

Kinetic Studies on the Hydroformylation of 1-Hexene Using $\text{RhCl}(\text{AsPh}_3)_3$ as a Catalyst

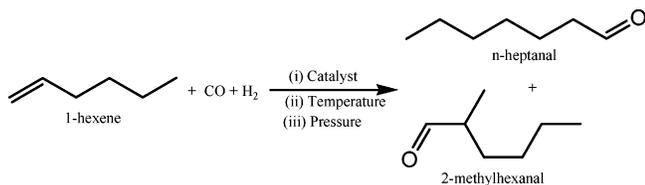
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The detail kinetic study of 1-hexene hydroformylation using $\text{RhCl}(\text{AsPh}_3)_3$ as a homogeneous catalyst has been investigated. The present kinetic study involves the effect of concentrations of 1-hexene and catalyst, partial pressures of CO and H_2 , agitation speed, and temperature on the rate of hydroformylation. Additionally, the studies of deactivation of the catalyst $\text{RhCl}(\text{AsPh}_3)_3$ with temperature have also been done. It was observed that the rates of hydroformylation reaction were increased on increasing the initial concentrations of 1-hexene, catalyst, and partial pressures of CO and H_2 at lower ranges. The activation energy was found to be 42.74 kJ/mol. A nonlinear semiempirical kinetic model was also developed to be the best fit with 11.6% error.

1. Introduction

Homogeneous hydroformylation, a reaction between olefinic double bond and the mixture of hydrogen and carbon monoxide (synthesis gas) leading to aldehydes and alcohols as the principal products, is an important reaction from industrial and academic viewpoints.^{1,2}



Worldwide,³ approximately 8.8 million t/yr of oxo (aldehydes and alcohols) chemicals are produced using hydroformylation reaction. These oxo chemicals find applications in the manufacture of soaps, detergents, adhesives, plastisizers, and solvents. Commercially, hydroformylation of olefins is done with the metal complexes of Co and Rh with triphenylphosphine (PPh_3) as well as triphenylphosphine trisulfonate (TPPTS) in homogeneous and biphasic medium, respectively.

Presently the efforts in hydroformylation research are mainly focused toward developing novel catalyst/ligand synthesis, moderate reaction conditions, regio-selectivities of products, and facile separation of the catalysts from reaction products.⁴ The triphenylphosphine ligand and its derivatives are most the cited ligands in the catalysts reported for the hydroformylation of olefins.^{5,6} Studies on the use of the ligands of other group V elements for hydroformylation catalysts are sparse. As the electronic properties of triphenylarsine (AsPh_3) are similar to its phosphorus counterpart in their ligand behavior, hence it may be reasonable to expect that

AsPh_3 like PPh_3 would stabilize the lower oxidation state of transition metals. Furthermore, the σ -donor/ π -acceptor ratio for EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) ligand shows^{7–9} the following trend: $\text{SbPh}_3 > \text{PPh}_3 > \text{AsPh}_3$. Generally, the ligands with low basic character having less σ -donor ability favor faster reaction rates toward hydroformylation. Therefore, due to lower σ -donor ability and lower basicity, one would expect a faster rate of hydroformylation reaction with AsPh_3 ligand as compared to those for PPh_3 and SbPh_3 . In fact, in recent reports^{10,11} on the hydroformylation of olefins, higher catalytic activity of transition metal complexes of arsine is also reported. The synthesis of complex $\text{RhCl}(\text{AsPh}_3)_3$, an analogue of $\text{RhCl}(\text{PPh}_3)_3$, has been reported by Magee and Wilkinson,¹² but they have not studied hydroformylation with this complex. In comparative studies¹³ on hydroformylation of 1-hexene with Rh, Co, and Ru complexes having group V elements ligands (PPh_3 , AsPh_3 , and SbPh_3), we recently observed similar activities for Rh/ PPh_3 and Rh/ AsPh_3 catalyst systems with the former showing higher n/iso ratio of aldehydes. Due to its commercial significance, kinetics and mass transfer analysis of the hydroformylation reaction using PPh_3 and its derivatives as a ligand are reported.^{14,15} However, similar studies with AsPh_3 as a ligand are not reported so far. In this paper, we present the first report on the kinetic analysis of the hydroformylation of 1-hexene using $\text{RhCl}(\text{AsPh}_3)_3$ as a catalyst. Ideally, the complex $\text{RhH}(\text{CO})(\text{AsPh}_3)_3$ could have been chosen to have proper comparison with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ catalyst in place of presently used $\text{RhCl}(\text{AsPh}_3)_3$ catalyst for hydroformylation reactions. It is worthy to mention here that the hydroformylation activity of $\text{RhCl}(\text{AsPh}_3)_3$ would be lower than that of $\text{RhH}(\text{CO})(\text{AsPh}_3)_3$ unless a strong base is added to remove the HCl formed during active catalyst formation with $\text{RhCl}(\text{AsPh}_3)_3$. However, the complex $\text{RhH}(\text{CO})(\text{AsPh}_3)_3$ could not be synthesized and isolated, hence the present study was focused on the $\text{RhCl}(\text{AsPh}_3)_3$ complex. The present study describes the effect of concentrations of 1-hexene and catalyst, partial pressures of CO and H_2 , reaction temperature, and agitation speed on the rate of hydroformylation.

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Finally, a rate equation has been anticipated based on these rate data. It was observed that, on increasing the temperature, the conversion of 1-hexene and selectivity toward the aldehydes decreased significantly. This could be due to the deactivation of catalyst on increasing temperature. Therefore, deactivation of $\text{RhCl}(\text{AsPh}_3)_3$ catalyst due to thermal pretreatment under syn-gas atmosphere was also studied in the present work.

2. Experimental Section

2.1. Materials. 1-Hexene (99.9%), benzene (99.8%), and *n*-decane (99.9%) were purchased from Sigma-Aldrich, USA. Rhodium trichloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) and triphenylarsine (AsPh_3) were procured from E. Merck, USA. CO (99.8%) and H_2 (99.8%) were purchased from Alchemie Gases and Chemicals Pvt. Ltd., India. The catalyst $\text{RhCl}(\text{AsPh}_3)_3$ was synthesized using procedure reported by Mague and Wilkinson¹² and characterized by FT-IR spectroscopy (Perkin-Elmer FT-IR Spectrum GX). The appearance of ν (Rh-As) band at 473 cm^{-1} in the FT-IR spectra confirms the formation of $\text{RhCl}(\text{AsPh}_3)_3$ complex. The elemental analysis (Perkin-Elmer CHNS/O 2400 analyzer) CHN; %C (calcd) 60.8 (61.3); %H (calcd) 4.0 (4.2).

2.2. Hydroformylation Reactions and Products Analysis. All kinetic experiments were carried out in 100 mL stainless steel autoclave reactor (Autoclave Engineers, USA, model E 01055A) equipped with a controlling unit. The autoclave is designed with a three-gas liner; one for gas inlet, second for gas ventilation, and third for a sampling valve. The autoclave is provided with four-blade propeller-type magnetic stirrer. The propellers in the reactor are fixed at a position in which an improved gas distribution is observed leading to intensive gas-liquid contact with gas bubbles reacting at all parts of the liquid.

In a typical experiment, the desired quantity of 1-hexene, catalyst, *n*-decane (as an internal gas chromatography (GC) standard), and benzene (50 mL) were charged in the autoclave. The autoclave was flushed twice with N_2 prior to successively introducing CO and H_2 at a desired pressure. The reactor was then brought to a desired reaction temperature. At that time, a sample of the reaction mixture was withdrawn, which was considered as the zero time reading. The hydroformylation reaction was then initiated by starting the stirrer. The reaction was then continued at constant pressure, by supplying CO and H_2 (1:1) from the reservoir vessel. For kinetic studies, liquid samples were withdrawn during the experiment by a sampling valve at fixed time interval. Sampling resulted in a pressure loss of 2–3 psig each time. After the set reaction time, the reaction was quenched by disconnecting the gas supply to the reactor. The autoclave was then brought to room temperature with the help of a cooling system, and the pressure drops were also noted. The product analysis was carried out using GC (Shimadzu 17A, Japan), having 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.32 mm diameter) and flame ionization detector (FID). The initial column temperature was increased from 40 to 200 °C at the rate of 10 °C/min. N_2 gas (3.4 mL/min) was used as a carrier gas. The temperature of injection port and FID were kept constant at 200 °C during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical GC conditions.

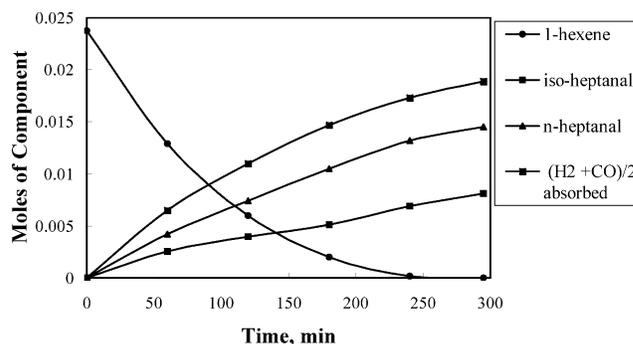


Figure 1. Concentration profile of 1-hexene hydroformylation at $[\text{1-hexene}] = 0.50\text{ mol/L}$; $[\text{catalyst}] = 20.00 \times 10^{-5}\text{ mol/L}$; $p_{\text{CO}} = 2.00\text{ MPa}$; $p_{\text{H}_2} = 2.00\text{ MPa}$; temperature = 353 K; and agitation speed = 850 rpm.

2.3. Thermal Deactivation of $\text{RhCl}(\text{AsPh}_3)_3$ Catalyst. It is worthy to mention here that the purpose behind the thermal deactivation studies was to test the activity of the $\text{RhCl}(\text{AsPh}_3)_3$ catalyst after preheat treatment temperature under syn-gas atmosphere, and no attempt has been taken for regeneration of the catalyst. In a typical thermal deactivation study, a known amount of the catalyst $\text{RhCl}(\text{AsPh}_3)_3$ dissolved in solvent benzene (50 mL) was charged into the reactor, and the reactor was flushed with N_2 before introducing syn-gas at desired pressure to the reactor. The reactor was then brought to desired preheat treatment temperature. After the set reaction time of preheat treatment, the reaction mixture was cooled to room temperature rapidly to avoid any side reaction. Then a fixed amount of 1-hexene (0.50 mol/L in all case) along with *n*-decane as an internal standard were charged in the reactor and the conventional hydroformylation reaction as described in earlier section 2.2 was started at 353 K in order to test the activity of the catalyst.

During the preheat treatment reactions, all other parameters were kept constant except temperature. The studies were done at the partial pressure of CO and H_2 at 2.00 MPa (1:1), olefin concentration 0.50 mol/L, and catalyst concentration $20.00 \times 10^{-5}\text{ mol/L}$. The preheat treatment of catalyst was done for 60 min at 353, 423, and 473 K and also for 30 min at 373, 423, and 473 K.

2.4. Reproducibility and Material Balance. To ensure the reproducibility of hydroformylation of 1-hexene using $\text{RhCl}(\text{AsPh}_3)_3$ as a catalyst, four experiments were done under identical conditions. The conversions, selectivities, and *n*/iso ratio of the aldehydes were found within 10% variation, confirming the reproducibility of results. The amounts of products formed and amount of 1-hexene and CO + H_2 consumed were compared in order to ensure the material balance of the reaction. During all the kinetic experiments, the aldehyde selectivity was observed in the range of 92–98%. A typical concentration profile of reactants and products are given in Figure 1 and Table 1.

2.5. Kinetic Analysis and Selectivity Studies. The parameters, which might have pronounced effects on the rate of hydroformylation, include concentration of olefin and catalyst, partial pressure of carbon monoxide and hydrogen, agitation speed, and temperature. The experiments were carried out by varying these parameters. The range of conditions used for kinetic analysis is given in Table 2. Under the employed reaction conditions, *n*-heptanal and 2-methylhexanal were the

Table 1. Material Balance of Hydroformylation of 1-Hexene Using $\text{RhCl}(\text{AsPh}_3)_3$ as a Catalyst^a

run	1-hexene $\times 10^2$, mol		partial pressure of CO and H ₂ , MPa		total aldehyde $\times 10^2$, mol	material balance (%) 1-hexene
	initial	final	CO	H ₂		
1	1.18	0.0	2.00	2.00	1.16	98.30
2	1.78	0.0	2.00	2.00	1.70	95.50
3	2.14	0.0	2.00	2.00	1.97	92.05
4	2.38	0.0	2.00	2.00	2.25	94.53
5	4.75	0.0	2.00	2.00	4.50	94.74
6	9.50	0.0	2.00	2.00	9.10	95.78

^a Reaction conditions: [catalyst] = 20.00×10^{-5} mol/L, temperature = 353 K, and agitation speed = 850 rpm. Reaction time = 300 min.

Table 2. Range of Conditions Studied for the Kinetics of Hydroformylation Using $\text{RhCl}(\text{AsPh}_3)_3$

concentration of 1-hexene, mol/L	0.25–1.95
concentration of catalyst, mol/L	4.92×10^{-5} – 49.20×10^{-5}
temperature, K	333–373
pCO, MPa	0.20–2.50
pH ₂ , MPa	0.50–3.00
solvent	benzene
reaction volume, mL	50
agitation speed, rpm	50–850

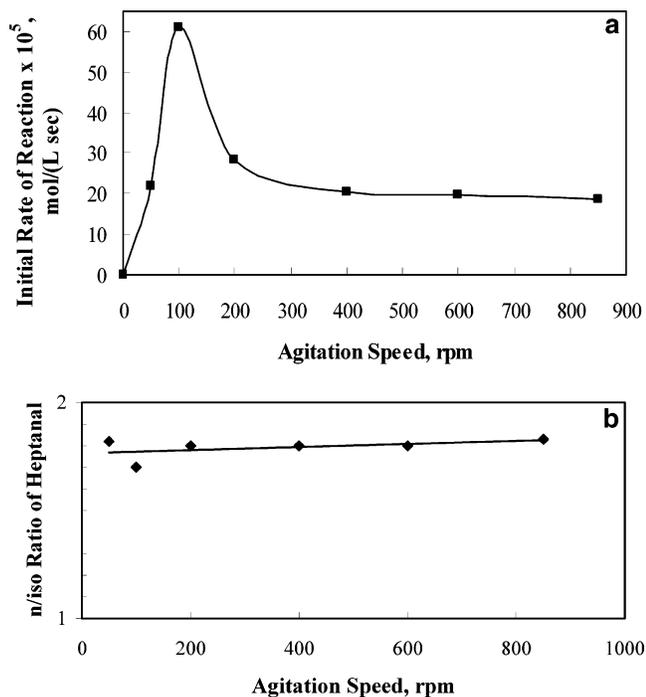


Figure 2. Effect of agitation speed on hydroformylation reaction at [1-hexene] = 0.50 mol/L; [catalyst] = 20.00×10^{-5} mol/L; pCO = 2.00 MPa; pH₂ = 2.00 MPa; temperature = 353 K; and agitation speed = 50–850 rpm.

major products formed during $\text{RhCl}(\text{AsPh}_3)_3$ catalyzed hydroformylation of 1-hexene.

3. Results and Discussion

3.1. Effect of Agitation Speed. The dependence of rate on agitation speed (Figure 2a) shows that the rate of hydroformylation increased on increasing the agitation speed from 50 to 100 rpm followed by a decrease with further increasing agitation speed before reaching a steady state. At the lower agitation speed, the initial concentration of dissolved gases is less, which indicates diffusion-controlled reaction; hence, the rate of reaction increases. Furthermore, on increasing the agitation

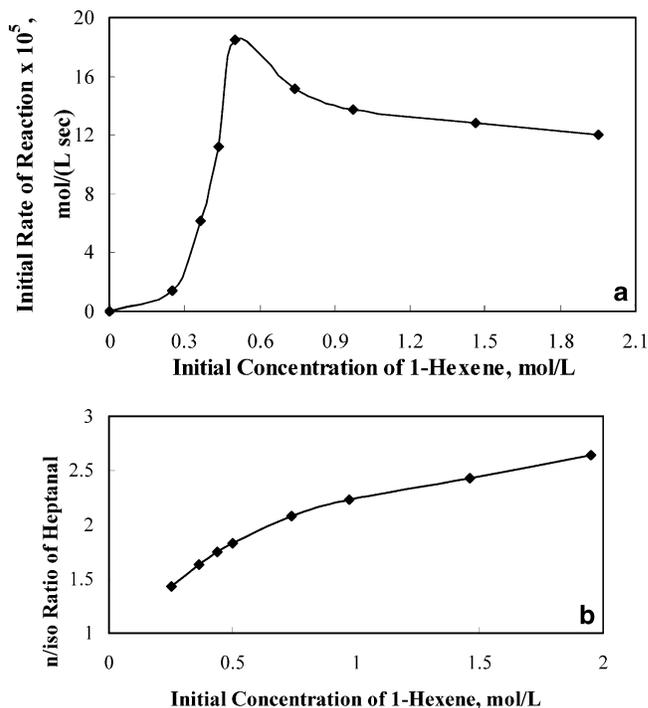


Figure 3. Effect of 1-hexene concentrations on hydroformylation reaction at [1-hexene] = 0.25–1.95 mol/L; [catalyst] = 20.00×10^{-5} mol/L; pCO = 2.00 MPa; pH₂ = 2.00 MPa; temperature = 353 K; and agitation speed = 850 rpm.

speed, the initial concentrations of dissolved gases significantly¹⁵ increased and the concentration of dissolved CO in reaction mixture becomes higher as solubility of CO > H₂ in benzene, which leads to a decreased rate. The agitation speed above 400 rpm has no effect upon the reaction rate (Figure 2a), which indicates the absence of mass transfer resistance, and the reaction is under kinetic regime. To ensure the purely kinetic regime, all the experiments were carried out at 850 rpm. The dependence of n/iso ratio of formation of aldehyde on agitation speed is shown in Figure 2b. The n/iso ratio of heptanal was found to be nearly constant by varying the agitation speed from 50 to 850 rpm.

3.2. Effect of 1-Hexene and Catalyst Concentration. The rates of reaction were increased (Figure 3a) on increasing the concentration of 1-hexene up to a certain limit, beyond which rates decrease with increasing concentration of 1-hexene. In the present study, the Rh/AsPh₃ system is showing substrate-inhibited kinetics for 1-hexene, which is an indication of an alteration of the rate-determining step and, consequently, a change in reaction pathway. Similar results were reported for the Rh/PPh₃ system.¹⁴ A positive order dependence on olefin concentration until a critical substrate/catalyst ratio is reached, after which a negative or even independence is reported,¹⁶ which is termed as saturation kinetics and is usually attributed to a shift in the rate-determining step. The dependence of n/iso ratio of the formation of heptanal is shown in Figure 3b. The n/iso ratio of heptanal was found to increase linearly on increasing the initial concentration of 1-hexene. On increasing 1-hexene concentration 7.8-fold (from 0.25 to 1.95 mol/L), the n/iso ratio was observed to increase 1.8-fold (from 1.4 to 2.6).

The observed trend on the effect of catalyst concentration (Figure 4a) on the rate of reaction shows that

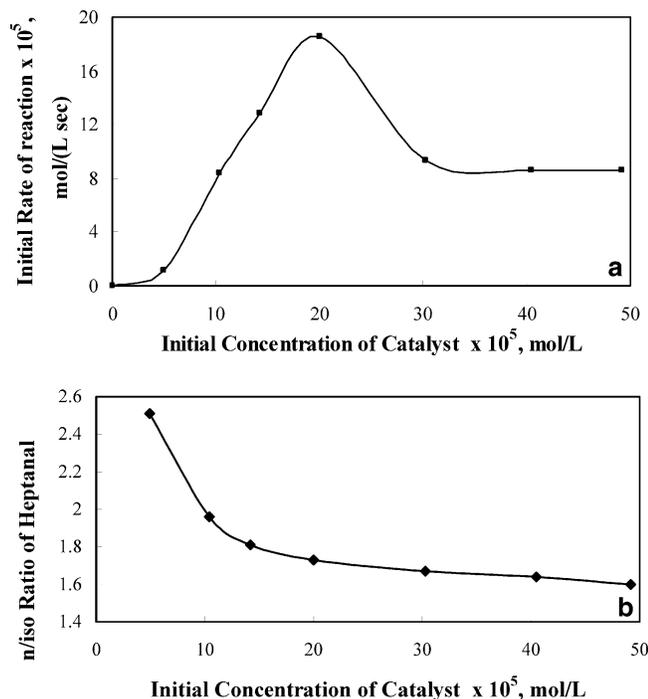
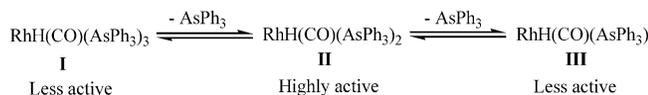


Figure 4. Effect of catalyst concentrations on hydroformylation reaction at [1-hexene] = 0.50 mol/L; [catalyst] = 4.92×10^{-5} – 49.2×10^{-5} ; $p_{\text{CO}} = 2.00$ MPa; $p_{\text{H}_2} = 2.00$ MPa; temperature = 353 K; and agitation speed = 850 rpm.

initially the rate of hydroformylation increases on increasing catalyst concentration up to 20.00×10^{-5} mol/L followed by a decrease and then becomes independent of catalyst concentration. It is observed that there is a critical catalyst concentration (4.92×10^{-5} mol/L) of $\text{RhCl}(\text{AsPh}_3)_3$ below which reaction does not proceed. Similar observation is also reported¹⁴ with Rh/PPh_3 . However, additionally it was observed in the present study that, above a certain catalyst concentration, the rate of hydroformylation of 1-hexene is independent of the catalyst concentration. These observations can be explained in terms of the Rh-intermediate species present at various catalyst concentrations as described by Brown and Wilkinson.¹⁷ According to the following equilibrium, at very low catalyst concentration the concentration of species (I) will be abundant, which is less active toward hydroformylation; hence, the rate is slow or even zero. On the other hand, at very high catalyst concentration, the concentration of less active species (III) for hydroformylation will be dominant. Moreover, the Rh–As bond in $\text{RhH}(\text{CO})(\text{AsPh}_3)_2$ is more liable^{7–9} to break than the Rh–P bond in $\text{RhH}(\text{CO})(\text{PPh}_3)_2$.



The trend of the n/iso ratio with catalyst concentrations is shown in Figure 4b. Unlike, the Rh/PPh_3 system¹⁷ the n/iso ratio with the present Rh/AsPh_3 system decreases on increasing catalyst concentrations. The n/iso ratio of heptanal falls from 2.5 to 1.5 by increasing catalyst concentration from 4.92×10^{-5} to 49.20×10^{-5} mol/L. Furthermore, on increasing the catalyst concentration, the concentration of the ligand AsPh_3 having higher π -acidity would be enhanced.

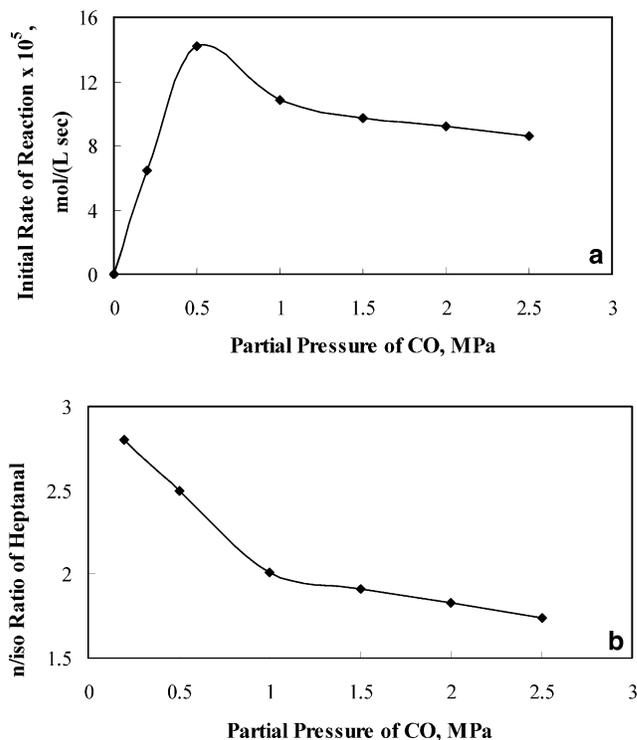
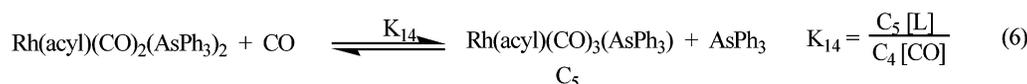
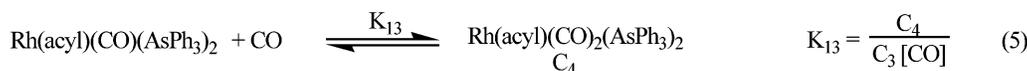
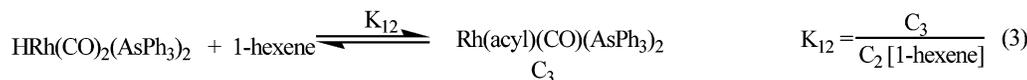
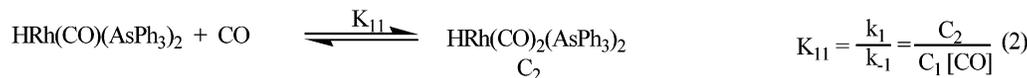


Figure 5. Effect of partial pressure of carbon monoxide on hydroformylation reaction at [1-hexene] = 0.50 mol/L; [catalyst] = 20.00×10^{-5} mol/L; $p_{\text{CO}} = 0.20$ – 2.50 MPa; $p_{\text{H}_2} = 2.00$ MPa; temperature = 353 K; and agitation speed = 850 rpm.

Consequently, the polarity of the Rh–H bond will increase,¹⁸ which will further increase the extent of Markovnikov addition leading to lower n/iso ratio for the aldehydes.

3.3 Effect of Partial Pressure of Carbon Monoxide. The rate of hydroformylation increases up to a certain limit and is followed by a decrease of further increasing the CO partial pressure (Figure 5a). A rate inhibition trend at higher partial pressure of CO confirms the formation of hydroformylation inactive acyl species, $(\text{RCO})\text{Rh}(\text{CO})_2(\text{AsPh}_3)_2$ and/or $(\text{RCO})\text{Rh}(\text{CO})_3(\text{AsPh}_3)$ (R = alkyl groups). Davis and Erkey¹⁶ reported that there might be some possibility of shifting of rate-determining step in hydroformylation reaction when the basicity of ligand varies. The first possibility is that the rate-determining step is the dissociation of CO from species 1 (Scheme 1). In case of a less basic ligand (like AsPh_3), the alkyl intermediate species 5 (Scheme 1) becomes the dominant species. This was attributed to a shift in the rate-determining step from dissociation of CO from species 1 to a step after formation of species 5 for less basic intermediate complex because of weakening of the Rh–carbonyl bond due to decreased basicity of ligand. The dependence of n/iso ratio of formation of heptanal is shown in Figure 5b. For the Rh/AsPh_3 system, the n/iso ratio of heptanal was found to decrease on increasing partial pressure of CO. The n/iso ratio drops down from 2.8 to 1.7 on increasing the partial pressure of CO from 0.20 to 2.50 MPa. Generally, it is assumed that at low partial pressure of CO the metal center becomes sterically more crowded. Accordingly, the formation of normal aldehyde is favored through anti-Markovnikov addition.

3.4. Effect of Partial Pressure of Hydrogen. The rate of hydroformylation was found (Figure 6a) to increase on increasing partial pressure of hydrogen. The

Scheme 2. Some Important Reaction Steps Based on Actual Mechanism**Table 3. Consumption of 1-Hexene with Time after Heat Treatment of the Catalyst $\text{RhCl}(\text{AsPh}_3)_3^a$**

time, min	temperature of preheat treatment, K/ time for preheat treatment, min					
	353/60	373/30	423/30	423/60	473/30	473/60
	Concentration of 1-Hexene, mol/L					
0	0.50	0.50	0.50	0.50	0.50	0.50
60	0.50	0.50	0.50	0.50	0.50	0.50
120	0.50	0.50	0.50	0.50	0.50	0.50
180	0.28	0.33	0.37	0.41	0.50	0.50
240	0.10	0.14	0.18	0.23	0.50	0.50
300	0.06	0.08	0.17	0.20	0.39	0.49

^a Reaction conditions: [1-hexene] = 0.50 mol/L; [catalyst] = 20.00×10^{-5} mol/L; pCO = 2.00 MPa; p H_2 = 2.00 MPa; and agitation speed = 850 rpm.

for the catalyst preheated at 353 K (for 60 min) and is zero after preheating at 473 K (for 30 and 60 min). Only slight consumption of 1-hexene at 300 min was observed with the catalyst preheated at 473 K, which was sufficient for complete consumption of 1-hexene when the catalyst was not subjected to preheat treatment (normal hydroformylation reaction). The consumption of 1-hexene decreased on increasing the preheat treatment temperature and time due to the higher concentration of inactive species; hence, the formation of the inactive species depends on the extent of temperature and time of preheat treatment. However, the initial rate of hydroformylation of 1-hexene was zero, irrespective of temperature and time of preheat treatment.

4. Kinetic Modeling

To develop a suitable rate equation representing the intrinsic kinetic, the data were analyzed for the significance of mass transfer resistance. It was assumed that since the pure gases were used, therefore the gas side mass transfer resistance is negligible; Henry's law is applicable; and the reaction takes place in liquid-phase only. The independency of agitation speed (850 rpm) upon the reaction rate is further supported by comparing the maximum rates of mass transfer of carbon monoxide and hydrogen with the hydroformylation reaction rates under identical conditions.

For that purpose, the enhancement factors ϕ_1 and ϕ_2 were calculated as described in the literature.¹⁴ The

values of ϕ_1 and ϕ_2 calculated for all the rate data were found to be less than 0.10 in each case. This clearly shows that the rates observed in the entire range of conditions studied are much smaller than the mass transfer rates; hence, the rate data are in the kinetic regime.

For the purpose of the quantitative analysis of the complex relationship between different factors and the reaction rate, different empirical models were attempted. However, it is more meaningful to derive a rate equation model based on the actual mechanism of hydroformylation, assuming oxidative addition of hydrogen to acylrhodium species 6 (Scheme 1) as the rate-controlling step. Therefore, from reaction 4 (Scheme 2) the rate of reaction is given as

$$\text{rate} = k C_3 [\text{H}_2] \quad (5)$$

Since, the total concentration of the catalyst species known as

$$C = C_1 + C_2 + C_3 + C_4 + C_5 \quad (6)$$

Then eq 5 becomes

$$\text{rate} = \frac{k_0 e^{-E/RT} [\text{1-hexene}] [\text{H}_2] [\text{CO}] [\text{C}]}{(1 + K_1 [\text{CO}] + K_2 [\text{CO}] [\text{1-hexene}] + K_3 [\text{CO}]^2 [\text{1-hexene}] + K_4 [\text{CO}]^3 [\text{1-hexene}])} \quad (7)$$

where K_1 , K_2 , K_3 , and K_4 are the constants.

The rate parameters from complex rate model (eq 7) were evaluated by a nonlinear least-squares optimization using a modified Levenberg–Marquart (LM) algorithm. Based on minimized sum of squares of the errors (ϕ_{\min}) between calculated and experimental rates, we choose the best-fit model. ϕ_{\min} was calculated as

$$\phi_{\min} = \sum_{i=1}^N (\text{rate}_{\text{calc}(i)} - \text{rate}_{\text{exp}(i)})^2 \quad (8)$$

It was found that the experimental data were not fitted properly in eq 7 since the minimized sum of root-mean-squares error (ϕ_{\min}) was up to 26%. Therefore, this model was not found suitable for present system, which means that the RDS is not the only oxidative addition of H_2 on the acyl species 6 (Scheme 1). In addition, our

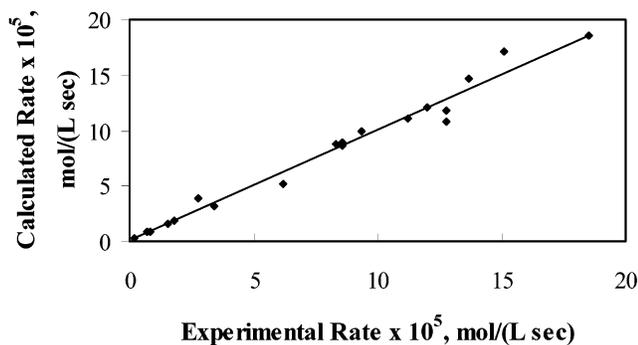


Figure 7. Comparison of hydroformylation reaction rates calculated from the empirical model (eq 9) with experimental data.

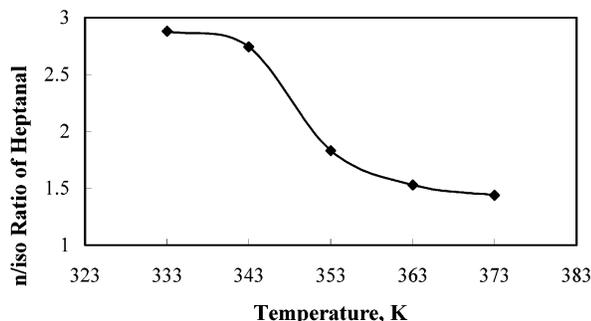


Figure 8. Effect of reaction temperature on the *n/iso* heptanal at [1-hexene] = 0.50 mol/L; [catalyst] = 20.00×10^{-5} mol/L; p_{CO} = 2.00 MPa; p_{H_2} = 2.00 MPa; temperature = 333–373 K; and agitation speed = 850 rpm.

experimental results as discussed earlier (in the effects of 1-hexene concentration and partial pressure of CO) also gave indication of shifting of the RDS.

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 experimental data, and unreliable parameter values would be obtained. Therefore, it is preferred to introduce simplified semiempirical rate equations, which are consistent with the observed reaction behavior, and rate model (eq 9) was found to be the best representing the experimental data:

$$\text{rate} = \frac{4008.22[A]^{0.75}[B]C^{0.35}D}{((1 + 102.0[B] + 10.99D)^3D)} \quad (9)$$

which have minimized sum of root-mean-squares deviation (variance), 2.98×10^{-7} , and an average error (ϕ_{\min}) between experimental and calculated rates was found to be 11.6% (Figure 7), which is under a kinetic range.

5. Effect of Temperature and Activation Energy

The observed trend of the *n/iso* of heptanal with the variation of reaction temperature (333–373 K) is shown in Figure 8. The *n/iso* ratio is found to fall from 2.8 to 1.4 on increasing the reaction temperature. At higher temperatures, it can be expected that the steric factors decrease significantly and thermal motion increases resulting in increase in the polarity of the M–H bond, which favor Markovnikov addition.

Activation energy was found to be 42.74 kJ/mol (Figure 9) with RhCl(AsPh₃)₃ catalyst, which is less than

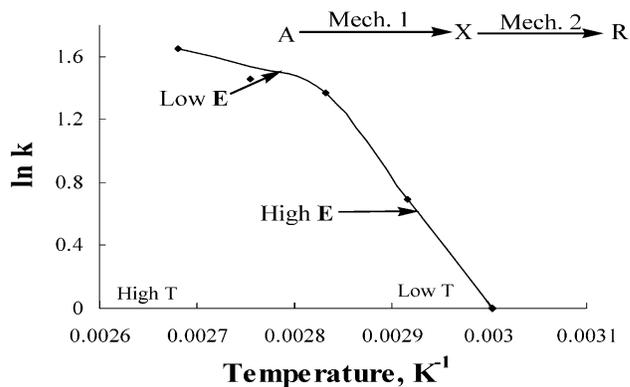


Figure 9. Arrhenius plot for activation energy.

the reported value for Rh/PPh₃ system.¹⁴ The calculated value of preexponential factor is 1.62×10^6 . The entropy of activation for the studied range of temperature, found to be -0.22 ± 0.01 kJ/(K mol), indicated that the catalyst system is favorable being associated with significant low entropy.

However, it may be noted that conventional straight line in Arrhenius plot was not found in the present study. It was observed the lower activation energy at higher temperature and vice versa. As it is well-known that for the multiple reactions,²² like hydroformylation, a change in activation energy with temperature indicates a shift in controlling mechanism of the reaction and consequently a change of RDS. The observed substrate-inhibited kinetics for 1-hexene concentration and CO partial pressure under employed kinetic conditions supports the above statement. Moreover, the average error (ϕ_{\min}) between experimental and calculated rates were found up to 26% when the oxidative addition of H₂ to acyl intermediate **6** (Scheme 1) was considered to be as a RDS.

7. Conclusions

RhCl(AsPh₃)₃ complex was used as a catalyst for homogeneous hydroformylation of 1-hexene in which the observed catalytic activity of RhCl(AsPh₃)₃ complex was found to be comparable with its analogue, RhCl(PPh₃)₃ complex. The rate increased on increasing catalyst concentration up to 20.00×10^{-5} mol/L followed by a decrease and then saturation obtained. At lower concentrations, the rates were increased on increasing 1-hexene followed by substrate-inhibited kinetics at higher concentrations. The dependence of partial pressure of hydrogen showed first-order kinetics. The rates were found to be increased with increasing the partial pressure of carbon monoxide up to a certain limit and after that followed inhibition. Agitation speed dependence indicated that a moderate speed of 100 rpm is sufficient for the hydroformylation reaction. The RhCl(AsPh₃)₃ catalyst system is observed to be more susceptible than RhCl(PPh₃)₃ toward the temperature and time of the preheat treatment during the study of thermal deactivation. The activation energy and the entropy of activation were calculated as 42.74 kJ/mol and -0.22 ± 0.01 kJ/K mol, respectively. The nonlinear semiempirical kinetic model representing the data was found to be the best with 11.6% error (ϕ_{\min}) between experimental and calculated rates.

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Nomenclature

A = species A, hydrogen
 [A], C_A = concentration of hydrogen in liquid, mol/L
 B = species B, carbon monoxide
 [B], C_B = concentration of carbon monoxide, mol/L
 C = concentration of catalyst, mol/L
 D = concentration of 1-hexene, mol/L
 k = reaction rate constant
 p_{H_2} = partial pressure of hydrogen, MPa
 p_{CO} = partial pressure of carbon monoxide, MPa
 E = activation energy, kJ/mol
 k_0 = preexponential factor
 R = gas constant (0.082057 atm/(g mol K))
 rpm = revolution per min
 T = reaction temperature, K
 n/iso = ratio of normal to isomeric aldehyde
 ϕ_{min} = minimized sum of square of errors between calculated and experimental rates
 cal = predicted values by kinetic models
 exp = observed values by kinetic experiments

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