The hydroformylation of vegetable oils and model compounds by ligand modified rhodium catalysis

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Abstract

The hydroformylation of vegetable oils (soybean, high oleic safflower, safflower, and linseed) and model compounds (methyl linoleate, methyl oleate, triolein, and trilinolein) using $Rh(CO)_2Acac$ ((acetylacetonato)dicarbonylrhodium(1)) as the catalyst precursor in the presence of triphenylphosphine (TPP) or $(PhO)_3P$ converted the olefins to polyaldehydes in quantitative yield. The reaction rate expressed as either initial rate or maximum turnover frequency (TOF) correlates with the olefin concentration of the substrate independent of the type of dominant triglyceride in vegetable oils. The relative rate constants (k_o/k_1) between methyl oleate and methyl linoleate at $90\,^\circ C$ and $1000\,psig$ measured separately (2.4) and measured competitively in a mixture (0.90 ± 0.08) indicate the formation of a π-allyl complex of the catalyst with the diolefin, methyl linoleate. The relative rate constants (k_o/k_1) of triglycerides (triolein and trilinolein) measured separately (1) and measured competitively in a mixture (0.94 ± 0.06) do not indicate any significant effect from π-allyll complex formation on the reaction speeds of vegetable oils. The co-catalyst, $(PhO)_3P$, showed a lesser reactivity compared to TPP in contrast to the rates of bulky phosphite ligands reported in the literature. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Because of the present interest in biological materials as renewable sources of energy and as chemical feed-stocks vegetable oils are receiving renewed attention as an important precursor for value added products such as high performance plastics, adhesives, lubricants, and coatings. Vegetable oils consist of triglyceride esters with three dominant fatty acids, oleic, linoleic and linolenic with internal double bonds. Hydroformylation, commonly known as the oxo process, is an environmentally friendly process by which these triglycerides can be converted into aldehydes. Once the aldehyde functionality is introduced, it could be a starting material for a number of products (see Scheme 1). There have been a number of reports on the hydroformylation of unsaturated fatty acid esters and vegetable oils with rhodium or cobalt catalysts [1–11]. However, systematic studies of the effects of reaction parameters on the kinetics of unsaturated fatty acid esters or triglycerides are limited [12–14].

We have previously reported the epoxidation of vegetable oils, specifically soybean oil, followed by ring opening to yield polyols [15,16]. These have low viscosity and high hydroxyl numbers that indicates the industrial feasibility of soybean oil as a chemical feedstock for value added materials. We now report the

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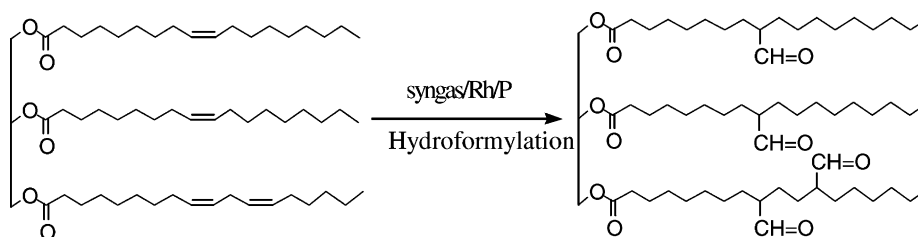
Scheme 1. The hydroformylation of a model triglyceride with oleic and linoleic functionality.

results of a systematic investigation of the conversion of vegetable oils and model compounds to aldehydes by the hydroformylation reaction using ligand modified rhodium catalysts. Reaction conditions relevant to industrial processes were used and the general kinetic features of the conversion of vegetable oils were evaluated with the aid of model compounds.

2. Experimental

2.1. Materials

The iodine values (IV) of soybean oil (ADM Chemicals, Decatur, IL), high oleic safflower oil (Ventura Foods, Opelousas, LA), linseed oil (Aldrich), and safflower oil (Aldrich) were measured and the oils were used as received. Acetone (HPLC grade), acetonitrile (HPLC grade), TPP (99%), and triphenyl phosphite (above 99%) purchased from ACROS Organics, NJ and toluene (HPLC grade, Fisher) were used as received. Methyl linoleate, methyl oleate, triolein, and trilinolein in >99% purity were purchased from Nu Check Prep Inc, MN.

2.2. Hydroformylation

The reactions were carried out in a high-pressure Parr mini-reactor (450 ml) equipped with temperature and stirrer speed controls and liquid sampling outlet. The experimental setup was similar to the one described by Bhanage et al. [17]. The samples (60–130 ml) of vegetable oils, neat or as solutions in toluene, plus the catalyst precursor, $Rh(CO)_2Acac$ and the ligand, TPP or $(PhO)_3P$, were charged into the reactor and sealed. The sealed reactor was flushed four times with syn-gas (100 psig), and pressurized to

400–450 psig before thermostating at the desired temperature. Once the temperature of the reactor reached a set value, the total syn-gas pressure (700–1600 psig) and the agitation speed (1000 rpm, gas dispersion stirrer) were increased. The consumption of syn-gas was monitored by the pressure drop of a gas reservoir. The pressure of the reactor was kept constant by a pressure regulator. The number of moles of olefins consumed with time was calculated based on the amount of carbon monoxide reacted. The initial rate of the reaction was determined by plotting moles of olefin reacted, n, with time, t, for the initial linear region of the reaction (<10% of the progress), i.e. $(\Delta n/\Delta t)_{ini}$, and also by plotting n/t versus t and extrapolating to zero time [18]. Both methods gave comparable results except for fast reactions of soybean oil with TPP ligand, in which the reaction commenced before the set temperature was reached. The turnover frequency (TOF) at time intervals was calculated by Eq. (1) in which $(\Delta n)_{re}$ refers to the number of moles of olefin reacted at the time interval Δt and n_{Rh} refers to the number of moles of the catalyst precursor $Rh(CO)_2Acac$. The conversions calculated by the gas consumption and the FT-IR determination of the aldehyde content of the final reaction mixtures gave comparable results. The rate measurements were reproducible within 3–7%.

$$TOF = \frac{(\Delta n)_{re}}{(\Delta t n_{Rh})} \tag{1}$$

2.3. Relative rate constant between methyl linoleate and methy oleate

A mixture of methyl linoleate and methyl oleate (1:1(molar), 0.75 M, 60 g) was prepared in toluene and hydroformylated at 90 °C and 1000 psig. Partially reacted samples were withdrawn at time intervals and analyzed by HPLC using Nova Pac C_{18} reverse

phase column with Waters 1525 binary HPLC pump and Waters 2410 IR detector and Waters 2487 dual λ absorbance detector. Acetone/acetonitrile mixture (15/55; 0.7 ml/min) was used as eluents. An external standard (9-octadecene) was added before HPLC analysis and the relative rate constant was calculated according to the Eq. (2), where A_1, A_o and A_s denote the peak areas of methyl linoleate, methyl oleate and the standard in partially reacted (<30%) mixtures.

$$\frac{k_o}{k_1} = \frac{\log[(A_o/A_s)_t/(A_o/A_s)_o]}{\log[(A_1/A_s)_t/(A_1/A_s)_o)]} \tag{2}$$

2.4. Relative rate constant between triolein and trilinolein

This was measured in a similar method as above using a mixture of triolein and trilinolein (1:1(molar); 0.075 M, 51 g) in toluene. Acetone/acetonitrile mixture (70/30; 1.2 ml/min) was used in HPLC analysis. HPLC analysis of the reaction mixtures of soybean oil was performed using acetone/acetonitrile mixtures (65/35; 1 ml/min).

2.5. Determination of aldehyde content by FT-IR

FT-IR measurements were made as thin films of liquid samples using an NaCl window by Perkin–Elmer FT-IR spectrometer (Spectra 1000). The aldehyde concentration of a sample of hydroformylated soybean oil was determined by a titrimetric method [19]. The FT-IR spectrum of this sample consisted of peaks at 1743 cm^{-1} (ester functionality) and 1727 cm^{-1} (aldehyde functionality). A series of samples were prepared by diluting with unreacted soybean oil and the absorbances of the two peaks, ester and aldehyde, were measured. A calibration curve was constructed using the ratio of absorbance and the aldehyde yield measured by the titration method. The aldehyde yield of an unknown sample could be determined by measuring the absorbance ratio of two carbonyl peaks. The conversions calculated by the pressure drop and FT-IR methods gave comparable results.

2.6. Determination of iodine value

The IV was determined by Hanus method in which excess iodine monobromide in an acetic acid/

carbontetrachloride was allowed to react with olefins and the unreacted iodine was titrated with a standardized sodium thiosulphate solution.

3. Results and discussion

3.1. General kinetic features

Hydroformylations were carried out using syn-gas (1:1 H$_2$:CO; 600–1600 psig) at 70–130 °C in neat liquids of vegetable oils or in toluene solutions using Rh(CO)$_2$Acac and either TPP or (PhO)$_3$P as catalyst precursors. The reactions converted the internal double bonds of vegetable oils (10–130 g) almost quantitatively to aldehydes within 2–5 h. The progress of the reaction, measured by the gas consumption, was essentially linear within experimental uncertainty for the first 10–15% of the reaction (see Fig. 1). The consumption of syn-gas begins after an induction period of 1–20 min during which the active catalytic species is presumably formed. The data satisfactorily fit for a first-order dependence on the substrate concentration (treated as the total olefin content) for the early stage (<25%) of the reaction. However, it is difficult to determine the reaction orders with such limited data. At higher conversions substantial deviation from a simple kinetic model is observed. This is expected for such a complicated multi step process. The complexity of the structure of vegetable oils, in which oleic, linoleic, and linolenic fragments may exhibit a diverse
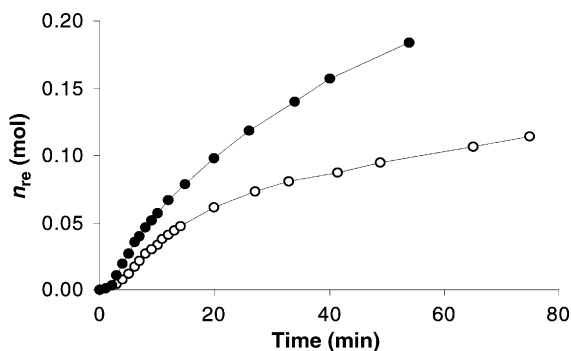
Fig. 1. The progress (olefins reacted, n_{re}, with time) of the hydroformylation reaction for soybean oil (100 g; 71% in toluene) at 80 °C with Rh(CO)$_2$Acac (0.0005 mol) in the presence of TPP (●) (0.0025 mol) and (PhO)$_3$P (O) (0.0025 mol).
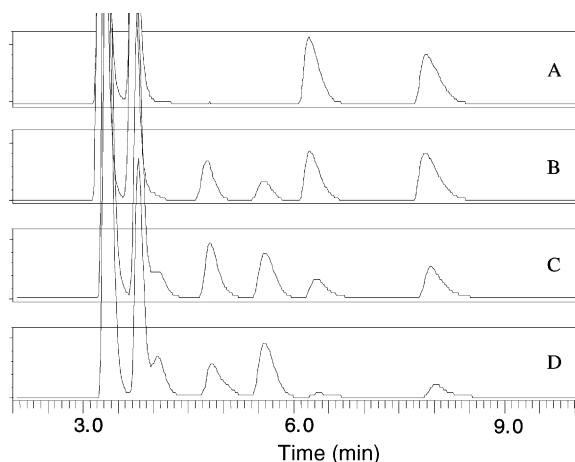
Fig. 2. The HPLC analysis of the progress of the hydroformylation reaction of a 1:1 mixture of methyl oleate and methyl linoleate at A: 0 min; B: 6.5 min; C: 30.5 min; and D: 85 min. The peaks were identified as HFML-2 (reaction time (T_R) = 4.10 min), HFML-1 (T_R = 4.85 min), HFMO (T_R = 5.60 min), ML (T_R = 6.35 min), and MO (T_R = 8.00 min).

range of reactivity; the possibility of different rates for secondary hydroformylations, and competing side reactions such as isomerizations and hydrogenations can explain this behavior. The HPLC analysis of partially reacted mixtures, both soybean oil and model compounds, shows the accumulation and subsequent disappearance of intermediate products (see Figs. 2 and 3).

The TOF of the reaction (number of moles of olefins reacted per mole of rhodium catalyst per hour) shows
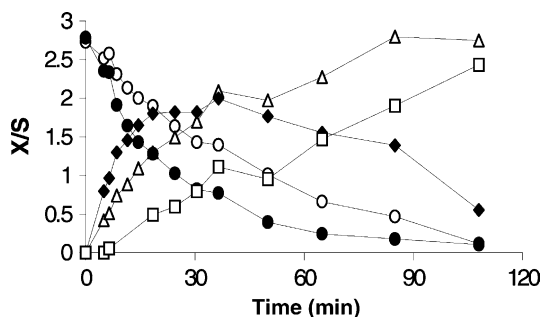

Fig. 3. The products formation (X/S where X denotes reactant and products and S stands for the external standard) from the reaction of a 1:1 mixture of methyl oleate (○) and methyl linoleate (●). The products are identified as HFMO (△), HFML-1 (◆), and HFML-2 (□).
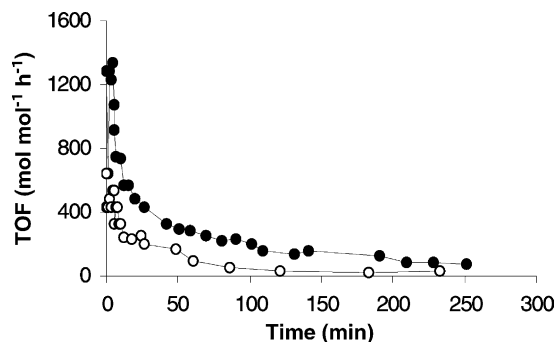

Fig. 4. The variation of TOF with time for the hydroformylation of soybean oil (75 g) with Rh(CO)2Acac catalyst (0.0004 mol) in the presence of 0.002 mol TPP (●) and (PhO)$_3$P O at 80 °C.

an initial increase due to the induction period followed by an exponential decline due to the decrease in substrate concentration (see Fig. 4). The maximum TOF values of up to 3000 mol mol^{-1} h^{-1} were observed.

The kinetically useful initial rate was measured from the initial linear part of the reaction (($\Delta n/\Delta t)_{ini}$, see Fig. 1) or by plotting n/t versus t and extrapolating to zero time (($\Delta n/\Delta t)_{ini}$). Both methods yield comparable rates, except for faster reactions in which the initial phase of the reaction could not be followed.

It was necessary to rule out the possibility of a mass transfer limited process for this gas–liquid phase reaction before applying any kinetic treatment to the results. Although, the large variations of reaction rates observed under different conditions render this possibility unlikely, there was no sufficient proof to exclude it. The effect of stirring speed was evaluated for soybean hydroformylation (Rh/TPP) and it was observed that indeed the reactions were limited by diffusion of syn-gas at low agitation speeds, i.e. less than 800 rpm (see Fig. 5). Furthermore, the use of a gas dispersion stirrer at high stirrer speeds (>1000 rpm) ensures excess syn-gas is available for the reaction at all times.

There is no evidence for substantial isomerization leading to conjugated or *trans* double bonds with TPP as a ligand. The (PhO)$_3$P modified catalyst under certain conditions (low pressure) gave up to 50% isomerization rendering the substrate inactive [20,21]. Although, the initial rate for (PhO)$_3$P was only about three times slower than TPP, the former achieves only about 50% conversion at extended reaction times while the latter gives complete reaction (see
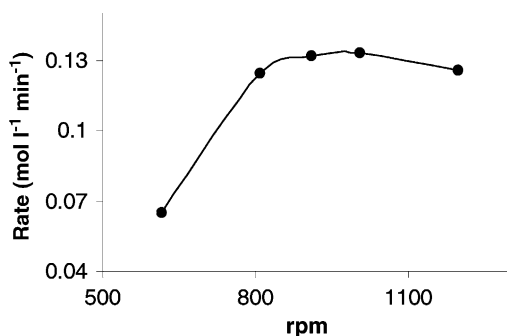
Fig. 5. The effect of agitation speed on the hydroformylation of soybean oil (120 g) with rhodium catalyst.

Fig. 1). Fast *cis–trans* isomerization of methyl oleate had been observed with bulky phosphite-modified rhodium catalyst [12].

The hydrogenation of double bonds appears to be insignificant with rhodium catalysts [22–24]. Since, more than 95% of olefin content is converted to aldehydes (estimated by both gas consumption and FT-IR analysis), the side reactions are minimal in most cases.

The speed of the reaction with $(PhO)_3P$ is 2–3 times slower than with TPP. This is in contrast to the observations with bulky phosphite ligands in which higher reaction rates were obtained than TPP [12,25,26].

Table 1 summarizes the IVs, initial rates, and maximum TOFs, for the hydroformylation of several

vegetable oils (soybean, safflower, high oleic safflower, and linseed) at 90 °C and 990–1030 psig. The conversions were determined by both gas consumption and FT-IR spectroscopy and, in the case of soybean oil and high oleic safflower oil, by the hydroxy number determination following catalytic hydrogenation of aldehydes to polyols using Raney-nickel and molecular hydrogen. The reactivity of the oils as well as model compounds triolein and methyl oleate correlates to their IVs, i.e. olefin concentration, and is independent of the source of the oil or the solvent. In fact, a log–log plot for the initial rate or TOF with the olefin concentration, irrespective of the source of the vegetable oil, gave an order of the reaction (1.08) which was consistent with the reaction order measured with a series of toluene solutions (see Fig. 6; TOFs were plotted as $-\log(\text{TOF})/2$ to display both sets of data on the same scale). However, methyl linoleate as a model compound does not follow this trend and displays a negative deviation. Dienes can form stable unsaturated π-allyl-rhodium phosphine complexes, which depending on the conditions may undergo slow hydroformylation. The type of the dominant triglyceride in a particular vegetable oil, i.e. oleic, linoleic, or linolenic, does not appear to have a bearing on the reaction rates probably because all of the reactions are limited by the effects of the formation of π-allyl-rhodium complexes between the

Table 1

The rates of hydroformylation of vegetable oils at 90 °C and 1000 psig in a 1:1 mixture of syn-gas[a]

Vegetable oil	IV (functionality)[d]	Ligand	[Olefin] (mol l^{-1})	Initial rate[e] (mol l^{-1} min^{-1})	TOF[f] (mol/mol h^{-1})
Soybean	125 (4.3)	TPP	4.61	0.171	2074
Soybean	125 (4.3)	$(PhO)_3P$	4.61	0.062	1254
High oleic Safflower	96 (3.3)	TPP	3.54	0.132	1956
Safflower	134 (4.6)	TPP	4.93	0.183	2049
Linseed	177 (6.1)	TPP	6.53	0.236	3026
Soybean[b]	125 (4.3)	TPP	3.25	0.090	1465
Soybean[c]	125 (4.3)	TPP	2.51	0.063	1103
Methyl linoleate[c]	(2)	TPP	3.06	0.051	814
Methyl oleate[c]	(1)	TPP	1.52	0.062	933
Triolein[c]	(3	TPP	1.53	0.054	897

[a] Neat oils (75 g) or solutions in toluene with 6.0×10^{-3} M $Rh(CO)_2Acac$ and 2.4×10^{-2} M TPP or $(PhO)_3P$.

[b] 71% Solution in toluene.

[c] 50% Solution in toluene.

[d] The average number of double bonds in a molecule.

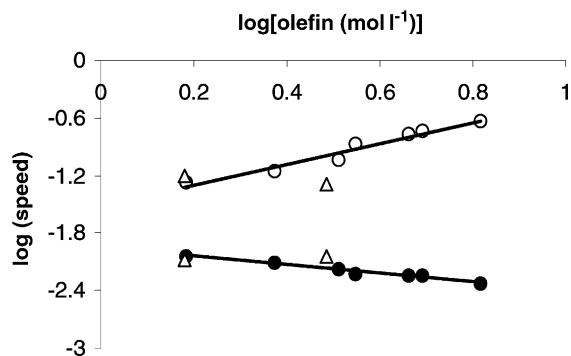[e] An average from two methods.

[f] Observed maximum (initial) TOF.

log[olefin (mol l⁻¹)]

Fig. 6. The variation of the reaction speed with the concentration of olefins in vegetable oils. Log (initial rate/mol l^{-1} min^{-1}) vs. [olefin]/mol l^{-1} for vegetable oils, and triolein, ($\bigcirc$), for methyl linoleate, and methyl oleate ($\triangle$), and $-\log$(TOF (mol mol^{-1} h^{-1}))/2 vs. [olefin] (mol l^{-1}) for vegetable oils, and triolein, ($\bullet$) and methyl linoleate, and methyl oleate ($\triangle$).

double bonds of side chains. Apparently, the complex formation within linoleic or linolinic chains are not significant in triglycerides unlike methyl esters of fatty acids [12].

3.2. Relative rate measurements

In order to substantiate the magnitude of the effects of π-allyl complex formation, the relative rate constant of hydroformylation of methyl oleate to methyl linoleate, k_o/k_1, was determined. The Table 1 shows the initial rates and maximum TOF values of these substrates (50% in toluene) when they were reacted individually. Methyl oleate reacted about 1.2 times faster than methyl linoleate. However, if the rates are statistically corrected for the functionality, the monoolefin methyl oleate is about 2.4 times faster. An experiment was conducted using a 1:1 (mol.%) mixture of these two methyl esters and their relative rate of hydroformylation was measured by product analysis using HPLC (see Section 2 for details). Eqs. (3)–(5) show the possible products from these two substrates in which MO, ML, HFMO, HFML-1 and HFML-2 denotes the starting materials methyl oleate, methyl linoleate, and the monoaldehyde from methyl oleate, and mono and dialdehyde from methyl linoleate respectively. Figs. 2 and 3 describe the formation of products with time in which the yield of HFMO increased as MO is consumed while the yield of HFML-1 shows an increase

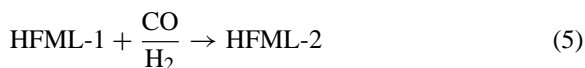Table 2
The relative rate measurements of model compounds

Substrates	k_{rel} (separate)[a] (k_o/k_1)	k_{rel} (mixture)[b] (k_o/k_1)
Methyl oleate Methyl linoleate	2.43	0.90 ± 0.08
Triolein Trilinolein	~ 1[c]	0.94 ± 0.06

[a] Individual reaction rate of each compound was measured separately by gas consumption and statistically corrected for the number of double bonds (see Table 1).

[b] Measured in a mixture by HPLC product analysis and statistically corrected for the number of double bonds in a molecule.

[c] Estimated to be unity since the rates of all vegetable oils and triolein fall in-line in Fig. 6.

followed by a formation of HFML-2 at the expense of HFML-1.

$$MO + \frac{CO}{H_2} \rightarrow HFMO \qquad (3)$$

$$ML + \frac{CO}{H_2} \rightarrow HFML\text{-}1 \qquad (4)$$

$$HFML\text{-}1 + \frac{CO}{H_2} \rightarrow HFML\text{-}2 \qquad (5)$$

The relative rate constant, k_o/k_1, measured using this competitive method was determined to be 0.45 ± 0.04 (0.90 if a statistical correction (2) was applied) indicating an inhibition of the hydroformylation of oleic acid methyl ester in the presence of a diolefin. However, the relative rate constant between triolein and trilinolein were comparable in both noncompetitive separate measurements (the rate of triolein falls in line in Fig. 3 indicating a relative rate constant of unity) or measured in a mixture (0.94 ± 0.06). The observation that triolein, trilinolein, and trilinolenin side chains have comparable rates in vegetable oils is consistent with these results (see Table 2).

4. Conclusions

General kinetic features of the oxo process of vegetable oils and model compounds by modified rhodium catalysis have been studied. The reactions of triglycerides (the constituents of vegetable oils) show a reactivity independent of the type of triglyceride, i.e. whether mono, di or tri olefin, unlike methyl

esters of fatty acids in which polyolefins show a lesser reactivity presumably due to the π-allyl complex formation with rhodium. Triphenyl phosphite as a catalyst modifier was less effective in hydroformylation than TPP. A detailed kinetic analysis of this reaction is presented in the next paper.

Acknowledgements

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