Kinetics of the Hydroformylation of Soybean Oil by Ligand-Modified Homogeneous Rhodium Catalysis

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ABSTRACT: The kinetics and mechanism of the hydroformylation of soybean oil by homogeneous ligand-modified rhodium catalysts were investigated at 70–130°C and 4000–11,000 kPa. The effects of reaction rates on systematic variations in reaction parameters were evaluated in order to develop an industrial process to convert vegetable oils to polyaldehydes. The activation energies in the presence of triphenylphosphine (Ph_3P) (61.1 ± 0.8 kJ/mol) (mean ± SD) and triphenyl phosphite [$(PhO)_3P$] (77.4 ± 5.0 kJ/mol) were determined. The catalyst was deactivated at temperatures higher than 100°C. An evaluation of the effects of the reaction parameters on initial rates yielded the rate laws for Ph_3P {rate = k [olefin]$[Rh(CO)_2Acac]^{1.1}[Ph_3P]^{-0.5}(pH_2 + pCO)^{1.4}$, where $Rh(CO)_2Acac$ is (acetylacetonato)dicarbonylrhodium (I)} and $(PhO)_3P$ {rate = [olefin] $[Rh(CO)_2Acac]^{1.2}$ $[(PhO)_3P]^{-0.8}$ $(pH_2 + pCO)^{0.9}$ at total pressures lower than 7000 kPa, and rate = [olefin] $[Rh(CO)_2Acac]^{1.2}$ $[(PhO)_3P]^{-0.8}(pH_2 + pCO)^{1.7}$ at total pressures higher than 7000 kPa}.

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KEY WORDS: Catalysis, hydroformylation of soybean oil, kinetics, rate law, rhodium.

Strategic research in the development of new technologies for the conversion of biobased feedstocks such as vegetable oils to value-added products is important for economic growth in the environmentally conscious, yet highly competitive, global economy. The chemical composition of vegetable oils consists of TG esters with three dominant FA, oleic, linoleic, and linolenic acids having internal double bonds. Hydroformylation, commonly known as the oxo process, is an environmentally friendly process by which those TG can be converted to polyaldehydes (1–4). Whereas the kinetics and mechanism of simple olefin hydroformylation over phosphine- or phosphite-modified rhodium catalysts have been reported (5–16), the effects of reaction parameters on the reaction rates of unsaturated FA esters, TG, or vegetable oils have not been extensively investigated (17–19).

We now report the results of a kinetic investigation of the conversion of soybean oil to polyaldehydes by the hydroformylation reaction using homogeneous rhodium catalysis under the reaction conditions relevant to industrial processes. Scheme 1 shows the hydroformulations of a model TG ester having one (oleic) and two (linoleic) double bonds.

EXPERIMENTAL PROCEDURES

The iodine value of soybean oil (ADM, Decatur, IL) was measured, and the oil was used as received. Acetone (HPLC grade), acetonitrile (HPLC grade), triphenylphosphine (Ph_3P; 99%), and triphenyl phosphite [$(PhO)_3P$; 99+%] were purchased from Acros Organics (Fairlawn, NJ), as was toluene (HPLC grade, Fisher, Fairlawn, NJ); these were used as received. FTIR measurements were made as thin films of liquid samples on NaCl windows by a PerkinElmer (Spectra 1000) spectrometer. HPLC analysis was performed by using a Waters 1525 binary pump, a Waters 2410 refractive index, and Waters 2487 dual λ absorbance detectors.

A detailed description of the hydroformylation reactor and the kinetic procedure are reported elsewhere (3). The experimental setup used to evaluate the kinetics of the reaction by measuring gas consumption was similar to the one described by Bhanage *et al.* (16). The reactions were carried out in a high-pressure Parr mini-reactor (450 mL) equipped with temperature and stirrer speed controls and a liquid sampling outlet. The samples (60–130 mL) of vegetable oils, neat or as solutions in toluene, plus the catalyst precursor, (acetylacetonato)dicarbonylrhodium (I) [$Rh(CO)_2Acac$], and the ligands, Ph_3P or $(PhO)_3P$, were charged into the reactor and sealed. The sealed reactor was flushed four times with syngas and pressurized to 2700–3100 kPa. Once the temperature of the reactor reached a set value, the total syngas pressure (4800–11,000 kPa) and the agitation speed (1000 rpm, gas dispersion stirrer) were increased. The consumption of syngas inside the constant pressure reactor was monitored by the pressure drop in the gas reservoir. The number of moles of olefins consumed with time was calculated based on the amount of carbon monoxide reacted. The partially reacted soybean samples were withdrawn from the reactor and analyzed by FTIR and HPLC (Nova Pac C18 reversed-phase column using a 3:1 acetone/acetonitrile mixture).

The initial rate of the reaction, $(\Delta n/\Delta t)_{ini}$, and the turnover frequency, TOF (Eq. 1), were measured as described previously while systematically varying reaction parameters such as temperature, pressure, olefin concentration, $Rh(CO)_2Acac$ and ligand [Ph_3P or $(PhO)_3P$] concentrations. The activation energy was determined by Arrhenius plots using the temperature profile for initial rates. The observed rate expressions for the catalyst systems, Rh/Ph_3P and $Rh/(PhO)_3P$, were formulated based on the data collected (Eqs. 2,3):

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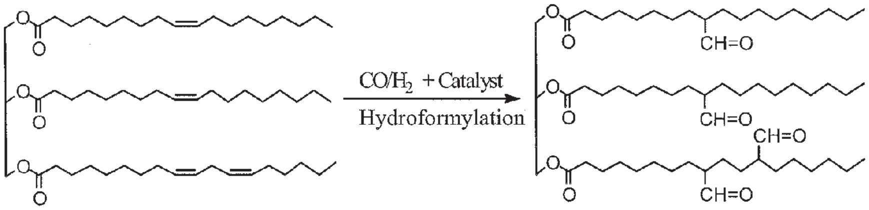

SCHEME 1

$$\mathrm{TOF} = (\Delta n)_{\mathrm{re}} / (\Delta t \times n_{\mathrm{Rh}}) \quad [1]$$

where n_{Rh} is the number of moles of rhodium used, $(\Delta n)_{\mathrm{re}}$ is the number of moles of double bonds reacted at time interval Δt, and

$$\text{polyolefin} + \mathrm{Rh(CO)_2Acac} + \text{ligand} + \mathrm{CO} + \mathrm{H_2} \rightarrow \text{polyaldehyde} + \text{catalyst} \quad [2]$$

$$\text{rate} = k[\text{olefin}]^a[\mathrm{Rh}]^b[\text{ligand}]^c(\mathrm{pH_2} + \mathrm{pCO})^d \quad [3]$$

The total olefin content of the soybean oil (determined by the iodine number) was taken as the substrate concentration, since it was apparent that the reaction rate was independent of the type of dominant TG present in the vegetable oils (3). The reaction orders with respect to olefin content (*a*), rhodium (*b*), ligand (*c*), and total syngas pressure (*d*) were experimentally measured as the slopes of log–log plots.

A comparative study of the effects of hydroperoxides was done using soybean oil purified of hydroperoxides by vacuum distillation at 100°C. The initial rates of soybean oil at 90°C and 10,000 kPa with and without hydroperoxides were measured as described above. The reactions in the presence of $\mathrm{Ph_3P}$ were not affected by hydroperoxides because at elevated temperatures $\mathrm{Ph_3P}$ will remove peroxides from the oils. However, the reaction rates remained constant with or without peroxides whether $\mathrm{Ph_3P}$ or $\mathrm{(PhO)_3P}$ was used. Moreover, the amount of hydroperoxides in the oil feedstock was estimated to be about 0.01 mol% based on the amount of double bonds.

RESULTS AND DISCUSSION

Effects of the ligands. Trialkyl or arylphosphines used in modified rhodium or cobalt catalysts in industrial oxo processes can stabilize the catalyst system even at low carbon monoxide pressures. The presence of phosphines in rhodium catalysis virtually eliminates the side reactions such as olefin isomerization and hydrogenation, in addition to improving selectivity and providing good thermal stability (14).

The effects of the ligands, $\mathrm{Ph_3P}$ and $\mathrm{(PhO)_3P}$, were determined by systematically changing the ligand concentrations while keeping the other parameters constant. The reactions were carried out at 80°C and total syngas pressures of 7250–7600 kPa with soybean oil (71%) in toluene (using $\mathrm{Ph_3P}$) and at 90°C and total syngas pressure of 8000–8400 kPa in neat soybean oil [using $\mathrm{(PhO)_3P}$]. The turnover frequencies, initial rates, and percentage conversions were measured with time, and the total aldehyde content in the final reaction mixtures was estimated by FTIR. The reaction speed, measured as the initial rate or TOF, increased when the ligand/Rh ratio was increased from 2 to 5, followed by a steady decrease at higher ligand/Rh ratios (Table 1). The order of reaction *c,* with respect to the ligand concentration [$c = -0.52 \pm 0.03$ for $\mathrm{Ph_3P}$ and $c = -0.81 \pm 0.18$ for $\mathrm{(PhO)_3P}$], was determined using the ligand/Rh > 4 region. Comparable values for *c* were obtained from either the initial rate or the maximum observed TOF as a measure of the reaction speed, and an average value is reported. It should be noted that although the ligand/Rh ratio of about 5 gave the maximal initial speed, it may not necessarily be the optimal practical ratio for this reaction; higher ligand concentrations may delay the deactivation of the catalyst, thereby improving the final yields.

Substrate concentration. The average functionality of soybean oil (average number of double bonds per TG molecule) was estimated to be 4.36 based on its iodine value (127 mg KOH/g). The reactions were carried out using toluene solutions (see Table 2) at 90°C and 8950–9300 kPa (using $\mathrm{Ph_3P}$) and 7150–7370 kPa [using $\mathrm{(PhO)_3P}$]. The nonpolar solvent toluene did not appear to have any significant mechanistic bearing on the reaction since the rates for the neat substrate fell in line in concentration profiles (the highest concentration being for the neat oil). Also, no evidence was found for any changes in product composition in toluene solutions compared to neat oils, i.e., no alcohols or hydrogenated products were found. The order of the reaction with respect to olefin concentration of the substrate was determined by using both initial rates and maximum TOF as before, and comparable results were obtained. The average values for reaction order *a* were obtained for $\mathrm{Ph_3P}$ ($a = 1.18 \pm 0.04$) and $\mathrm{(PhO)_3P}$ ($a = 0.92 \pm 0.07$). A value of 1.08 was obtained when the rates of various vegetable oils, toluene solutions, and model compounds were correlated with their olefin concentrations (3,4). When the experimental uncertainties were taken into account, a first-order dependence on the substrate concentration was apparent.

Catalyst precursor. Figure 1 displays the increase in the reaction speed as the concentration of the catalyst precursor, $\mathrm{Rh(CO)_2Acac}$, was increased. The reactions with $\mathrm{(PhO)_3P}$ (at 9650 kPa) were carried out under a constant ligand/Rh ratio of about 5. Although both the rhodium and ligand concentrations were varied at the same time, the measured initial rates could be corrected for the changes in $\mathrm{(PhO)_3P}$ concentration, since the reaction order with respect to the phosphite ligand was already known (–0.8). In the case of $\mathrm{Ph_3P}$ (at 9900 kPa), the rhodium concentrations were varied so as to keep the

TABLE 1
Effects of the Ligand/Rhodium Ratio on the Hydroformylation of Soybean Oil[a]

Ligand	[Ligand] (mol L^{-1})	[Ligand]/[Rh][b]	Initial rate (mol L^{-1} min^{-1})	Maximum TOF (mol mol^{-1} h^{-1})	Conversion[c] (%)
$(PhO)_2P$	0.0099	2.1	0.070	954	27.3
$(PhO)_3P$	0.0139	3	0.078	1042	31.0
$(PhO)_3P$	0.0189	4.1	0.082	1088	34.8
$(PhO)_3P$	0.0237	5	0.073	904	49.5
$(PhO)_3P$	0.0281	6.1	0.056	832	34.8
$(PhO)_3P$	0.0374	8.1	0.045	692	30.2
$(PhO)_3P$	0.0556	12	0.029	553	26.4
Ph_3P	0.0109	2.7	0.063	951	74.5 (84)
Ph_3P	0.0195	4.8	0.080	1094	84.3 (88)
Ph_3P	0.0252	6.3	0.060	1007	
Ph_3P	0.0307	7.6	0.057	854	79.0 (83)
PH_3P	0.0348	8.6	0.062	894	
PH_3P	0.0477	11.8	0.042	728	
PH_3P	0.0760	18.8	0.037	568	68.2 (72)

[a] Reactions with triphenyl phosphite $[PhO)_3P]$ were run at 90°C and 8000–8400 kPa in neat oil, and the reactions with triphenylphosphine (Ph_3P) were run at 80°C and 7250–7600 kPa in a 71% solution in toluene. TOF, turnover frequency.

[b] Ligand concentration was changed while keeping the (acetylacetonato)dicarbonylrhodium (I) $[Rh(CO)_2Acac]$ concentration constant.

[c] The conversions of olefins at 60 min $[using (PhO)_3P]$ and 120 min (using Ph_3P). The conversions based on aldehyde content (from FTIR) are given in parentheses.

ligand/Rh ratio greater than 5 while keeping the amount of Ph_3P constant, so that no correction was necessary for the Ph_3P concentration. Both methods yielded satisfactory results. The average values of the slopes of the log–log plots using both initial rates and maximum TOF yielded reaction order *b*, with respect to the catalyst precursors for Ph_3P ($b = 1.09 \pm 0.29$) and $(PhO)_3P$ ($b = 1.24 \pm 0.08$).

Effects of pressure. Interpreting changes in the reaction speed with the total syngas (1:1) pressure is complicated by the opposing influences of CO and H_2 on the reaction rate. High carbon monoxide pressures can inhibit the reaction by the formation of inactive catalyst species (see Eqs. 4 and 5, where L denotes a ligand). Both $RCORh(CO)_2L_2$ and $RCORh(CO)_3L$, in which rhodium is coordinatively saturated, are inactive catalyst species. Low hydrogen pressures can also yield inactive rhodium dimers (Eq. 6); however, higher hydrogen pressures can accelerate the reaction since the oxidative addition of hydrogen to the acyl rhodium complex depends on the partial pressure of hydrogen (Eq. 7).

$$\mathrm{RCORh(CO)}L_2 + \mathrm{CO} \rightleftharpoons \mathrm{RCORh(CO)_2}L_2 \qquad [4]$$

$$\mathrm{RCORh(CO)_2}L_2 + \mathrm{CO} \rightleftharpoons \mathrm{RCORh(CO)_3}L + L \qquad [5]$$

$$2\mathrm{HRh(CO)_2}L_2 \rightleftharpoons [\mathrm{Rh(CO)_2}L_2]_2 + \mathrm{H_2} \qquad [6]$$

$$\mathrm{RCORh(CO)}L_2 + \mathrm{H_2} \rightarrow (\mathrm{H_2})\mathrm{RCORh(CO)}L_2 \qquad [7]$$

The ligands Ph_3P and $(PhO)_3P$ show similar behavior with respect to the total pressure (see Fig. 2). The existence of two pressure regimes is apparent with $(PhO)_3P$, where it shows a

TABLE 2
Effects of Olefin Concentration on the Rates of Hydroformylation of Soybean Oil at 90°C[a]

[Olefin] (mol L^{-1})	Ligand[b]	$[Rh(CO)_2Acac]$ (mol L^{-1}) × 10^3)	Initial rate (mol L^{-1} min^{-1})	Maximum TOF (mol mol^{-1} h^{-1})
1.15	$(PhO)_3P$	5.81	0.024	318
1.54	$(PhO)_3P$	5.81	0.036	490
2.02	$(PhO)_3P$	5.81	0.049	567
2.52	$(PhO)_3P$	5.81	0.054	715
4.03	$(PhO)_3P$	5.81	0.078	907
4.61	$(PhO)_3P$	5.81	0.101	1097
0.51	Ph_3P	5.04	0.009	123
0.84	Ph_3P	5.04	0.018	216
1.69	Ph_3P	5.04	0.036	488
2.36	Ph_3P	5.04	0.070	1103
4.61	Ph_3P	5.04	0.117	1277

[a] Solutions in toluene (100 mL) except for 4.61 M (neat). For abbreviations see Table 1.

[b] Reactions with $(PhO)_3P$ were run at 7150–7370 kPa, and reactions with Ph_3P were run at 8950–9300 kPa.

TABLE 3
The Activation Energy and Rate-Law Coefficients for the Hydroformylation of Soybean Oil

Ligand	ΔE_a (kJ/mol)	*a*	*b*	*c*	*d*
$(PhO)_3P$	77.4 ± 5.0	0.29 ± 0.07	1.24 ± 0.08	−0.81 ± 0.18	0.9^a (1.7^b)
Ph_3P	61.1 ± 0.8	1.18 ± 0.04	1.09 ± 0.29	−0.52 ± 0.03	1.39 ± 0.11

[a] Total pressure <7000 kPa (0.93 ± 0.03).

[b] Total pressure >7000 kPa (1.69 ± 0.12).

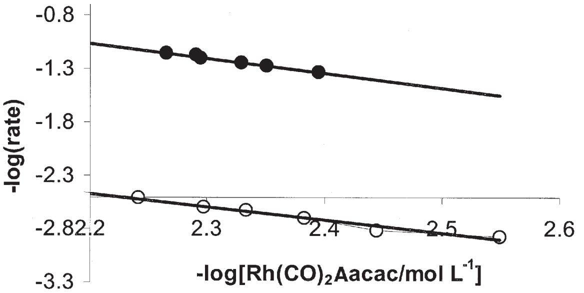

FIG. 1. The effect of the rhodium precursor concentration [$Rh(CO)_2Acac$] at 90°C on the initial rate for Ph_3P (triphenylphosphine) [log (rate/mol L^{-1} min^{-1}] (●) and $(PhO)_3P$ (triphenyl phosphite) (log {rate/[$(PhO)_3P]^{-0.8}$}) (○).

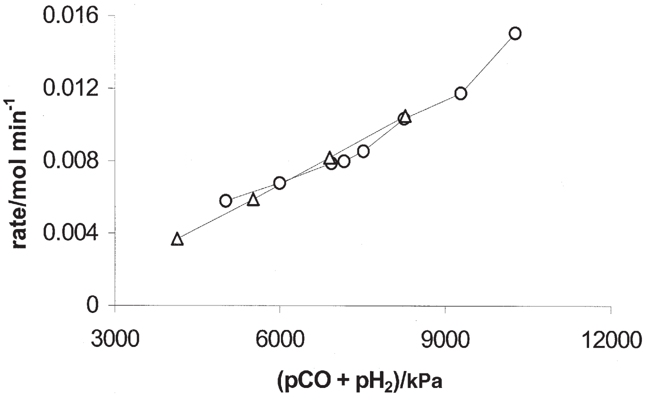

FIG. 2. The variation of the initial rate of hydroformylation of soybean oil with total syngas pressure at 90°C for $(PhO)_3P$ (○) and at 80°C for Ph_3P (△). For abbreviations see Figure 1.

reaction order *d* of 0.93 ± 0.03 (<7000 kPa) and 1.69 ± 0.12 (>7000 kPa) at 90°C, whereas Ph_3P yielded an order of 1.39 ± 0.04. The reaction rates increased with increasing total pressure. It is possible to have higher reaction orders with respect to hydrogen (15) by the combined effects of the rate-limiting oxidative addition of hydrogen to the acyl rhodium complex, $RCORh(CO)L_2$ (see Eq. 7) and inhibition of rhodium dimer formation at increased hydrogen pressure (see Eq. 6).

Although the migratory insertion of the alkene substrate to the catalyst is the rate-determining step for these types of reactions using the Ph_3P and $(PhO)_3P$ ligands, the addition of hydrogen to the acyl rhodium complex (Eq. 6) could not be ruled out from these results. The kinetic parameters obtained from varying the total syngas pressure (without changing partial pressures) do not provide conclusive evidence in this regard.

Effects of temperature. Matsubara *et al.* (20) studied the potential energy profile of olefin hydroformylation catalyzed by $RhH(CO)_2(PH_3)_2$ using *ab initio* molecular orbital methods (20). The oxidative addition of hydrogen to the acyl rhodium intermediate had the highest barrier, consisting of the desolvation energy and the intrinsic activation energy. The experimental activation energy (76 kJ/mol) for an internal olefin, cyclohexene, could be calculated based on the results of Van Rooy *et al.* (9) using a bulky phosphite ligand.

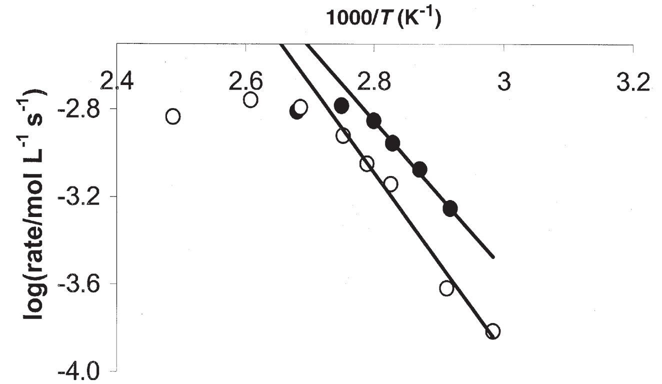

FIG. 3. The Arrhenius plots for the hydroformylation of soybean oil with Ph_3P (●) and $(PhO)_3P$ (○). For abbreviations see Figure 1.

Figure 3 displays the temperature behavior of the reaction for both Ph_3P (10,300 kPa) and $(PhO)_3P$ (10,700 kPa) ligands. The speed of the reaction increases until the temperature reaches *ca.* 100°C, followed by an apparent inhibition of the process accompanied by the formation of a dark-brown rhodium compound. The formation of catalytically inactive dimeric phosphido-bridged clusters at high temperatures has been invoked to explain this behavior (14). The activation energies are calculated using the linear region of the temperature profiles. The activation energies for Ph_3P (61.1 ± 0.8 kJ/mol) and $(PhO)_3P$ (77.4 ± 5.0 kJ/mol) are consistent with the values reported in the literature (9). The measured reaction coefficients (Eq. 3) and activation energies are summarized in the Table 3.

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