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Supported Aqueous-Phase, Rhodium Hydroformylation Catalysts

II. Hydroformylation of Linear, Terminal and Internal Olefins

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Hydroformylation of 1-, 2-, and 3-heptene by supported aqueous-phase (SAP) catalysts shows that the conversion to aldehydes and the regioselectivity are functions of the position of the double bond. 1-Tetradecene and 1-heptadecene give results similar to 1-heptene while data obtained from *t*-7-tetradecene compare well to those observed from *t*-2-heptene indicating the independence of chain length. Linear dienes are shown to be hydroformylated as well. Effects of temperature and pressure and water content are illustrated using linear, terminal, and internal olefins.

INTRODUCTION

An important use of the hydroformylation reaction is in the production of linear aldehydes (alcohols) from internal olefins (*1*). Usually, cobalt is the catalyst of choice for this reaction because its low cost makes the inevitable loss of catalyst economically feasible and also, and perhaps more importantly, because it has a high activity for isomerization. Since terminal olefins are more readily hydroformylated than internal olefins the isomerization activity results in the migration of the double bond to the end of the chain where it is hydroformylated. In this manner good normal/branched ratios (*n*/*b*) are achieved even with internal olefins as the reaction feed. In addition to cobalt (*2*) other metals, including Pt/Sn, Rh, and Re (*3–5*) have been studied for the hydroformylation of internal olefins. The best results have been achieved with phosphine-modified Co catalysts (*6*). Cobalt catalysts are also used for the hydroformylation of terminal dienes such as 1,9-decadiene (the linear monohydroformylated product is used in the perfume industry as a fragrance modifier (*7*)).

Recently, we reported that supported aqueous-phase (SAP) catalysis can be used for the liquid-phase hydroformylation of olefins (*8, 9*). SAP catalysis uses a supported, water soluble, organometallic complex to promote interfacial reactions of substrates soluble in organic solvents.

The objective of this work is to study the influence of processing variables, e.g., temperature and pressure, on the hydroformylation reaction with SAP catalysts as well as to systematically study the hydroformylation of linear, terminal and internal olefins.

EXPERIMENTAL

Materials. $HRh(CO)(TPPTS)_3$ was prepared as previously described (*9*). The SAP catalysts were prepared as before with exception of the hydration procedure which was modified and is as described in our accompanying paper (*10*). The impregnation procedure, except in those cases where it is specifically noted, was the same as before (*8, 9*). The SAP catalysts, except where noted, contained 0.0208 mmol Rh/g SAP catalyst. The P/Rh ratio, except where

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TABLE 1

Hydroformylation of Heptenes (100°C, 1000 psig H_2/CO (1/1), Reactor A)

Alkene	Conversion (%)		n/b	b_i/b_{i+1}
	Total	Aldehydes		
1-Heptene	13.3	13.3	2.83	2.83
c-2-Heptene	11.6	5.4	0.057	2.01
t-2-Heptene	3.1	1.9	0.010	1.44
c-3-Heptene	7.0	4.0	0.0018	1.10
t-3-Heptene	6.3	5.3	0	1.04

noted, was 9.0. Dry olefins and solvent were purchased in the highest purity available and handled under Ar or N_2.

Low P/Rh ratio SAP catalyst impregnation procedure. Method B, as described in our accompanying paper (*10*), was used to prepare SAP catalysts with P/Rh ratios of 0, 2, and 3, catalysts SAPC0, SAPC2 and SAPC3, respectively.

Reaction conditions. The hydroformylation reactors used were standard batch stainless-steel stirred vessels heated either by thermostatic oil bath or by a thermostatic furnace. A small reactor denoted A had a usable volume of 0.5 ml and a larger reactor denoted B had a usable volume of 15 ml. The details of these procedures are described in the accompanying paper (*10*).

RESULTS

Hydroformylation of internal olefins. Due to the availability of all the possible isomers, heptenes were chosen as the model olefins for the study of the influence of the position of the double bond on the activity and selectivity of the hydroformylation reaction with SAP catalysts. The hydroformylation reactions were all conducted at 100°C and 1000 psig of H_2/CO (1/1) for a fixed time of 5 h in reactor A. Amounts of 20 mg of the dried SAP catalyst (2.9 wt% H_2O), 0.1 ml of the olefin, and 0.4 ml of cyclohexane were loaded into the reactor. Each reaction was performed twice to assure reproducibility; the results for conversion, n/b, and b_i/b_{i+1} are presented in Table 1 (n = linear aldehyde, b = summation of all branched aldehydes, b_i/b_{i+1} represents either 2-methyl heptanal/2-ethyl hexanal or 2-ethyl hexanal/2-propyl pentanal depending on whether 2-heptene or 3-heptene, respectively, is hydroformylated).

Hydroformylation of other alkenes. 1-Tetradecene, 1-heptadecene, and *t*-7-tetradecene were also hydroformylated using the same procedure as the one used for the heptenes above so that the results can be compared to those from the heptenes. The conversions of the two higher molecular weight terminal olefins are, within experimental error, the same as 1-heptene while the conversion to aldehydes for *t*-7-tetradecene equals the conversion to aldehydes for *t*-2-heptene (see Table 1). The n/b ratios obtained with the terminal olefins are the same and the n/b ratio for *t*-7-tetradecene is zero. 1,5-Hexadiene, 1,7-octadiene, and 1,9-decadiene were hydroformylated under the same conditions as outlined above for the heptenes; the results are shown in Table 2. Figure 1 shows the conversion and selectivity to monoaldehydes as a function of time for the hydroformylation of 1,9-decadiene (performed in reactor B).

Influence of temperature and pressure. The influence of temperature and pressure on the rate and selectivity for the hydroformylation of 1-heptene is presented in Figs. 2 and 3. In each reaction, 0.5 g of the dried SAP catalyst (2.9 wt% H_2O), 0.4 ml 1-heptene, and 11 ml cyclohexane were loaded into reactor B. Two temperatures, 100 and 75°C were studied, and at each tem-

TABLE 2

Hydroformylation of Dienes (100°C, 1000 psig H_2/CO (1 : 1), Reactor A)

	1,5-Hexadiene	1,7-Octadiene	1,9-Decadiene
Conversion (%)	18	15	17
Aldehydes (%)	18	14	14
Monoaldehydes (%)	86	88	87
n/b, Monoaldehydes	2.6	2.5	2.8

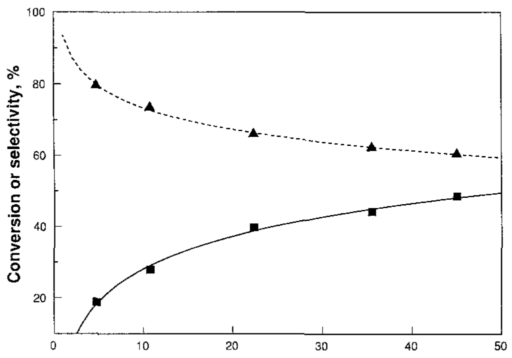

FIG. 1. Hydroformylation of 1,9-decadiene. T = 110°C, P = 1000 psig, rpm = 400, reactor B. ---▲--- selectivity to monoaldehydes; —■— conversion to aldehydes.

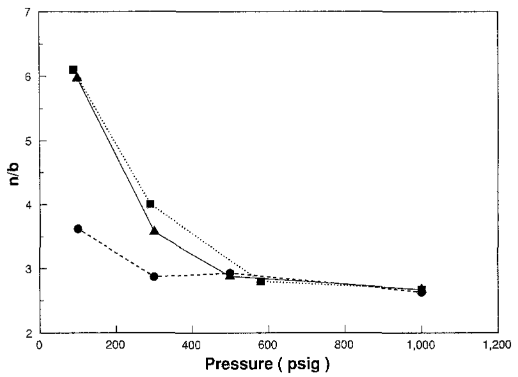

FIG. 3. Hydroformylation of 1-heptene using the dried SAP catalyst. Influence of T and P on selectivity; reactor B —▲— 100°C; ---●--- 75°C; ···■··· from Ref. (*11*), substrate: 1-octene, solvent: toluene, catalyst: Rh-triphenylphosphite, T = 90°C.

perature, runs at 1000, 500, 300, and 100 psig of H_2/CO (1/1) were performed. In Fig. 2 the runs at the three higher pressures, 1000, 500, and 300 psig are grouped together in one dashed line for each temperature since there is very little difference observed between 300 and 1000 psig. The results from the reaction at 100 psig are denoted with the solid line. Figure 3 shows the *n*/*b* ratios for the runs in Fig. 2. Also shown in Fig. 3 (dotted line) are the values obtained from Ref. (*11*) for the homogeneous hydroformylation of 1-octene in toluene using a Rh–triphenylphosphite as catalyst (the *n*/*b* ratio at 1000 psig has been interpolated from the values given in the reference). Table 3 shows the dependence of *n*/*b* ratios, selectivity toward aldehydes, and initial (t = 0) turnover frequencies (TOF) for the hydroformylation reactions of 1-heptene and *c*-2-heptene with respect to variations in reaction temperature. Figure 4 shows the results from a series of reactions run in reactor A under the same reaction conditions as those used in Table 1 with *c*-2-heptene in order to illustrate the effects of activity and selectivity as a function of temperature with an internal olefin.

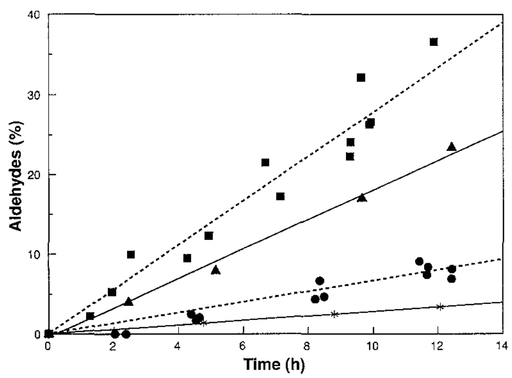

FIG. 2. Hydroformylation of 1-heptene using SAP catalysis, influence of temperature and pressure. Reactor B ---■--- T = 100°, P = 1000, 500 and 300 psig; —▲— T = 100°C, P = 100 psig; --●-- T = 75°, P = 1000, 500 and 300 psig; —✱— T = 75°C, P = 100 psig.

Influence of P/Rh ratio. Table 4 shows the influence of the P/Rh ratio on the activity and selectivity of SAP catalysis using 1-heptene or *c*-2-heptene as substrates at 1000 psig H_2/CO (1/1) and 100°C (reactor A).

Influence of hydration. Table 5 illustrates the results of hydrating the SAP Catalyst. As before, the TOFs are at t = 0.

DISCUSSION

Hydroformylation of internal olefins. From data shown in Table 1 it is clear that the activity of SAP catalysts for the hydroformylation of internal olefins is of approxi-

TABLE 3

Hydroformylation of Linear Olefins Using the Dried SAP Catalyst (2.9 wt% Water; 100 psig H_2/CO (1/1), Reactor B)

T (°C)	1-Heptene			c-2-Heptene		
	Aldehyde			Aldehyde		
	n/b	Selectivity (%) (conversion)	TOF (s^{-1})	n/b	Selectivity (%) (conversion)	TOF (s^{-1})
75	3.6	100 (3.4)	2.2E-04	—	—	—
100	6.7	80 (29)	1.2E-03	—	—	—
120	12.9	64 (58)	1.6E-03	2.6	19.0 (4.5)	5.3E-05
140	—	—	—	2.6	5.6 (19)	5.0E-05

mately the same order of magnitude as for the hydroformylation of terminal olefins. However, the rate of isomerization for the internal olefins is higher than for 1-heptene. Also, the degree of isomerization is greater for 2-heptene than for the 3-heptene, which is reasonable since the most stable isomer of heptene is t-3-heptene. Correspondingly t-3-heptene shows the least amount of isomerization of all the heptenes. Also noticeable is the higher reactivity of the *cis*-isomers than the *trans*-isomers toward isomerization. In general the *trans*-isomer is more stable than the corresponding *cis*-isomer. Also, the *cis*-isomer is more easily coordinated to the metal than the *trans*-isomer (*12*). Although SAP catalysts are effective for the hydroformylation of internal olefins it can be seen from the data in Table 1 that if the linear aldehyde is the desired product, the hydroformylation of internal olefins using SAP catalysts does not efficiently yield the desired end product at these conditions. Table 1 shows that the n/b ratio significantly declines if the double bond is not in the terminal position. Also, the data in Table 1 show that for *cis*-isomers, the formyl group is placed closer to the end of the chain in proportions larger than those for the *trans*-isomers, i.e., b_i/b_{i+1} for *cis* > *trans*.

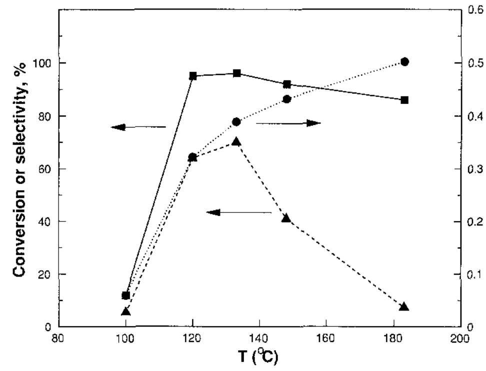

FIG. 4. Hydroformylation of c-2-heptene using the dried SAP catalyst, influence of temperature. Reactor A; P = 1000 psig, time = 5 h. —■— total conversion; --▲-- conversion to aldehydes; ··●·· n/b.

Hydroformylation of other alkenes. The results for the hydroformylation of longer molecular weight terminal alkenes and dienes show that the n/b ratio does not depend to a significant degree on the length of the chain. From Fig. 1 it can also be seen that the hydroformylation of the dienes essentially takes place sequentially.

Influence of temperature and pressure. At a constant temperature, the rate of reaction increases with pressure (Fig. 2). However, larger changes in reaction rate are observed

TABLE 4

Variations in the P/Rh Ratio with the Dried SAPC (2.9 wt% Water; 1000 psig H_2/CO (1/1), 100°C, Reactor A)

Catalyst: Substrate(s):	SAPC9		SAPC3[a]		SAPC2[a]		SAPC0[a] *c*-2-Hept	SAPC90 1-Hept
	1-Hept	*c*-2-Hept	1-Hept	*c*-2-Hept	1-Hept	*c*-2-Hept		
P/Rh:	9		3		2		0	90
% Conversion	21	12	82	99	93	97	99	22
% Aldehydes	21	5.5	42	94	50	73	90	22
n/*b*	2.8	0.06	2.5	0.20	2.4	0.25	0.24	2.9
mg Catalyst	20	20	2	20	2	2	20	40
Time (h)	5	5	5	5	5	5	5	25

[a] Extensive Rh leaching detected.

in the pressure range between 100 and 300 psig. Above this range the rate is only a weak function of total pressure. The scattering of the data from different runs in Fig. 2 may be due to small amounts of water which may have been adventitiously adsorbed. Catalytic activity is strongly dependent on total water content.

The *n*/*b* values do not change significantly in the range of conversions spanned. Thus, average *n*/*b* ratios are given in Fig. 3. The comparison in Fig. 3 of the results obtained with SAP catalysis (100°C) with the results from homogeneous catalysis (90°C) (*11*) shows that similar selectivities are obtained.

Table 3 illustrates that very high *n*/*b* ratios can be obtained using SAP catalysis at high temperatures and 100 psig. The data in Table 3 also show the increase in the activity of the catalyst toward hydroformylation with increasing temperature. However, the trade off in the selectivity toward aldehydes is also noticeable: isomerization becomes increasingly important at high temperatures and low pressures. This may explain the consistency in the aldehyde TOF at temperatures greater than 100°C. An Arrhenius plot can be drawn from the TOFs for 1-heptene listed in Table 3; however, the plot of ln(TOF) vs $1/T$ is not linear in the temperature range spanned. The reasons could be twofold: (A) a limitation in the mass transfer rate and also (B) the competing isomerization reaction. A mass transfer limitation is unlikely since a 100-fold increase in the activity of the catalyst is observed upon hydration at exactly the same reaction conditions. An estimate of 18 kcal/mol for the activation energy can be obtained from the hydroformylation data taken at the lower temperatures. This is similar to the values shown for homogeneous catalysts (*13*).

TABLE 5

Hydroformylation of Linear, Terminal Olefins (100 psig H_2/CO (1 : 1), P/Rh = 9, Reactor B)

T (°C)	TOF (s^{-1})	*n*/*b*	Catalyst	Substrate
70	0.06	3.9	Hydrated SAPC[a]	1-Tetradecene (neat)
85	0.1	4.7		
100	0.2	5.9		
75	0.00022	3.6	Dried SAPC[b]	1-Heptene (3.5% v/v in cyclohexane)
100	0.0012	6.7		

[a] 62 mg CPG-240 (19 wt% water), 15 ml olefin, 0.5 g dried SAPC (2.9 wt% water).

[b] 2.9 wt% water.

Two important features are apparent at low pressures and high temperatures: (i) the increase of *n*/*b* ratio and (ii) the increase in the isomerization activity. The realization that these two features are desired in the preparation of linear aldehydes from internal olefins leads to the experiments shown in Fig. 4. Thus, at 120 to 140°C and at 100 psig the hydroformylation of *cis*-2-heptene yields *n*/*b* ratios of ca. 2.6. However, also clear in this figure are the very low initial reaction rates. This is understandable since the majority of the substrate must have been isomerized to 1-heptene to give *n*/*b* ratios in the range of 2.6. In contrast, at higher pressures (see Table 1 for *c*-2-heptene), the internal double bond was hydroformylated with very little isomerization to 1-heptene.

The optimum catalyst should show high rates for isomerization and low rates for the hydroformylation of internal olefins compared to terminal olefins. This is difficult to achieve with the SAP catalysts. The generation of a more active catalyst, by hydrating the SAPC catalyst, is possible but yields a less stable catalyst (*10*). At 100 psig and 100°C the hydrated SAP catalyst (62 mg CPG-240 (19 wt% H_2O), 12 ml cyclohexane, 0.5 ml *c*-2-heptene, and 0.50 g dried SAP catalyst (2.9 wt% H_2O)) gives the following results: TOF = 0.0018 s^{-1} and *n*/*b* = 1.7 for the hydroformylation of *c*-2-heptene. This catalyst is more than 40 times more active than the dried SAP catalyst (2.9% H_2O). However, as noted above, the hydrated catalyst is darker after reaction indicating some degradation.

Influence of excess ligand. As noted in the previous paper (*10*) an excess of phosphine is necessary for the stability of SAP catalysts. However, when the P/Rh ratio is 9 or greater the *n*/*b* ratios do not parallel the values for homogeneous catalysts. Using $HRh(CO)(PPh_3)_3$ as catalyst for the homogeneous hydroformylation of 1-pentene at 100 psig H_2/CO 1/1 and 80°C the *n*/*b* ratios are 3.0 and 7.6 for P/Rh = 5 and 50, respectively (*4*). However, an experiment run at 75°C and 100 psig using the hydrated SAP catalyst (same conditions as previously described) with P/Rh = 90 (0.0021 mmol Rh/g SAP catalyst) yields *n*/*b* = 3.45. This value is similar to the value obtained at the same *T* and *P* using dried or hydrated SAP catalyst with P/Rh = 9. The data in Table 5 illustrate that the *n*/*b* values for the dried SAP catalysts are approximately the same as the ones for hydrated SAP catalysts. However, the TOFs differ by more than two orders of magnitude. These data reveal that SAP catalysts do not respond in the same way as homogeneous catalysts with $HRh(CO)(PPh_3)_3$ to an increase in the P/Rh ratio.

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