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Kinetics of hydroformylation of propylene using $RhCl(CO)(TPPTS)_2$/TPPTS complex catalyst in aqueous system

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Abstract

The kinetics of $RhCl(CO)(TPPTS)_2$/TPPTS catalyzed hydroformylation of propylene was studied by an orthogonal experimental design. The hydroformylation reaction was carried out batchwise in a 500 ml stirred autoclave. The effects of temperature, total pressure, molar ratio of hydrogen/carbon monoxide, partial pressure of propylene, molar ratio of rhodium/TPPTS and concentration of rhodium catalyst on the initial rate of reaction were determined by margin and variance analysis. Several empirical rate equations were proposed to represent the experimental data. The kinetic parameters were evaluated and the activation energy was found in the range of $75 \sim 85$ kJ/mol. The regioselectivity of hydroformylation was also determined and the molar ratio of normal/isomeric aldehyde varied from 3.9 to 56.1. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Propylene; Hydroformylation; Kinetics; Orthogonal experimental design

1. Introduction

Hydroformylation of propylene is an important reaction for commercial production of *n*-butyraldehyde and isobutyraldehyde, which are widely used as intermediates in the manufacture of plasticizers and solvents [1]. Extensive work has been done on the role of different types of metal complex catalysts, ligands and solvents on the activity and selectivity in propylene hydroformylation. Many efforts were also devoted to develop heterogeneous catalysts, e.g. water-soluble rhodium phosphine complexes, to overcome the typical trouble of separation of catalyst from the product mixture in conventional homogeneous catalyst systems [2,3]. Since water is an environment-friendly and safe solvent for reaction as compared to organic solvents, the “biphasic” hydroformylation of olefin using an aqueous reaction mixture is considered as a clean catalytic process. In the biphasic process, the catalysts are immobilized in the water phase without leak into environment and products remain in the organic phase that is easily separated from the aqueous phase by simple phase separation.

Studies on the kinetics of hydroformylation of olefins not only are instructive for improvement of the catalytic system but also provide the basic information for design and scale-up of appropriate reactors. The kinetics of hydroformylation of different olefins, such as ethylene, propylene, 1-hexene, 1-octene and 1-dodecene, using homogeneous catalyst [4–8] or supported catalyst [9–13] have been reported in the literature. However, the literature on the kinetics of hydroformylation in aqueous systems is very limited. The kinetics of 1-octene hydroformylation in two-phase media was reported and different rate models were proposed [14,15]. Zhang [16] studied the macrokinetics of hydroformylation of 1-dodecene and analyzed the influence of interphase mass transfer. Deshpande et al. [4] compared the kinetics of

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Nomenclature

A_0	pre-exponential factor of kinetic rate model
C	concentration of various component (kmol/m^3)
e	error of experiment
E	activation energy of hydroformylation reaction (kJ/mol)
$k_1 \sim k_7$	constants in different rate equations
N	total number of kinetic experiments
p	pressure of various gas components (MPa)
r	kinetic rate of hydroformylation reaction (kmol/(m^3 s))
R_G	universal gas constant (8.3144×10^{-3} kJ/(mol K))
t	reaction time (s)
T	reaction temperature (K)
V^G	gas volume in the reactor (m^3)
V^L	liquid volume in the reactor (m^3)
y	molar fraction of gas component
Z_m	compressibility factor of gas mixture

Greek letter

$\phi_{\min}$	minimized sum of square of errors between calculated and experimental rates

Superscripts

cal	predicted values by kinetic models
exp	observed values by kinetic experiments

Subscripts

0	initial
CO	carbon monoxide
H_2	hydrogen
L	ligand TPPTS
P	propylene
Rh	rhodium complex catalyst

hydroformylation of ethylene in organic and aqueous systems, but the rate of hydroformylation reaction in aqueous medium was studied at the temperature of 313 K only. Wachsen et al. [17] proved that the aqueous biphasic catalysis took place at the interfacial region for hydroformylation of propylene with aqueous rhodium complex catalysts, but no detailed kinetic data were reported and further effort of modeling also required.

Although the water-soluble catalyst was first commercially applied for hydroformylation of propylene in Germany [18,19], no practical kinetics of biphasic hydroformylation of propylene was ever reported for such catalyst systems. In this paper, the kinetics of hydroformylation of propylene with aqueous RhCl(CO)(TPPTS)$_2$/TPPTS catalyst was investigated. Several kinetic equations were also evaluated based on the experimental data and the available knowledge on mechanism of hydroformylation.

2. Experimental

2.1. Reagents and apparatus

The water-soluble ligand tri(sodium-*m*-sulfonatophenyl) phosphine (TPPTS) and the rhodium catalyst precursor RhCl(CO)(TPPTS)$_2$ were provided by Sichuan University, China [20,21]. Propylene (≥99.9% purity), hydrogen (≥99.99%) and carbon monoxide (≥99.99%) were purchased from Huayuan Gas Chemicals Co., China.

Hydroformylation of propylene was carried out in a stirred autoclave with capacity of 500 ml. A schematic of experimental setup for kinetic studies is shown in Fig. 1. The reactor was equipped with an automatic temperature control system, which consists of an external electric heating jacket and an internal cooling loop. A pressure transducer-monitor system with high precision was also connected to the reactor for on-line measurement of pressure drop in the autoclave in the course of batch hydroformylation reaction. The gaseous reactants, i.e. C_3H_6, H_2 and CO, were purified by passing through dehydration, decarbonylation, desulfurization and deoxidation columns before charged into the reactor.

2.2. Experimental procedure

The catalyst solution was formed in situ by mixing known amounts of RhCl(CO)(TPPTS)$_2$ and TPPTS in

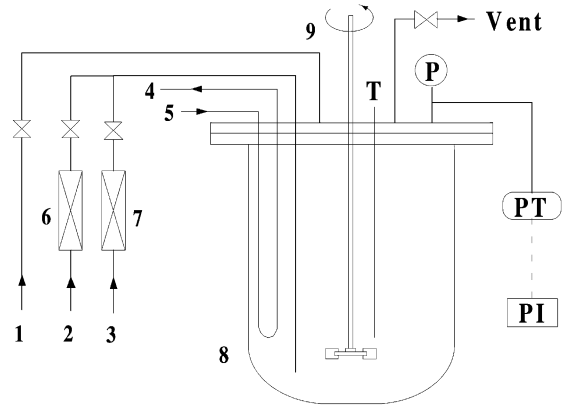

Fig. 1. Scheme of experimental setup for kinetic studies: (1) nitrogen; (2) syngas (H_2 and CO); (3) propylene; (4) cooling water out; (5) cooling water in; (6 and 7) columns of pre-treatment (including dehydration, decarbonylation, desulfurization and deoxidation); (8) autoclave; (9) stirrer; (T) thermocouple; (P) pressure gauge; (PT) pressure transducer; (PI) pressure monitor.

deionized water. It was added to the reactor under N_2 atmosphere and then heated to the desired temperature. The volume of aqueous phase was fixed at 100 ml in all experimental runs. The reactor was flushed with nitrogen and propylene successively, and propylene was then charged into the reactor up to the desired pressure. After that, the autoclave was charged with the syngas of CO and H_2 with specified ratio to a desired total pressure according to the experimental schedule. The above-mentioned procedures were done at very low agitation speed to ensure that no reaction took place up to this point. Hydroformylation reaction was allowed to start by increasing the agitation speed, meanwhile the pressure in the reactor was measured and recorded at regular time intervals. Since only hydroformylation products were observed under the experimental conditions, the corresponding stoichiometric equation is as follows:

$$C_3H_6 + CO + H_2 \xrightarrow{\text{catalyst}} n\text{- or } iso\text{-}\,C_3H_7CHO \qquad (1)$$

Therefore, the total pressure in the reactor at any instant can be described by [4]

$$p = p_0 - \int_0^t \frac{3Z_m R_G T V^L}{V^G} r \, dt \qquad (2)$$

where Z_m is the compressibility factor of gaseous reactant mixture at the reaction temperature (T) and was calculated by the Redlich–Kwong equation and the mixing rule proposed by Prausnitz–Chueh was adopted [22].

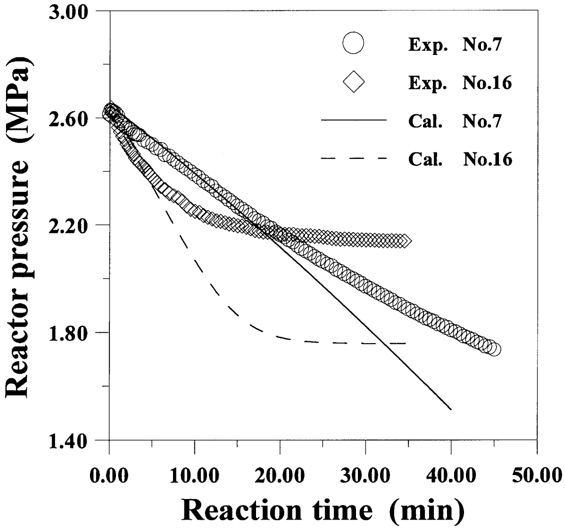

Fig. 2. Typical plots of experimental and calculated total pressure against reaction time of hydroformylation. Numbers 7 and 16 are the experimental serial number of the orthogonal table.

The typical pressure drop in the reactor is a function of reaction time, which is presented in Fig. 2. The initial rates of hydroformylation of propylene were then calculated from the plots of pressure drop with time using Eq. (2).

2.3. Analytical method

The contents of gas phase were analyzed using a gas chromatograph (SQ-206, Beijing Analytical Instrument Co., China) equipped with two columns: (i) a 4 m × 2 mm 5 Å molecular sieve for the analysis of syngas; (ii) a 2 m × 3 mm *n*-hexadecane on 6201 support for the analysis of olefin and CO. Argon and hydrogen were used as carrier gases, respectively. The chromatographic columns were connected to a thermal conductivity detector.

The liquid samples were extracted with ether and the extract was analyzed by the same gas chromatograph at the end of each run. A 4 m × 2 mm PEG-20M on 6201 support column and the thermal conductivity detector with hydrogen as the carrier gas were used.

3. Results and discussion

3.1. Effect of agitation speed

The effect of agitation speed on the initial rate of hydroformylation of propylene was investigated in preliminary runs. As shown in Fig. 3, the rate became independent of the agitation speed beyond 750 rpm. Hence, all the subsequent experiments were conducted with the agitation speed of 900 rpm with the confidence that the mass transfer resistance for gas reactants and catalyst was negligible in comparison with the intrinsic kinetics and the overall hydroformylation reaction was in the kinetic regime.

3.2. Orthogonal experimental design

The reaction pathway of hydroformylation of propylene using water-soluble catalyst is very complicated. It is necessary to study the effects of a number of factors, such as reactant and catalyst concentrations, pressure and temperature, on the hydroformylation reaction. Therefore, in this work the kinetics of hydroformylation were investigated by an orthogonal experimental design and an orthogonal table of $L_{18}(2^1 \times 3^7)$ was adopted to select the influencing factors and corresponding levels. The range of reaction conditions was selected by reference to the work on catalytic chemistry of propylene hydroformylation by Li et al. [23].

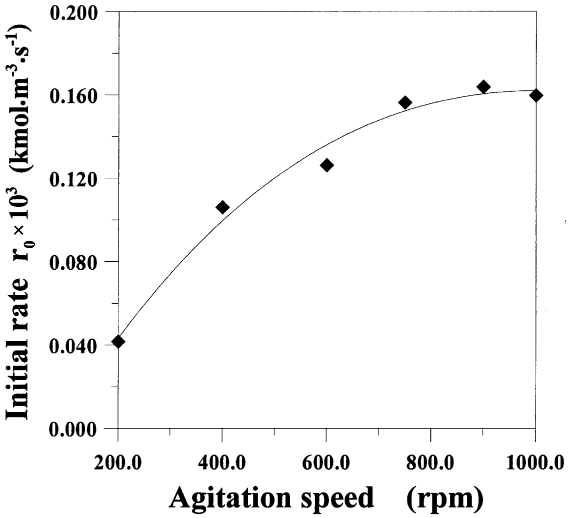

Fig. 3. Effect of agitation speed on the initial rate of propylene hydroformylation. Reaction conditions: $T = 373$ K, $p_0 = 3.1$ MPa, $p_P = 0.7$ MPa, $y_{H_2}/y_{CO} = 1/1$, $C_{Rh} = 1.0 \times 10^{-3}$ kmol/m^3, $C_L/C_{Rh} = 45/1$.

The schedule of kinetic experimental results are given in Table 1, in which the effects of total pressure, molar ratio of hydrogen/carbon monoxide, partial pressure of propylene, molar ratio of rhodium/TPPTS, catalyst concentration and temperature on the initial rate of propylene hydroformylation were evaluated comprehensively. The relative importance of factors to the hydroformylation rate and the optimal set of factor levels were determined by margin and variance analysis. According to the margin analysis presented in Table 1, the order of importance of the investigated factors on reaction rate and the optimal levels corresponding to the maximum rate are shown in Table 2. It was observed that the hydroformylation rate increased rapidly with the increase of reaction temperature. High partial pressure of hydrogen would enhance the reaction rate, while increasing the partial pressures of CO and C_3H_6 or molar ratio of ligand to rhodium was not beneficial to hydroformylation of propylene.

As shown in Table 3, the variance analysis of experiments was also made to evaluate the influence of various factors. Temperature was the most influential parameter while the influence of propylene partial pressure on the rate was the least significant. The results of variance analysis are similar to those of margin analysis, besides the different influence sequence of two secondary factors, i.e. the total pressure and catalyst concentration.

3.3. Normal/isomeric aldehyde ratio

n-Butyraldehyde and isobutyraldehyde were generally formed as the major products of propylene hydroformylation. Many efforts were made for achieving preferential formation of *n*-butyraldehyde owing to its high market price. In this work the regioselectivity of hydroformylation of propylene was also investigated and the ratio of normal/isomeric aldehyde was shown in Table 4. It can be observed that the molar ratio of *n*-butyraldehyde to isobutyraldehyde is in a wide range from 3.9 to 56.1 among investigated experimental conditions. Moreover, some runs showed industrially attractive high activity and selectivity.

Table 1
Orthogonal table of $L_{18}(2^1 \times 3^7)$ for kinetic experimental design and the corresponding margin analysis[a]

No.		p_P (MPa)	p_0 (Mpa)	y_{H_2}/y_{CO}		T (K)	$C_{Rh} \times 10^3$ (kmol/m^3)	C_L/C_{Rh}	$r_0 \times 10^3$ (kmol/(m^3 s))
1	1	1 (0.8)[b]	1 (2.6)	1 (1/4)	1	1 (363)	1 (0.5)	1 (30/1)	0.05181
2	1	1	2 (3.1)	2 (1/1)	2	2 (373)	2 (1.0)	2 (45/1)	0.1589
3	1	1	3 (3.6)	3 (4/1)	3	3 (383)	3 (1.5)	3 (60/1)	0.1060
4	1	2 (0.7)	1	1	2	2	3	3	0.04730
5	1	2	2	2	3	3	1	1	0.3684
6	1	2	3	3	1	1	2	2	0.06439
7	1	3 (0.6)	1	2	1	3	2	3	0.1877
8	1	3	2	3	2	1	3	1	0.1605
9	1	3	3	1	3	2	1	2	0.09027
10	2	1	1	3	3	2	2	1	0.3169
11	2	1	2	1	1	3	3	2	0.1644
12	2	1	3	2	2	1	1	3	0.03485
13	2	2	1	2	3	1	3	2	0.04020
14	2	2	2	3	1	2	1	3	0.1619
15	2	2	3	1	2	3	2	1	0.2074
16	2	3	1	3	2	3	1	2	0.3787
17	2	3	2	1	3	1	2	3	0.03035
18	2	3	3	2	1	2	3	1	0.1544
T_{r1j}[c]	1.246	0.8466	1.031	0.6042	0.7957	0.3844	1.096	1.272	
T_{r2j}	1.508	0.8970	1.060	0.9541	0.9973	0.9385	0.9733	0.9086	
T_{r3j}		1.011	0.6624	1.196	0.9612	1.431	0.6849	0.5737	
R_{rj}[d]	0.2620	0.1644	0.3976	0.5918	0.2016	1.047	0.4111	0.6983	

[a] $r_T = \sum_{k=1}^{18} r_{0k} = \sum_{i=1}^{n_j} T_{rij}$, n_j is the number of levels of factor j ($r_T = 2.754$).

[b] Selected parameter values at different levels: p_P at 16 °C; p_0 at reaction temperature.

[c] Total values of rates at level i of factor j, i.e. $T_{rij} = \sum_{k=1}^{m_i} r_{0k}$, m_i is the number of replicate experiments at level i of factor j ($i = 1, 2, 3$; $j = 1, 2, \ldots, 8$).

[d] $R_{rj} = \max(T_{rij}) - \min(T_{rij})$.

For example, the turnover frequency (TOF) of no. 14 in Table 1 is about 0.3 kmol product/(kmol catalyst s) with a normal/isomeric aldehyde ratio of about 30, which coincides with the reported activity of Rh/TPPTS complex catalysts (14–16 min^{-1}) [24] and is close to that of homogeneous catalysis with Co complexes (below 0.35 s^{-1}) [5]. Although no obvious relationship between reaction process parameters and normal/isomeric aldehyde ratio was found, very high selectivity to *n*-butyraldehyde could be obtained under suitable reaction conditions.

Table 2
Relative importance of various factors to the initial rate of hydroformylation determined by margin analysis

Relative importance	Primary → Secondary					
Factor	T	C_L/C_{Rh}	y_{H_2}/y_{CO}	C_{Rh}	p_0	p_P
Level	383	30/1	4/1	0.5	3.1	0.6

3.4. Kinetic rate model

For the purpose of quantitative analysis of the complex relationship between different factors and the reaction rate, a variety of rate models were attempted to describe the kinetics of propylene hydroformylation in the aqueous system. Above all, the following simple power rate equation was used to fit the experimental data by means of multiple linear regression:

$$r_0 = A_0 \exp\left(\frac{-E}{R_G T}\right) p_{H_2}{}^{k_1} p_{CO}{}^{k_2} p_P{}^{k_3} C_{Rh}{}^{k_4} C_L{}^{k_5} \quad (3)$$

The logarithmic of the above equation was adopted for linear regression. The fitting objective function was chosen as the least square of error between predicted and experimental logarithmic rates as defined by

$$\phi_{\min} = \sum_{i=1}^{N} (\ln r_{0i}^{\text{cal}} - \ln r_{0i}^{\text{exp}})^2 \quad (4)$$

Table 3
Results of variance analysis of the orthogonal table

Source of variance	S_j[a]	f_j[b]	S_j/f_j	F_j[c]	F_j^{Δ}	Significance level
Blank column no. 1	0.003584	1	0.003584			
p_{P}	0.002620	2	0.001310	0.4888		
p_0	0.01585	2	0.007926	2.957	3.463	<0.1
$y_{\mathrm{H_2}}/y_{\mathrm{CO}}$	0.02998	2	0.01499	5.593	6.549	<0.025
Blank column no. 5	0.004042	2	0.002021			
T	0.08892	2	0.04446	16.59	19.42	<0.005
C_{Rh}	0.01517	2	0.007587	2.831	3.315	<0.1
$C_{\mathrm{L}}/C_{\mathrm{Rh}}$	0.03981	2	0.01990	7.425	8.694	<0.025
e	0.01340	5	0.002680			
e^{Δ}	0.01602	7	0.002289			
S_T	0.2058	17	0.01210	4.515	5.286	<0.025

[a] $S_j = m_i\sum_{i=1}^{n_j}(T_{rij}/m_i - r_{\mathrm{av}})^2 = \frac{1}{m_i}\sum_{i=1}^{n_j}T_{rij}^2 - r_T^2/18$, $S_T = \sum_{k=1}^{18}(r_k - r_{\mathrm{av}})^2$, $S_e = S_T - \sum_{i=1}^{K_i}S_i$, m_i is the number of replicate experiments at level i of factor j, K_i is the total number of non-blank columns ($i = 1, 2, 3$; $j = 1, 2, \ldots, 8$).

[b] Degree of freedom $f_j = n_j - 1$, $f_e = f_T - \sum_{i=1}^{K_i}f_i$, n_j is the number of levels of factor j.

[c] $F_j = (S_j/f_j)/(S_e/f_e)$, $F_j^{\Delta} = (S_j/f_j)/(S_e^{\Delta}/f_e^{\Delta})$, Δ indexes the column p_{P} merged into the error.

Table 4
Molar ratio of *n*-butyraldehyde/isobutyraldehyde obtained from part of experiments in the orthogonal table

Run number	Normal/isomeric aldehyde
2	12.5
3	56.1
4	11.6
5	3.9
11	8.5
14	30.5
15	5.7
18	9.3

The values of rate parameters are presented in Table 5. The rates predicted using Eq. (3) were found to agree with the experimental data with an average relative error of 16.1%. The apparent activation energy is about 77 kJ/mol, which was calculated using the Arrhenius equation. As shown in Fig. 4, the

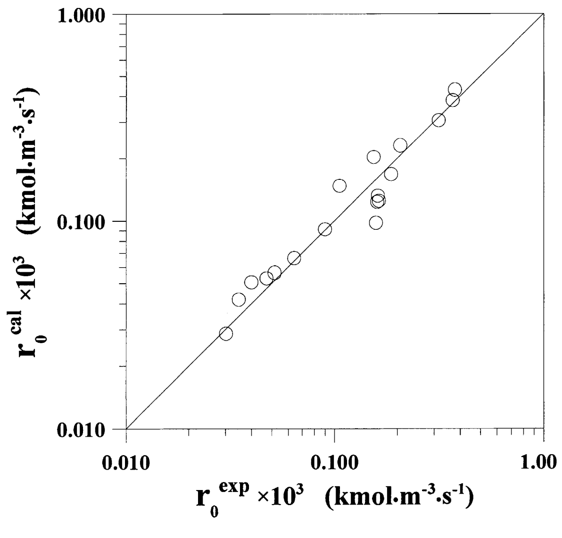

Fig. 4. Comparison of hydroformylation reaction rates calculated from the empirical model of Eq. (3) with experimental data.

Table 5
Values of $\phi_{\min}$ and kinetic parameters of two kinetic equations[a]

Model	A_0	E	k_1	k_2	k_3	k_4	k_5	$\phi_{\min}$[b]
Eq. (3)	1.286×10^{8}	76.78	0.2515	−0.6403	−0.9808	0.9789	−1.188	1.555×10^{-8}
Eq. (6)	7.545×10^{15}	83.15	13.67	5.641	4.995	–	18.23	1.155×10^{-8}

[a] The units of r_0, E and partial pressure (p_i) are kmol/(m^3 s), kJ/mol and MPa, respectively.

[b] $\phi_{\min} = \sum_{i=1}^{N}(r_{0i}^{\mathrm{cal}} - r_{0i}^{\mathrm{exp}})^2$.

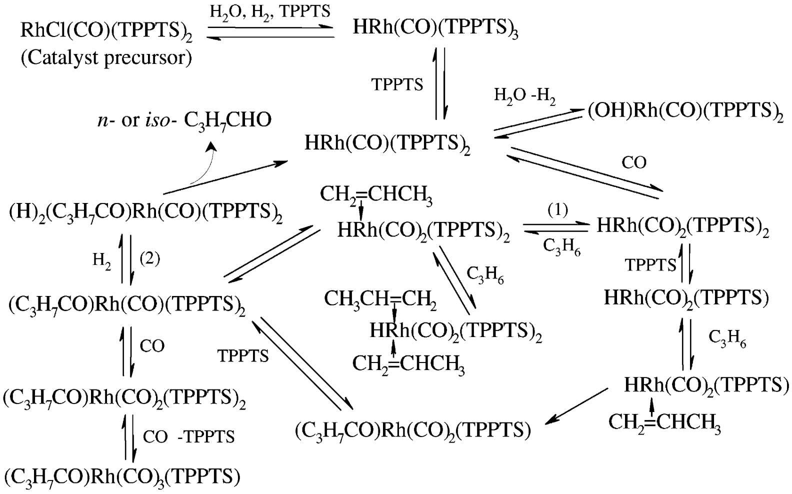

Fig. 5. Conjecture of the mechanism of propylene hydroformylation using water-soluble catalyst.

calculated rates of hydroformylation were compared reasonably well with the observed rates.

Normally, it is more meaningful to derive rate models on the basis of the actual mechanism, assuming different rate-controlling steps. Up to now, the mechanism of hydroformylation of propylene using a water-soluble rhodium complex catalyst has not been completely understood. Different reaction mechanisms proposed in the literature [4,6–8,15,25] for homogeneous hydroformylation of olefins were summarized in Fig. 5, which shows the possible reaction pathway. Brown and Wilkinson [26] suggested that the oxidative addition of hydrogen to the acylcarbonyl species (step (1) in Fig. 5) was the rate-limiting step. However, other investigators [15,27] suggested that the rate-limiting step might be the addition of olefin to the active catalyst species (step (2) in Fig. 5) in certain cases.

If the addition of C_3H_6 to the active species $HRh(CO)_2(TPPTS)_2$ was a rate-determining step, the following complex rate equation was derived through some simplification of the mechanism:

$$r_0 = \frac{k_1 C_{H_2} C_{CO} C_P C_{Rh}}{k_2 + k_3 C_{H_2} + k_4 C_{CO} + k_5 C_{H_2} C_{CO} + k_6 C_P + k_7 C_{CO}^2 / C_L + C_{H_2} C_L} \tag{5}$$

where $k_1 \sim k_7$ are positive constants derived from the equilibrium constants of different steps in the hydroformylation mechanism, thus these constants are dependent upon the reaction temperature. Some other highly complicated rate models with a large number of parameters can also be derived if various steps are assumed as rate-controlling steps and different simplifications are adopted. In this case, more unknown parameters should be evaluated from limited experimental data and unreliable parameter values would be obtained. Therefore, it is preferred to introduce some simplified semi-empirical rate equations, which are consistent with the observed reaction behavior. Various empirical rate equations were taken into consideration in this work and Eq. (6) was found to be the best for representing the experimental data.

$$r_0 = \frac{A_0 \exp(-E/(R_G T)) p_{H_2} p_{CO} p_P C_{Rh}}{(1 + k_1 p_{H_2})(1 + k_2 p_{CO})^2 (1 + k_3 p_P)^2 (1 + k_5 C_L)^3} \tag{6}$$

$$\phi_{\min} = \sum_{i=1}^{N} (r_{0i}^{\mathrm{cal}} - r_{0i}^{\mathrm{exp}})^2 \tag{7}$$

The parameters in Eq. (6), as shown in Table 5, were evaluated by a non-linear least square optimization routine using a modified Levenberg–Marquardt algorithm. It was found the fitting to Eq. (6) was more satisfactory. The average deviation between the predicted and the experimental data was about 14.1%. The parity plot in Fig. 6 also indicates a better deviation distribution. The activation energy of this reaction

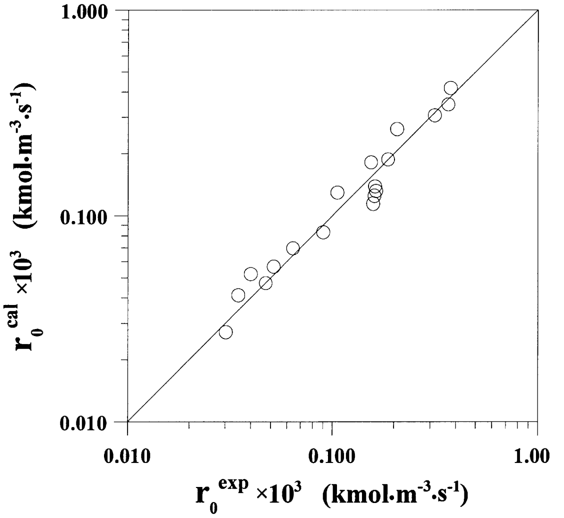

Fig. 6. Comparison of hydroformylation reaction rates calculated from the semi-empirical model (Eq. (6)) with experimental data.

evaluated from Eq. (6) was about 83 kJ/mol and close to that obtained from Eq. (3).

According to above kinetic rate models, the increase of hydrogen partial pressure or rhodium catalyst concentration would lead to the increase of the hydroformylation rate, but the rate decreased with the increase of the partial pressure of CO or C_3H_6. Excessive TPPTS ligand in the catalyst solution would slow down the initial rate of propylene hydroformylation.

In order to verify the applicability of the empirical kinetics, Eqs. (2) and (6) were used to calculate the pressure drop in the autoclave during hydroformylation runs. Fig. 2 compares the change of the calculated and measured total pressures with reaction time. At the initial stage of hydroformylation reaction, the calculated pressure coincides with the observed pressure very well. However, the correspondence between calculated and measured pressures becomes unsatisfactory as reaction proceeds further, even though the same trends are observed. This suggests that the empirical kinetic equation represents well the initial period of hydroformylation only and is not directly applicable to the circumstances with decreased total pressure in the autoclave. The kinetic equation of initial reaction rate is certainly beneficial for studying the hydroformylation mechanism. In order to provide rate data for process design, the reaction rate during the whole experimental runs should be integrated into the kinetic equations.

4. Conclusions

The kinetics of hydroformylation of propylene using water-soluble $RhCl(CO)(TPPTS)_2$/TPPTS catalyst has been investigated by an orthogonal experimental design. The relative importance of various factors, such as temperature, pressure and catalyst concentration, to the initial rate of hydroformylation and the corresponding optimal factor levels were determined by margin and variance analysis. The kinetic rate models showed fractional order of dependence with respect to partial pressure of H_2, CO and C_3H_6, catalyst concentration and TPPTS concentration. The kinetic rate was found to be in positive order with respect to hydrogen partial pressure and rhodium catalyst concentration. However, higher CO and C_3H_6 pressure or TPPTS concentration showed substrate-inhibited kinetics. The activation energy of hydroformylation of propylene was about $75 \sim 85$ kJ/mol. Some runs of orthogonal experiments showed very high selectivity to *n*-butyraldehyde up to 56.1, which is industrially beneficial. Experimental data and observations provide relevant information for further engineering study on hydroformylation of propylene and other low carbon olefins.

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