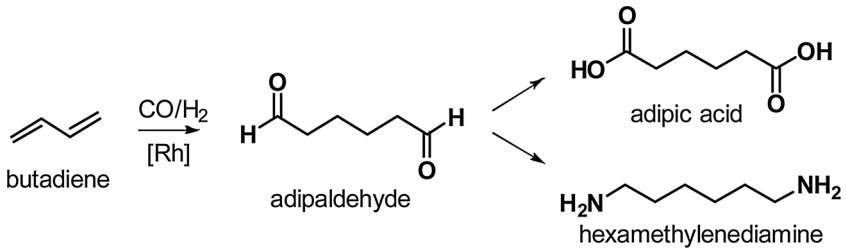
Adipaldehyde is an attractive precursor for synthesizing C_6 compounds such as adipic acid and hexamethylenediamine, important industrial monomers for the production of polyamides (e.g., Nylon-6,6), polyesters and polyurethanes [1,2]. The current commercial process for adipic acid manufacture is based on multistep oxidation of cyclohexane using nitric acid as the oxidant. The over oxidation of cyclohexane and release of large amounts of N_2O emissions are major environmental problems associated with the conventional technology [3]. Hexamethylenediamine is mainly produced by Ni-catalyzed hydrocyanation and subsequent hydrogenation, but it requires handling of relatively expensive and extremely toxic HCN gas. However, adipaldehyde as a starting material provides a promising alternative route for the production of adipic acid by oxidation and hexamethylenediamine by reductive amination (Scheme 1).

The selective hydroformylation of butadiene is an atom economical process for producing adipaldehyde [4–15]. With increased availability of inexpensive natural gas liquids, the use of butadiene as the feedstock is receiving renewed interest. Among homogeneous catalysts [16–19], transition-metal-complexes are the most reported for butadiene hydroformylation to adipaldehyde. The use of either Co/monophosphine [10] or Rh/monophosphine catalysts [6,9] requires severe reaction conditions (120 − 175 °C, 200 − 300 bar), resulting in complex aldehyde products with low C_6-dialdehyde selectivity (< 20%). Rhodium/diphosphine catalysts provide better selectivities and activities under mild conditions (p < 20 bar, T < 100 °C) [4,7,8,11]. Ohgomori et al. [4] reported 37% adipaldehyde selectivity with a catalyst composed of Rh and the commercially available DIOP ligand. Smith et al. [5] reported a higher adipaldehyde selectivity of 50% with congeners of the bisphosphine triptyphos as ligands. By using the concept of isomerizing hydroformylation, Mormul et al. achieved 73% selectivity toward adipaldehyde bis-acetal derivative [20]. However, the adipaldehyde yield (50 %) is still low for practical viability.

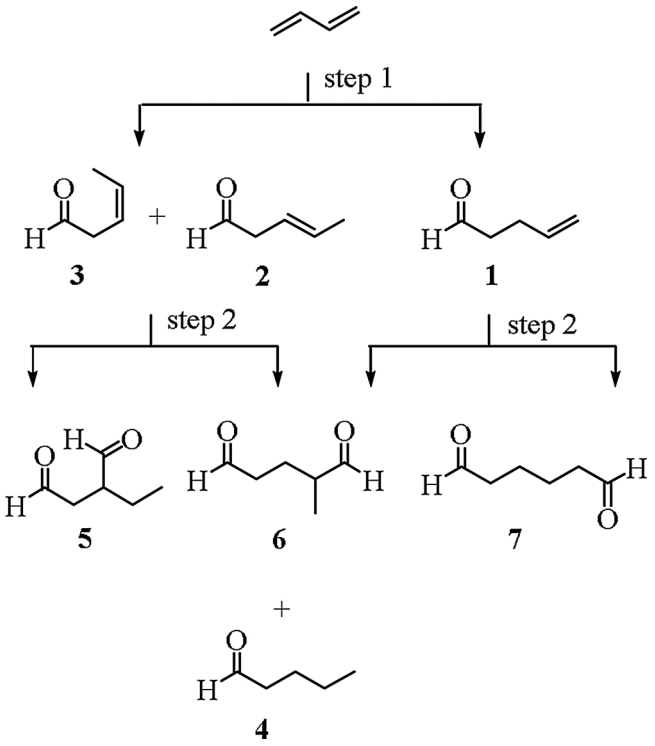
Compared to terminal mono-alkene, conjugated dienes as substrates are very resistant to hydroformylation and show atypical reaction behavior resulting in much slower reaction rates and lower regioselectivity [21]. Even though the hydroformylation of several conjugated dienes (such as butadiene [22], isoprene [23], 1,3-pentadiene [24] and myrcene [25,26]) has been reported, systematic investigations of the correlation between phosphine structure and catalytic performance are rare. Previous literature on the subject of butadiene hydroformylation

* Corresponding author at: Center for Environmentally Beneficial Catalysis, The University of Kansas, Lawrence, KS, 66047, United States.
E-mail address: bsubramaniam@ku.edu (B. Subramaniam).

https://doi.org/10.1016/j.mcat.2019.110721
Received 15 October 2019; Received in revised form 13 November 2019; Accepted 15 November 2019



Scheme 1. Butadiene as building block for commodity chemicals.



Scheme 2. Overall reaction stoichiometry for formation of adipaldehyde and other byproducts from butadiene hydroformylation.

typically reports product selectivity at the end of fixed-time batch runs lasting several hours. Given that butadiene conversion to adipaldehyde requires two sequential hydroformylation steps with various competing reactions (Scheme 2), temporal product evolution profiles are needed to better discern the relative contributions of the two steps toward adipaldehyde yield. In this work, we measured product evolution profiles by periodic sampling to monitor the reaction progress. This allowed us to systematically investigate the effects of reaction parameters and ligands on the two hydroformylation steps. We found that for butadiene hydroformylation with a given ligand, the adipaldehyde selectivity was independent of the ligand/Rh ratio, Rh concentration, substrate concentration and syngas pressure. Rh/DIOP catalyst provided the best 4-pentenal selectivity (48%) at short reaction times (i.e., low butadiene conversion), and 40% adipaldehyde selectivity at the end of a run. In contrast, for 4-pentenal hydroformylation, the 6-DPPon ligand performed much better than the DIOP ligand, providing nearly 93% adipaldehyde selectivity. These insights provide new leads for catalyst selection and process optimization aimed at maximizing adipaldehyde selectivity.

2. Experimental

2.1. Materials

$(CO)_2Rh(acac)$ and phosphine ligands L1-L8 were purchased from commercial suppliers and stored in an argon atmosphere in a glovebox before usage. Butadiene (chemically pure) and syngas (99.99% purity, molar H_2/CO ratio of 1:1) were supplied by Matheson in cylinders. The toluene solvent (anhydrous, 99.8%) was purchased from Alfa Aesar and stored under an atmosphere of argon.

2.2. General procedure for hydroformylation experiments

The butadiene hydroformylation experiments were carried out in a 50 mL Parr reactor equipped with a six-port valve for periodic sampling of reactor contents (see Fig. S1 for a schematic of the unit). $(CO)_2Rh(acac)$ (10 mg, 0.039 mmol) and ligand (0.116 mmol) were dissolved in 13 mL toluene, and 0.1 mL decane was added as an internal standard. After purging the mixture with Ar (high purity) thrice, the reactor was heated to 80 °C, and then 0.5 mL pure butadiene (metered with an ISCO pump at −6 °C/~12 bar) was charged into the reactor followed by 2 mL of toluene from a HPLC pump. Once the reactor temperature stabilized at a predetermined value, syngas (molar $CO/H_2 = 1$) was charged into the reactor from an external reservoir to the desired reactor pressure. Following this step, the stirrer was promptly started and set at 1000 rpm to initiate the hydroformylation reaction. Samples from the liquid phase were collected by a six-port valve equipped with a 50 μL sample loop which was flushed thrice with N_2. The first sample that typically showed the maximum 4-pentenal selectivity was collected immediately (< 1 min) after syngas was charged into the reactor and the stirring was commenced. The concentrations of the various reactants and products in the reaction mixture were analyzed by GC/FID analysis. The continuous decrease in the external reservoir pressure following reaction initiation is due to syngas consumption and was monitored on a LabVIEW® data acquisition and control system. The overall carbon balance was estimated based on end-of-run analysis of the hydroformylation products in the liquid phase. To get an accurate estimate of butadiene remaining in the reactor following a batch run, the reactor was sufficiently cooled (to −20 °C) to totally condense the butadiene prior to sampling the liquid phase.

The chemoselectivity is defined as moles of aldehydes formed relative to moles of total products formed.

$$\text{Chemoselectivity}\,(\%) = \frac{\text{n(aldehydes formed)}}{\text{n(total products)}} \times 100 \quad (1)$$

The regioselectivity (n/i) is defined as the molar ratio of linear dialdehyde (adipaldehyde) to branched dialdehydes (2-methylpentanedial) in the products.

$$\text{Regioselectivity}(n/i) = \frac{\text{n(adipaldehyde)}}{\text{n(2-methylpentanedial)}} \quad (2)$$

Turnover frequency is estimated from the slope of the linear portion of the products' concentration vs time plots (Fig. S3) as follows.

$$\text{TOF}\,(h^{-1}) = \frac{\text{n(total products)}}{\text{n(Rh)} \times \text{time}} \quad (3)$$

The carbon balance for the hydroformylation of either butadiene or pent-4-enal is estimated as follows

$$\text{Carbon balance} = \frac{\text{nC(aldehydes + butadiene or 4-pentenal)}_{\text{product}}}{\text{nC(CO)} + [\text{nC(butadiene or 4-pentenal)}]_{\text{feed}}} \quad (4)$$

$$\text{nC(CO)} = [\text{n(syngas consumption from reservoir)-n(hydrogenation products)}] \times 0.5 \quad (5)$$

Clearly, the C balance will be 100% for total chemoselectivity to aldehydes. Any deviation is attributed to the formation of hydrogenation products. Details of carbon balance estimation for three temporal runs are shown in Tables S1-S3.

2.3. GC method

Gas chromatographic analysis was performed using an Agilent Technologies 7890A GC system equipped with a 30 m × 320 μm × 0.25 μm HP-5 column. The He flow rate was kept at 0.8 std mL/min. The column temperature was initially held at 35 °C for 8 min, then ramped at 20 °C /min to 90 °C and held for 3 min. This was followed by another ramp of 30 °C /min to 200 °C, where the temperature was held for 5 min. Details of calibration for quantifying the product species may be found in the Supplementary Materials (Table S4).

2.4. In situ ReactIR experiments

Reactions for *in situ* infrared spectroscopic analysis were performed in Mettler Toledo ReactIR 15. The reactor schematic is essentially similar to the one shown in Fig. S1 with the stirred reactor unit being replaced by another unit fitted with a ReactIR probe. Approximately, 77 mg (0.29 mmol) $(CO)_2Rh(acac)$ was dissolved in 13 mL toluene in an autoclave reactor. The solution was heated to 80 °C at a stirrer speed of 1000 rpm. Once the temperature reached 80 °C, the reactor was pressurized with 7 bar syngas and the measurement was started with 2 scans at 1 min intervals. After allowing 1 h for formation of the catalyst precursor, 0.5 mL butadiene and 2 mL toluene were introduced into the reactor by a HPLC pump. Syngas consumption from an external reservoir was monitored on a LabVIEW® data acquisition and control system.

3. Results and discussion

3.1. Temporal product evolution profiles

Fig. 1 shows the temporal syngas consumption and product selectivity profiles during butadiene hydroformylation using Rh/DIOP complex as a catalyst. As shown in Scheme 2, the first hydroformylation step rapidly produces 4-pentenal (**1**) and trans/cis-3-pentenal (**2** + **3**). The maximum 4-pentenal selectivity being approximately 48%. During the first 100 min, the 4-pentenal selectivity decays steadily and is completely consumed. The adipaldehyde (**7**) selectivity rises during this period reaching approximately 40% and remains fairly constant for the remaining duration of the batch run. Beyond 100 min, the 3-pentenal was further hydroformylated to 2-ethylbutanedial (**5**) and 2-methylpentanedial (**6**), resulting in a lower *n*/*i* ratio. Simultaneously, the 3-pentenal was isomerized to conjugated 2-pentenal, which is rapidly transformed into pentanal (**4**) by hydrogenation. At longer reaction times, pentanal and 2-methylpentanedial were the main products. Butadiene conversion to adipaldehyde requires the following two steps to occur preferentially: (i) butadiene (conjugated alkene) hydroformylation to monoaldehyde 4-pentenal via 1,2-addition; and (ii) 4-pentenal (terminal alkene) hydroformylation to adipaldehyde. In order to improve the overall selectivity of the desired adipaldehdye, we sought to systematically investigate the effects of reaction operating conditions and ligand on each of the sequential hydroformylation steps (i) and (ii).

3.2. Reaction parameter effects

The effects of the ligand/Rh ratio, rhodium concentration, butadiene concentration and syngas pressure are summarized in Table 1. Details of the syngas consumption profiles and temporal selectivity profiles corresponding to the various operating conditions are presented in the Supplementary Materials (Fig. S4 and Fig. S5). DIOP/Rh ratios were varied from 1–3 (entries 1–3, Table 1). At a molar [DIOP/Rh] = 1, the butadiene hydroformylation rate was lower compared to higher ratios (1.5–3). Temporal concentration profiles reveal that 3-pentenal (**2** + **3**) was apparently transformed to pentanal (**4**) and 2-methylpentanedial (**6**) beyond 80 min (Fig. S5). This could be due to degradation of the phosphine ligand [21,27], resulting in the formation of different phosphines with lower selectivity toward adipaldehyde. In the presence of excess DIOP ligand (entries 2 and 3, Table 1), both the hydrogenation and hydroformylation reactions involving 3-pentenal were suppressed, resulting in an increased adipaldehyde selectivity of 40%, which is consistent with literature values [4]. Increasing the $(CO)_2Rh(acac)$ concentration from 0.024 to 0.08 mmol (entries 5 and 4, Table 1) enhances the rate (See also Fig. S4). At higher $(CO)_2Rh(acac)$ concentration (entry 4, Table 1), the maximum 4-pentenal selectivity was slightly increased to 48%. The higher $(CO)_2Rh(acac)$ concentration also increases pentanal (**4**) and 2-methylpentanedial (**6**) formation, but the adipaldehyde selectivity (37 %) remains relatively constant. Similarly, the adipaldehyde selectivity was unaffected with increase in either the butadiene concentration from 1.1 to 11.4 mmol (entries 6 and 7, Table 1) or the syngas pressure from 7 to 24 bar (entries 8 and 9, Table 1). It is noteworthy however that, at lower butadiene concentration and syngas pressure (entries 7 and 9), the initial 4-pentenal selectivity was more than 60 %. However, end-of-run analysis showed that 3-pentenal was the main product in all cases and the overall adipaldehyde selectivity was ~40 %. The higher 4-pentenal selectivities (62–65 %) are caused by the formation of stable rhodium η^3-crotyl complex which does not favor 3-pentenal formation at low butadiene conversion. Importantly, the adipaldehyde selectivity is more or less independent of the ligand/Rh ratio, Rh concentration, butadiene concentration and syngas pressure.

3.3. Ligand effects

A series of commercially available bidentate phosphine and phosphite ligands L1-L8 (Fig. 2) were tested for butadiene hydroformylation. The reaction was carried out at 80 °C and 14 bar syngas with molar $[CO/H_2]$ ratio of 1 using 0.04 mmol $(CO)_2Rh(acac)$ with molar [P/Rh] ratio of 6. The product selectivities and TOF are summarized in Table 2. The syngas consumption profiles and temporal selectivity profiles obtained with the eight ligands are provided in the Supplementary Materials (Fig. S6 and Fig. S7). In general, monoaldehydes (4-pentenal and 3-pentenal) were the primary intermediate products. At the end of 260 min batch run, the 4-pentenal was totally consumed to form adipaldehyde.

The observed selectivities vary dramatically depending on the ligand used. The bis(diphenylphosphino) alkane ligands L1-L3, show progressively increasing 4-pentenal selectivity (from 14–39%) and adipaldehyde selectivity (from 1–30%). Ligands L3-L5 (Fig. 2), which are reported to be effective for butadiene hydroformylation [4,7], show high initial 4-pentenal selectivity (39–46 %) as well as high adipaldehyde selectivity (30–39%). For ligands L7 and L8, the maximum 4-pentenal selectivity decreased. At the end of the 260 min run, 3-pentenal was the major product with selectivity ranging from 73–82%. The adipaldehyde selectivities were correspondingly much lower (7 % and 16 %). Ligand L6, which can display typical bidentate ligand behavior by self-assembly through hydrogen bonding [28], showed moderate

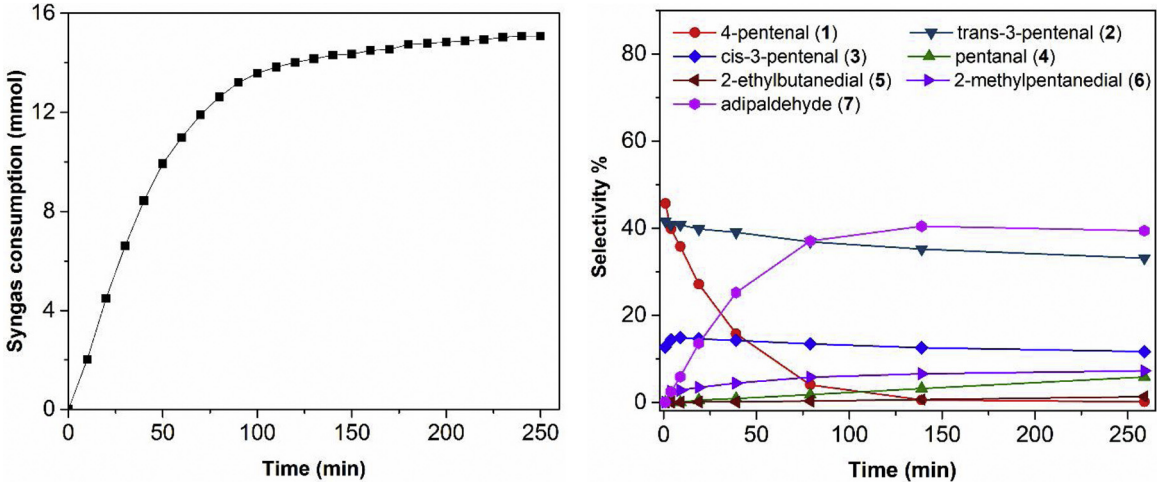


Fig. 1. Typical temporal profiles of syngas consumption and selectivity during butadiene hydroformylation with Rh/DIOP complex at 80 °C. Reaction conditions: 5.7 mmol butadiene, 0.04 mmol $(CO)_2Rh(acac)$, molar [DIOP/Rh] ratio = 3, syngas pressure =14 bar; molar [H_2/CO] ratio = 1, 15 mL toluene, 1000 rpm.

Table 1
Hydroformylation of butadiene catalyzed by $(CO)_2Rh(acac)$ with DIOP. Reaction conditions: 0.04 mmol $(CO)_2Rh(acac)$, molar [H_2/CO] ratio = 1, 15 mL toluene, 80 °C, 260 min, 1000 rpm.

Entry	DIOP/Rh	Butadiene, mmol	P, bar	Maximum 4-pentenal selectivity, %	End-of-run selectivities, %				TOF[c] h^{-1}
					2 + 3	**4**	**6**	**7**	
1	1.0	5.7	14	47	19	24	14	31	87
2	1.5	5.7	14	47	43	8	8	39	122
3	3.0	5.7	14	46	45	6	7	39	121
4[a]	1.5	5.7	14	48	33	13	10	37	115
5[b]	5.0	5.7	14	44	50	4	6	38	121
6	3.0	11.4	14	48	45	6	7	40	176
7	3.0	1.1	14	65	42	7	7	37	29
8	3.0	5.7	24	45	47	4	7	39	123
9	3.0	5.7	7	62	43	8	7	38	52

[a] 0.08 mmol $(CO)_2Rh(acac)$.
[b] 0.024 mmol $(CO)_2Rh(acac)$.
[c] Estimated using Eq. (3)].

selectivity towards 4-pentenal (24 %) and adipaldehyde (22 %). The maximum 4-pentenal selectivity followed an identical order: DPPE < DPPP < DPPB < DIOP > 6-DPPon > Xantphos > Biphephos. DIOP (L5) provided the best selectivity toward 4-pentenal (46 %) and adipaldehyde (39 %) as well as the highest activity (TOF).

3.4. 4-pentenal hydroformylation

The foregoing results prompted us to investigate ligand effects on 4-pentenal hydroformylation as well. Ligands L1-L8 were tested at 80 °C and syngas (molar [H_2/CO] = 1) pressure of 14 bar using 0.02 mmol $(CO)_2Rh(acac)$ with molar [P/Rh] ratio of 6. The results are shown in Table 3. The major products were adipaldehyde (**7**) and branched 2-methylpentanedial (**6**) followed by 3-pentenal (**2** + **3**) and pentanal (**4**).

For ligands L1 and L2, the adipaldehyde selectivity ranged from 37–46 %, and branched 2-methylpentanedial (**6**) was the favored product. Ligands L3-L5 showed progressively higher selectivity (84–91 %) towards the linear dialdehyde with moderate increases in the reaction rate. In sharp contrast to butadiene hydroformylation, the L6-L8 ligands

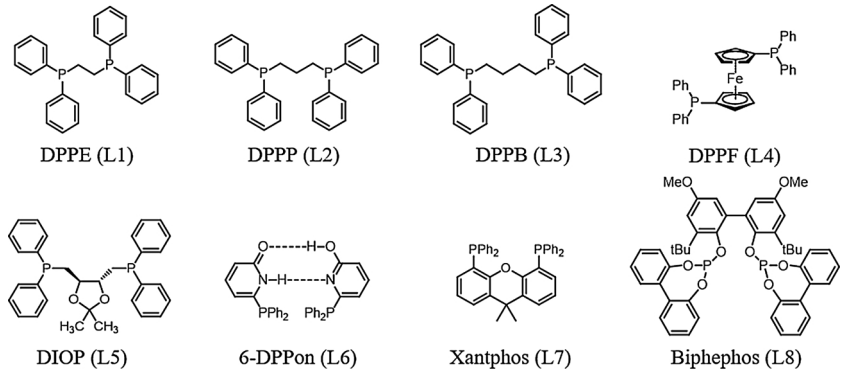


Fig. 2. Ligands tested in the hydroformylation of butadiene or 4-pentenal.

Table 2
Ligand effects for butadiene hydroformylation. Reaction conditions: 5.7 mmol butadiene, 0.04 mmol $(CO)_2Rh(acac)$, molar [P/Rh] = 6, syngas pressure =14 bar; molar [H_2/CO] ratio = 1, 15 mL toluene, 80 °C, 260 min, 1000 rpm.

Entry	Ligand	Natural bite angle, °	Maximum 4-pentenal selectivity, %	End-of-run selectivities, %						TOF[a] h^{-1}
				1	**2 + 3**	**4**	**6**	**7**	*n/i*	
L1	DPPE	85	14	0	10	81	4	1	0.3	59
L2	DPPP	91	19	3	70	10	7	4	0.6	44
L3	DPPB	98	39	0	49	6	9	30	3.3	93
L4	DPPF	96	42	0	48	9	9	31	3.4	96
L5	DIOP	98	46	0	42	6	7	39	5.6	116
L6	6-DPPon	–	24	0	43	25	6	22	3.7	34
L7	Xantphos	111	20	0	73	7	2	16	8.0	39
L8	Biphephos	120	11	6	82	5	0	7	–	10

[a] Estimated using Eq. (3).

Table 3
Ligand effects on 4-pentenal hydroformylation. Reaction conditions: 2 mmol 4-pentenal, 0.02 mmol $(CO)_2Rh(acac)$, molar [P/Rh] ratio = 6, syngas pressure = 14 bar; molar [H_2/CO] ratio = 1, 15 mL toluene, 80 °C, 80 min, 1000 rpm.

Entry	Ligand	Natural bite, °	End-of-run selectivity %					TOF[a] h^{-1}
			2 + 3	**4**	**6**	**7**	*n/i*	
L1	DPPE	85	3	0	45	37	0.8	68
L2	DPPP	91	0	0	53	46	0.9	20
L3	DPPB	98	0	0	16	84	5.3	105
L4	DPPF	96	0	0	12	88	7.3	78
L5	DIOP	98	0	0	9	91	10.1	198
L6	6-DPPon	–	0	0	7	93	13.3	435
L7	Xantphos	111	1	2	3	92	30.7	130
L8	Biphephos	120	3	8	1	87	87.0	4546

[a] Estimated using Eq. (3).

displayed much higher adipaldehyde selectivities (87–93 %) during 4-pentenal hydroformylation. The 6-DPPon ligand (L6) showed the best adipaldehyde selectivity (93 %) while the Biphephos ligand (L8) provided remarkably high reaction rate with a *n/i* ratio of 87. In sharp contrast, ligand L8 showed a rather low activity for butadiene hydroformylation (Table 2). The *n/i* ratio observed with various ligands for 4-pentenal hydroformylation ranked as follows: DPPE < DPPP < DPPB < DIOP < 6-DPPon < Xantphos < Biphephos.

The foregoing results reveal markedly different dependence on the various ligands tested, and suggest that the activity and selectivity towards the desired products result from the two sequential hydroformylation steps, viz., butadiene to 4-pentenal and 4-pentenal to adipaldehyde. As inferred from Table 3, the adipaldehyde selectivities correlate well with natural bite angle of the ligands. The DPPE (L1) and DPPP (L2) ligands with bite angles near 85° [29] showed the lowest selectivities towards the desired products for both the hydroformylation steps (Tables 2 and 3), thereby resulting in the lowest adipaldehyde selectivity. In contrast, for the first hydroformylation step, the DPPE ligand favors 3-pentenal [4,7] which is readily transformed to pentanal and the branched dialdehyde via hydrogenation and hydroformylation, respectively, in the second step (Tables 2 and 3). van Leeuwen et al. also reported high pentanal selectivity (90%) when using rhodium with DPPE ligand [7]. While the L6 and L8 ligands [28,30,31] with large bite angles ranging from 111-120° [32,33] are highly selective (87–93 %) towards the linear dialdehyde during 4-pentenal hydroformylation (Table 3), the maximum 4-pentenal selectivity when using butadiene as a feed is quite low (11–24 %). In comparison, the L3-L5 ligands with similar bite angle near 100° [29] provided higher 4-pentenal selectivity for the first step compared with other ligands (Table 2) but moderate adipaldehyde selectivity for the second step (Table 3). Thus, L3-L5 provide the best combination of selectivities towards the desired products from the two steps resulting in the highest overall selectivity towards adipaldehyde.

Ohgomori et al. also reported that diphosphine ligands with natural bite angle of 102-113° provided 37% adipaldehyde selectivity from butadiene hydroformylation [4]. Smith et al. reported increased adipaldehyde selectivity (50%) during butadiene hydroformylation with Rh complexes using chelating bisphosphate ligands [5]. To better characterize the structures of transient intermediate species, Ir analogs of the Rh complexes were investigated with bite angles of the ee and ea-coordinated isomers being 105.5° and 99.0°, respectively [38]. Based on our results and those reported in the literature, it follows that when employing Rh catalysts with a single ligand for butadiene hydroformylation, the natural bite angle should be close to 100° in order to maximize adipaldehyde selectivity. The fact that the 4-pentenal hydroformylation requires a different ligand to maximize adipaldehyde selectivity provides the motivation to develop a clear understanding of how the ligand structure affects the first hydroformylation step in selectively forming 4-pentenal.

3.5. ReactIR experiments

We employed *in-situ* ReactIR to investigate intermediate products formed during butadiene hydroformylation with DIOP/Rh catalysts (Fig. 3). The full IR spectra and the carbonyl region are shown in the Supplementary Materials (Fig. S8). The catalyst was prepared under 7 bar syngas from the precursors, 20 mmol/L $(CO)_2Rh(acac)$ and excess of DIOP (molar [DIOP/Rh] = 1.5) at 80 °C. The typical spectrum for the hydrido dicabonyl complex (I) was observed as shown in Fig. 3. The four carbonyl bands (at $\tilde{\nu}$ = 2041, 1995, 1976 and 1950 cm^{-1}) were assigned to the two trigonal bipyramidal isomers with DIOP ligand in an axial-equatorial position (ae) or in equatorial-equatorial position (ee) (Fig. 3a) [34,35]. After allowing 1 h for the catalyst precursors and syngas to react, butadiene was added, resulting in the immediate formation of new bands (1947 cm^{-1}) in the carbonyl region of the IR spectrum. This band is assigned to the η^3 crotyl complex (II) (Fig. 3b) [36]. Upon consumption of butadiene, the complex (I) was regenerated (Fig. 3c and 3d). The η^3-crotyl complex is a precursor to 3-pentenal formation, which is converted to either pentanal by hydrogenation or the branched dialdehyde by hydroformylation. The preferential formation of the stable rhodium η^3-crotyl complex thus appears to be the main reason for the relatively low adipaldehyde selectivity observed during butadiene hydroformylation. Stable rhodium η^3-crotyl complexes are also observed when using other ligands as shown in Figure S9. This explains why the adipaldehyde selectivity is more or less independent of the ligand/Rh ratio, Rh concentration, butadiene concentration and syngas pressure [37].

4. Conclusions

Temporal concentration profiles provide fresh insights into the effects of ligands and reaction parameters on adipaldehyde selectivity during butadiene hydroformylation on using Rh catalysts. The major

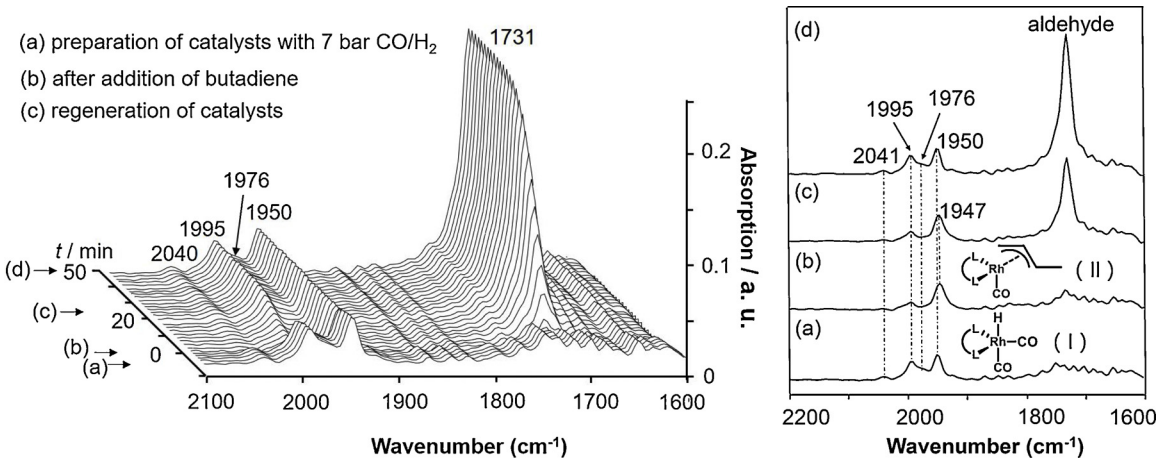


Fig. 3. *In-situ* IR spectra from butadiene hydroformylation with DIOP/Rh catalysts. $(CO)_2Rh(acac)$ and DIOP dissolved in toluene at 80 °C as background. (a) after adding 7 bar of CO/H_2 at 80 °C for 1 h; (b) immediately after adding butadiene; (c) after 26 min of hydroformylation; (d) after 50 min of hydroformylation.

determinant of adipaldehyde selectivity during the two-step butadiene hydroformylation appears to be the ligand structure. Of the eight biphosphine ligands tested, the DIOP ligand was preferred for the first hydroformylation step providing a maximum 4-pentenal selectivity of approximately 48 %, while the 6-DPPon ligand showed the best performance for the 4-pentenal hydroformylation step with adipaldehyde selectivity exceeding 93 %. The observed selectivity trends are consistent with previously reported correlations between ligand bite angles and product selectivity during Rh-catalyzed hydroformylation of olefins. Our finding that the two sequential butadiene hydroformylation steps require different ligands to maximize adipaldehyde selectivity suggests an opportunity to rationally design an optimum ligand that simultaneously maximizes the linear aldehyde selectivity during both steps.

CRediT authorship contribution statement

Si-min Yu: Methodology, Data curation, Writing - original draft, Visualization, Investigation. **William K. Snavely:** Methodology, Formal analysis, Writing - review & editing. **Raghunath V. Chaudhari:** Methodology, Supervision, Writing - review & editing. **Bala Subramaniam:** Conceptualization, Methodology, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors gratefully acknowledge support for this work by a grant from the joint National Science Foundation and Environmental Protection Agency program Networks for Sustainable Material Synthesis and Design program (NSF-EPA 1339661).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110721.

References

[1] H.-J. Arpe, K. Weissermel, Industrial-Organic Chemistry, Wiley-VCH, Weinheim, Germany, 2010.
[2] R. Franke, D. Selent, A. Börner, Chem. Rev. 112 (2012) 5675–5732.
[3] S. van de Vyver, Y. Roman-Leshkov, Catal. Sci. Technol. 3 (2013) 1465–1479.
[4] Y. Ohgomori, N. Suzuki, N. Sumitani, J. Mol. Catal. A Chem. 133 (1998) 289–291.
[5] S.E. Smith, T. Rosendahl, P. Hofmann, Organometallics 30 (2011) 3643–3651.
[6] H. Bahrmann, B. Fell, J. Mol. Catal. 8 (1980) 329–337.
[7] P.W.N.M. van Leeuwen, C.F. Roobeek, J. Mol. Catal. 31 (1985) 345–353.
[8] T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya, Tetrahedron 53 (1997) 7795–7804.
[9] B. Fell, W. Rupilius, Tetrahedron Lett. 10 (1969) 2721–2723.
[10] H. Adkins, J.L.R. Williams, J. Org. Chem. 17 (1952) 980–987.
[11] S. Bertozzi, N. Campigli, G. Vitulli, R. Lazzaroni, P. Salvadori, J. Organomet. Chem. 487 (1995) 41–45.
[12] B. Fell, H. Bahrmann, J. Mol. Catal. 2 (1977) 211–218.
[13] T. Maji, C.H. Mendis, W.H. Thompson, J.A. Tunge, J. Mol. Catal. A Chem. 424 (2016) 145–152.
[14] N. Herrmann, D. Vogelsang, A. Behr, T. Seidensticker, ChemCatChem 10 (2018) 5342–5365.
[15] M.J. Tenorio, R.V. Chaudhari, B. Subramaniam, Ind. Eng. Chem. Res. (2019), https://doi.org/10.1021/acs.iecr.9b05184.
[16] S. Rej, N. Chatani, Angew. Chem. Int. Ed. 58 (2019) 8304–8329.
[17] N. Chatani, Bull. Chem. Soc. Jpn. 91 (2018) 211–222.
[18] T. Ohkuma, N. Kurono, N. Arai, Bull. Chem. Soc. Jpn. 92 (2019) 475–504.
[19] X. Zhao, Y. Yang, R. Zhu, C. Liu, D. Zhang, Mol. Catal. 471 (2019) 77–84.
[20] J. Mormul, J. Breitenfeld, O. Trapp, R. Paciello, T. Schaub, P. Hofmann, ACS Catal. 6 (2016) 2802–2810.
[21] C. Claver, P.W.N.M. van Leeuwen, Rhodium Catalyzed Hydroformylation, Kluwer Academic Publishers, Dordrecht, 2000.
[22] S. Schmidt, E. Baráth, C. Larcher, T. Rosendahl, P. Hofmann, Organometallics 34 (2015) 841–847.
[23] H.J.V. Barros, C.C. Guimarães, E.N. dos Santos, E.V. Gusevskaya, Organometallics 26 (2007) 2211–2218.
[24] P. Neubert, S. Fuchs, A. Behr, Green Chem. 17 (2015) 4045–4052.
[25] C.M. Foca, H.J.V. Barros, E.N. dos Santos, E.V. Gusevskaya, J. Carles Bayon, New J. Chem. 27 (2003) 533–539.
[26] H.J.V. Barros, J.G. da Silva, C.C. Guimarães, E.N. dos Santos, E.V. Gusevskaya, Organometallics 27 (2008) 4523–4531.
[27] P.W.N.M. van Leeuwen, Appl. Catal. A Gen. 212 (2001) 61–81.
[28] B. Breit, W. Seiche, J. Am. Chem. Soc. 125 (2003) 6608–6609.
[29] P. Dierkes, P.W.N.M. van Leeuwen, J. Chem. Soc., Dalton Trans. (1999) 1519–1530.
[30] W. Seiche, A. Schuschkowski, B. Breit, Adv. Synth. Catal. 347 (2005) 1488–1494.
[31] J. Mormul, M. Mulzer, T. Rosendahl, F. Rominger, M. Limbach, P. Hofmann, Organometallics 34 (2015) 4102–4108.
[32] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, Organometallics 14 (1995) 3081–3089.
[33] C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney, D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535–5543.
[34] L.A. van der Veen, M.D.K. Boele, F.R. Bregman, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, J. Am. Chem. Soc. 120 (1998) 11616–11626.
[35] S. Schmidt, G. Abkai, T. Rosendahl, F. Rominger, P. Hofmann, Organometallics 32 (2013) 1044–1052.
[36] S. Schmidt, E. Barath, T. Prommnitz, T. Rosendahl, F. Rominger, P. Hofmann, Organometallics 33 (2014) 6018–6022.
[37] S. Schmidt, P. Deglmann, P. Hofmann, ACS Catal. 4 (2014) 3593–3604.
[38] G. Abkai, S. Schmidt, T. Rosendahl, F. Rominger, P. Hofmann, Organometallics 33 (2014) 3212–3214.