

Hydroformylation of Allyl Alcohol Using Homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ Catalyst: A Kinetic Study¹

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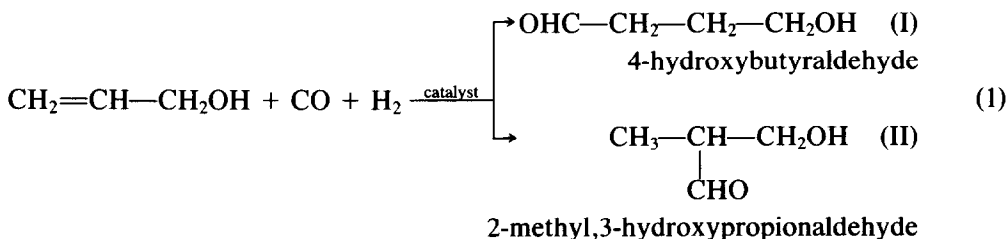
The hydroformylation of allyl alcohol using the homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst has been investigated in a temperature range of 60 to 80°C. The initial rate data were first examined to ensure that they were in the kinetic regime. The rate of hydroformylation was found to be first order with respect to the catalyst and 1.5th order with respect to hydrogen partial pressure. A critical partial pressure of H_2 was observed below which the rate of reaction was negligible. The rate of hydroformylation versus partial pressure of CO and allyl alcohol concentration plots passed through maxima, showing substrate inhibited kinetics in a certain range of concentrations. A rate equation has been proposed, which was found to represent the rate data satisfactorily. The activation energy was found to be 22.86 kcal mol⁻¹. © 1989 Academic Press, Inc.

INTRODUCTION

Hydroformylation of allyl alcohol is important in the synthesis of 1,4-butanediol which is an intermediate for the high-performance engineering plastics (1, 2). Conventionally, 1,4-butanediol is manufactured by the Reppe process based on acetylene (3). Hydroformylation of allyl alcohol provides an alternative route to 1,4-butanediol and is attractive since it is based on propylene, a petrochemical feedstock. In view of

this, several reports have been published on the hydroformylation of allyl alcohol using cobalt (4–6), and rhodium (7–10) complex catalysts. In the presence of the $\text{Co}_2(\text{CO})_8$ catalyst, lower yields of the aldehyde products were reported, while the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst has been found to work at milder conditions (7) with better selectivity.

The hydroformylation of allyl alcohol can be described as follows:



Of the two isomeric aldehydes, the linear aldehyde, 4-hydroxybutyraldehyde is of major interest since it can be hydrogenated to 1,4-butanediol.

The first detailed report on the hydroformylation of allyl alcohol using the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex catalyst was published by Pittman and Honnick (11), in which the effect of the PPh_3/Rh ratio, total pressure of syngas, temperature, and differ-

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ent ligands on the selectivity have been investigated. The aim of the present work is to investigate the intrinsic kinetics of the hydroformylation of allyl alcohol using the homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex catalyst. There is practically no published information on the kinetics of this reaction, using the homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst, except for the work of DeMunck *et al.* (12) wherein gas phase kinetics using a supported liquid phase catalyst (SLPC) has been studied.

For the purpose of kinetic study, the effects of the catalyst and allyl alcohol concentrations, and partial pressures of CO and H_2 on the rate of hydroformylation have been studied in a temperature range of 60–80°C. A rate equation has been proposed based on the experimental rate data and the dependence of the rate on different parameters has been discussed on the basis of a probable mechanism.

EXPERIMENTAL

Materials

Rhodium trichloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$), obtained from Arora-Mathey Ltd. was used. Triphenylphosphine (PPh_3) was procured from Fluka AG, Switzerland. Freshly distilled allyl alcohol and ethanol (solvent) were used in all the experiments. The catalyst, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, was prepared by the procedure given by Evans *et al.* (13). Hydrogen gas was supplied by Indian Oxygen Ltd., Bombay, and Carbon Monoxide with >99.8% purity was used directly from cylinders.

Experimental Setup

All the hydroformylation experiments were carried out in a 300 ml autoclave (made of SS 316). The autoclave supplied by Parr Instruments Co. Ltd., U.S.A., was provided with arrangements for sampling of liquid and gaseous contents, automatic temperature control, and variable stirrer speed. A safety rupture disk was also fitted to the reactor. The reactor was designed for a working pressure of 2000 psi and tempera-

tures up to 250°C. In order to monitor the consumption of CO and H_2 at constant pressure, a gas reservoir was used along with a constant pressure regulator. The pressure in the reservoir was recorded using a pressure transducer and a recorder system.

Experimental Procedure

In a typical experiment, known quantities of the catalyst, allyl alcohol, along with the solvent were charged into the autoclave and the contents were flushed with nitrogen. Then the contents were flushed with a mixture of CO and H_2 , and heated to the desired temperature. A mixture of H_2 and CO in the required ratio was then introduced into the autoclave up to a required pressure, a sample of the liquid was withdrawn, and the reaction was started by switching the stirrer on. The reaction was then continued at a constant pressure by supply of $\text{CO} + \text{H}_2$ (1 : 1) from the reservoir vessel. Since in this study the major products formed were isomeric aldehydes, supply of $(\text{CO} + \text{H}_2)$ at a ratio of 1 : 1 (as per the stoichiometry) was adequate to maintain a constant composition of H_2 and CO in the autoclave, as introduced in the beginning. This was confirmed in a few cases by analysis of the CO content at the end of the reaction. All the reactions were carried out for short durations such that the conversion in the liquid phase was minimum, to ensure differential conditions. In each of the kinetic runs, initial and final samples were analyzed for reactants and products in order to check the material balance. It was generally observed that in this low conversion range ($\leq 10\%$), the rates of hydroformylation were constant. The reproducibility of the experiments was found to be in a range of 5–7%. Following this procedure, the effects of the catalyst and olefin concentrations, partial pressures of H_2 and CO, and temperature on the rate of hydroformylation pressures of H_2 and CO and temperature on the rate of hydroformylation were studied.

TABLE I
Results Showing Mass Balance

Serial number	Allyl alcohol (mol)		Absorption (mol)	Mass balance with respect to CO and H ₂ absorption (%)
	Initial	Final		
1	0.253	0.209	0.048	91.76
2	0.256	0.199	0.058	98.27
3	0.252	0.181	0.077	92.2
4	0.249	0.155	0.097	96.91
5	0.253	0.158	0.098	96.94
6	0.253	0.180	0.077	101.30

Note. Conditions of reactions are the same as those in Fig. 2.

The analysis of reactants and products was carried out by a gas chromatographic method on a 5% PEG 20M on a Chromosorb W-AW column of 2 m length. For this purpose, an HP5840 gas chromatograph was used. The two aldehyde products were identified by GCMS. To confirm this, the aldehydes were reduced with LiAlH₄ and the products on analysis by GC were found to be 1,4-butanediol and 2-methyl,1,3-propanediol. The CO and H₂ contents in the gas phase were also analyzed by gas chromatography, using a molecular sieve 5-Å column of length 1.7 m.

RESULTS AND DISCUSSION

The main objective of this work was to investigate the kinetics of hydroformylation of allyl alcohol using the HRh(CO)(PPh₃)₃ complex catalyst. It was therefore thought necessary to first ensure the material balance and reproducibility of the experiments. For this purpose, a few experiments were carried out in which the amount of olefin consumed, products formed, and syngas consumed were compared. Some results are shown in Table 1. A typical concentration profile is shown in Fig. 1. In general it was observed that the material balance of (CO + H₂) and allyl alcohol consumed were consistent with the amount of total aldehyde products formed. Also, in the range of conditions covered in this work, the only products formed were 4-hy-

droxybutyraldehyde and 2-methyl, 3-hydroxypropionaldehyde. No hydrogenation or isomerization products were observed. Thus the overall hydroformylation kinetics could be followed by observing the consumption of syngas, at a 1:1 ratio of CO and H₂.

Solubility Data

For the purpose of kinetic study, a knowledge of the solubility of the gaseous reactants in the reaction medium is often essential. For the CO-ethanol system, the solubility data reported earlier (14) were used and the relevant data are presented in Table 2. For the H₂-ethanol system the solubility data were not available in the literature for the range of conditions used. Therefore, these data were obtained following the procedure described by Choudhary *et al.* (15), with an accuracy of 2-3%. These results are also presented in Table 2. These data were used in the calculation of the concentrations of dissolved CO and H₂ in the liquid medium.

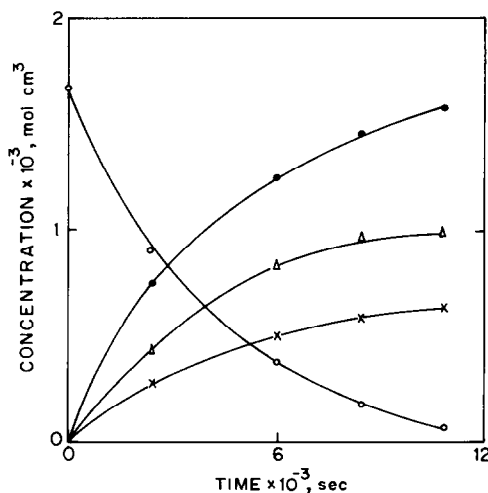


FIG. 1. Concentration profile of a batch reactor: Allyl alcohol hydroformylation. Concentration of catalyst = 1×10^{-6} mol cm⁻³. Concentration of allyl alcohol = 1.67×10^{-3} mol cm⁻³. $P_H = P_{CO} = 30.68$ atm. (○) Allyl alcohol, (Δ) 4-hydroxybutanal, (x) 2-methyl,3-hydroxypropanol, (●) CO or H₂ consumed.

TABLE 2
Solubility of H₂, and CO in Ethanol

Serial number	Temperature (°C)	Solubility × 10 ⁶ (mol cm ⁻³ atm ⁻¹)	
		H ₂	CO
1	60	3.82	9.378
2	70	4.01	9.688
3	80	4.26	10.020

TABLE 3
Range of Conditions Investigated for the Kinetic Study

Concentration of catalyst (mol cm ⁻³)	1.0 to 4.0 × 10 ⁻⁶
Concentration of allyl alcohol (mol cm ⁻³)	4.00 × 10 ⁻⁴ to 6.6 × 10 ⁻³
P _H (atm)	13.61 to 38.5
P _{CO} (atm)	3.48 to 40.8
Temperature (°C)	60–80
Solvent	Ethanol
Reaction volume (cm ³)	100

KINETIC STUDY

In order to study the intrinsic kinetics of the hydroformylation of allyl alcohol using the HRh(CO)(PPh₃)₃ catalyst in the ethanol medium, several experiments were carried out in the range of conditions given in Table 3. The procedure followed for the measurement of initial rates has been described earlier. In each of the experiments, the amount of CO and H₂ consumed as a function of time was observed and the initial and final liquid samples were also analyzed for allyl alcohol and products. The initial rates of hydroformylation were then calculated from the observed data on the consumption

of (CO + H₂) as a function of time, in the initial region where the conversion of allyl alcohol was ≤10%. A sample plot of adsorption of (CO + H₂) with time, showing the effect of P_{CO} on the rate of hydroformylation of allyl alcohol at 60°C is shown in Fig. 2. Under the conditions chosen for the kinetic study, no side reactions were found to occur and therefore the kinetic study described in the following sections would be representative of the overall hydroformylation of allyl alcohol to the corresponding aldehydes.

It was observed that in the initial period of the reaction, the rates of hydroformylation were essentially constant. Also, the

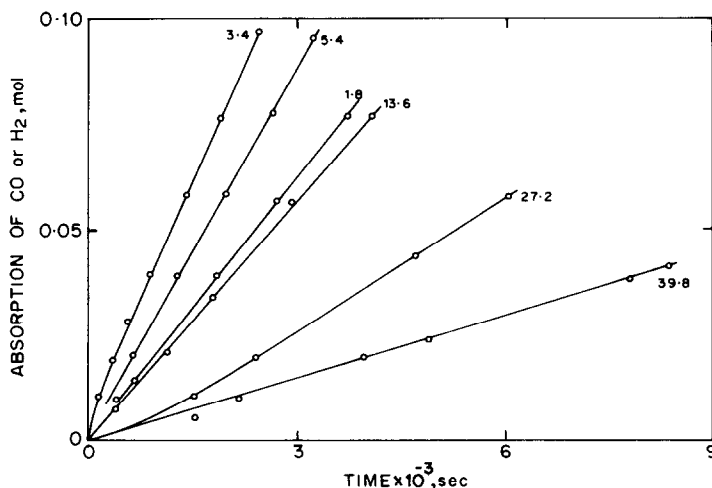


FIG. 2. Plot of absorption of CO or H₂ vs time: Effect of P_{CO}. Concentration of catalyst = 1 × 10⁻⁶ mol cm⁻³. Concentration of allyl alcohol = 2.5 × 10⁻³ mol cm⁻³. P_H = 27.2 atm; temperature = 60°C; reaction volume = 100 cm³.

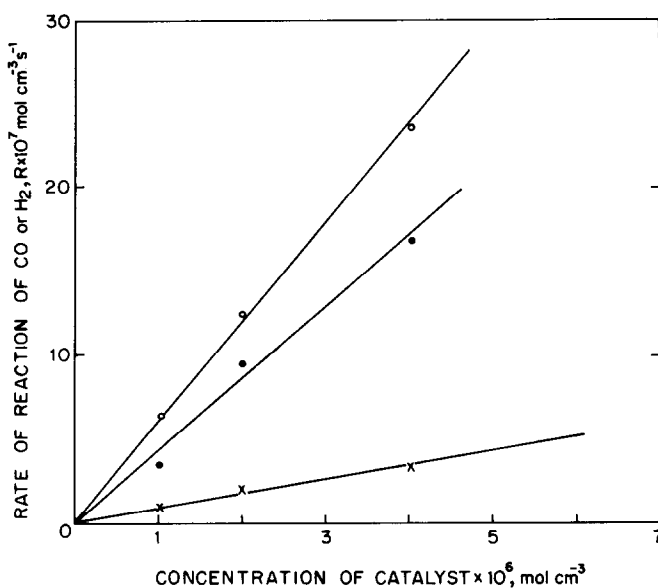


FIG. 3. Effect of catalyst concentration on the rate of hydroformylation. Concentration of allyl alcohol = $2.5 \times 10^{-3} \text{ mol cm}^{-3}$. $P_{\text{H}} = P_{\text{CO}} = 20.4 \text{ atm}$; temperature: (O) 80°C, (●) 70°C, (x) 60°C.

amount of $(\text{CO} + \text{H}_2)$ measured in all experiments at a 1:1 ratio would mean that the actual rate of hydroformylation would be half of this total consumption rate. Thus the rate of hydroformylation was calculated as follows:

$$R = \frac{\text{(slope of CO or H}_2\text{)} \text{ consumed vs time plot}}{\text{volume of liquid}} \quad (2)$$

These were essentially initial rates of reaction, observed under differential conditions. On comparison of the data on $(\text{H}_2 + \text{CO})$ and allyl alcohol consumed, and the formation of products I and II, it was observed that the material balance was in good agreement ($>95\%$) as per the stoichiometry shown by Eq. (1) (see Table 1). The results showing the dependence of the rates on different parameters, and a kinetic model based on these data, are discussed in the following section.

Effect of agitation speed. The rate was found to be independent of the agitation speed beyond 400 rpm, at all the temperatures studied, and therefore all the reac-

tions were carried out at an agitation speed of 900 rpm to ensure kinetic regime.

Effect of catalyst concentration. The effect of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ concentration on the rate of hydroformylation of allyl alcohol was studied in a temperature range of 60–80°C, allyl alcohol concentration of $2.5 \times 10^{-3} \text{ mol cm}^{-3}$, and a total pressure of $(\text{CO} + \text{H}_2) = 40.8 \text{ atm}$ ($\text{CO}/\text{H}_2 = 1$). The results are shown in Fig. 3. The rate was found to be linearly dependent on the catalyst concentration at all the temperatures studied, indicating first-order kinetics.

Effect of partial pressure of CO (P_{CO}). The effect of P_{CO} on the rate of hydroformylation of allyl alcohol was studied at a constant partial pressure of $\text{H}_2 = 27.2 \text{ atm}$, allyl alcohol concentration of $2.5 \times 10^{-3} \text{ mol cm}^{-3}$, and catalyst concentration of $1 \times 10^{-6} \text{ mol cm}^{-3}$. The results are shown in Fig. 4 for all the temperatures studied. The rate first increased with increase in P_{CO} , then passed through a maximum, and decreased with further increase in P_{CO} . It is a general observation that the hydroformylation rates are inversely proportional to the partial pressure of CO, however, there is a

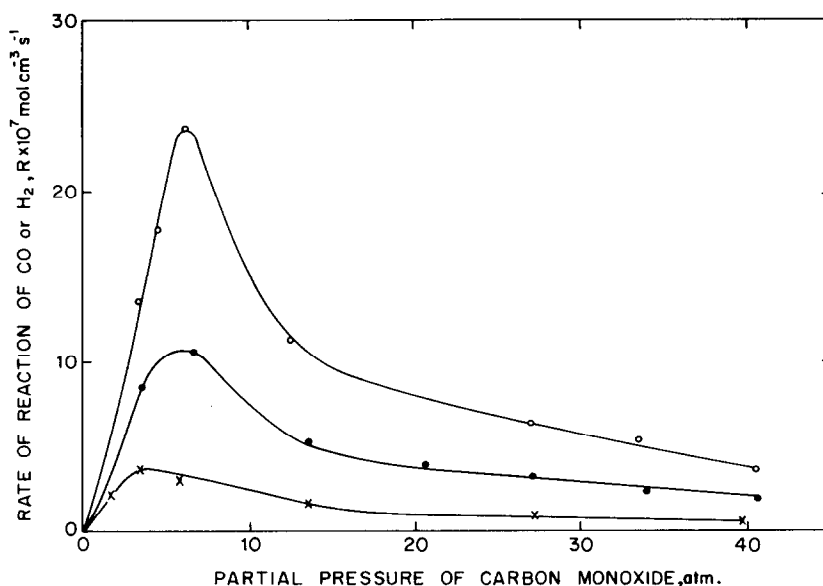


FIG. 4. Effect of partial pressure of carbon monoxide on the rate of hydroformylation. Concentration of catalyst = 1×10^{-6} mol cm^{-3} . Concentration of allyl alcohol = 2.5×10^{-3} mol cm^{-3} . $P_H = 27.2$ atm; temperature: (\circ) 80°C, (\bullet) 70°C, (\times) 60°C.

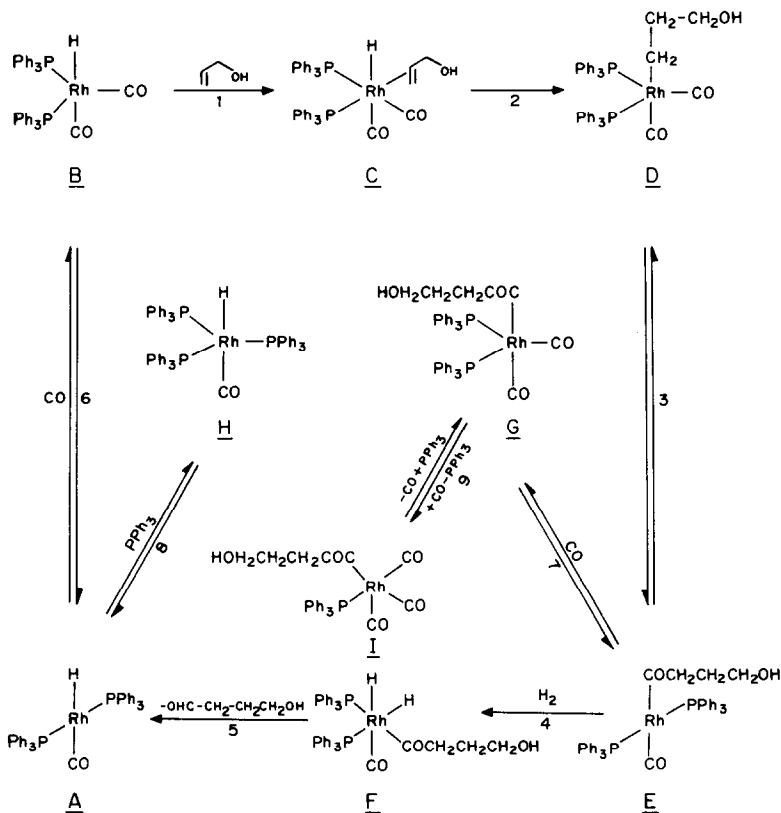


FIG. 5. Mechanism for hydroformylation of allyl alcohol (associative).

lack of information in the region of lower partial pressures of CO using the HRh(CO)(PPh₃)₃ catalyst. Similar observations also have been made for Co and Rh carbonyl catalysts (16, 17). In this work it is clearly observed that the rate increases with P_{CO} in the lower range of P_{CO} . An important observation made here is that the rate of hydroformylation is very sensitive to slight changes in the partial pressures of CO in this range. The sensitivity was found to be more pronounced with an increase in temperature. This observation can be explained reasonably on the basis of the mechanism proposed by Evans *et al.* (13, 18) shown in Fig. 5. As per the mechanism, inhibition of the rate of hydroformylation at higher partial pressures of CO is due to the side reactions (steps 7, 9, Fig. 5) leading to the formation of the inactive species (RCO)Rh(CO)₂(PPh₃)₂ and (RCO)Rh(CO)₃PPh₃ (G and I in Fig. 5). The formation of these species reduces the effective concentration of the active catalytic species, and hence the rate of reaction is retarded. The equilibrium leading to the formation of (RCO)Rh

(CO)₃PPh₃ will be more pronounced at still higher partial pressures of CO causing a sharp decrease in the rate of reaction, as has been observed in this work.

Effect of partial pressure of hydrogen (P_H). The effect of partial pressure of H₂ on the rate of hydroformylation of allyl alcohol was investigated at a constant partial pressure of CO = 27.2 atm, allyl alcohol concentration of 2.5×10^{-3} mol cm⁻³, and a catalyst concentration of 1×10^{-6} mol cm⁻³. The results are shown in Fig. 6. The rate of reaction was found to vary with an order of 1.5 with P_H , however, an unusual observation made in this case was that below a H₂ partial pressure of 10 to 12 atm, the rates were very low. This indicates that a certain critical partial pressure of H₂ is necessary for the reaction to proceed, which can be explained by the mechanism shown in Fig. 5, for a specific situation. For example, the competing reaction leading to the formation of species G (Fig. 5) is likely to be more dominant in comparison to the rate determining hydrogenation step, under these conditions. Also, the formation of di-

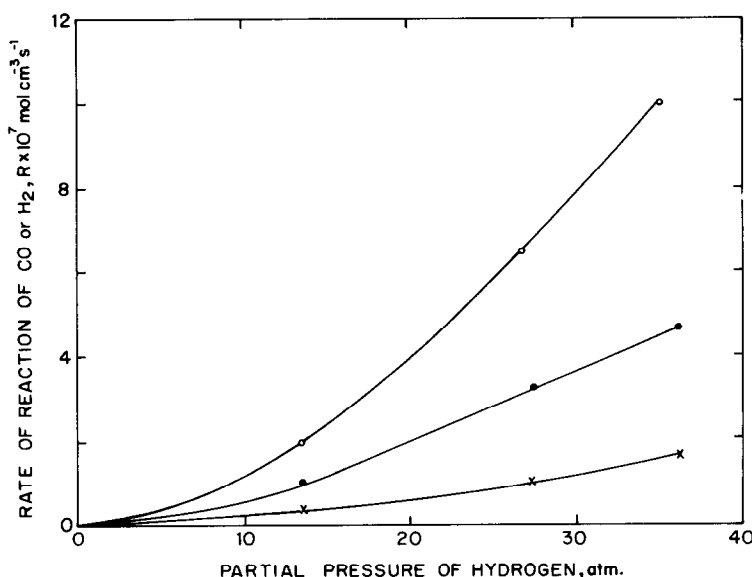


FIG. 6. Effect of partial pressure of hydrogen on the rate of hydroformylation. Concentration of catalyst = 1×10^{-6} mol cm⁻³. Concentration of allyl alcohol = 2.5×10^{-3} mol cm⁻³. P_{CO} = 27.2 atm; temperature: (O) 80°C, (●) 70°C, (x) 60°C.

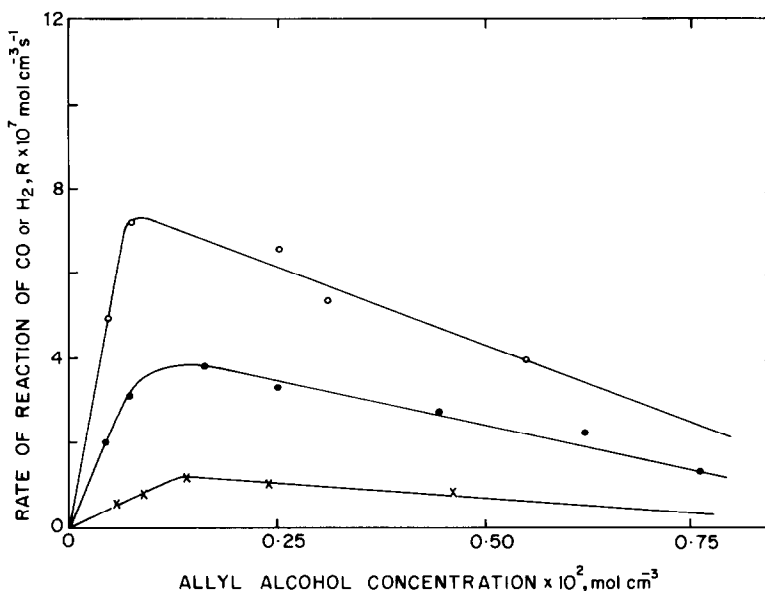
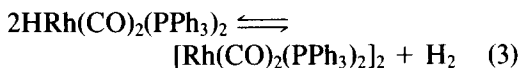


FIG. 7. Effect of allyl alcohol concentration on the rate of hydroformylation. Concentration of catalyst = 1×10^{-6} mol cm⁻³. $P_H = P_{CO} = 20.4$ atm; temperature: (O) 80°C, (●) 70°C, (x) 60°C.

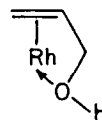
meric rhodium species in Eq. (3) is likely to be more pronounced in the lower range of partial pressures of H₂ (13). At very low P_H the equilibrium in the following reaction (3) will shift more to the right:



It is obvious from this reaction that a certain minimum P_H will be required to ensure that the reverse reaction dominates.

Effect of allyl alcohol concentration. Figure 7 shows the effect of allyl alcohol concentration on the rate of hydroformylation, at a total pressure of 40.8 atm ($\text{CO}/\text{H}_2 = 1$), a catalyst concentration of 1×10^{-6} mol cm⁻³, in a temperature range of 60–80°C. This is clearly a case of substrate inhibited kinetics and is a first report in which substrate inhibition with olefin species has been observed in the hydroformylation of allyl alcohol using the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst. The present knowledge of the hydroformylation mechanism is insufficient to explain this behavior. Such observation, however, has been reported in the hydroge-

nation of allyl alcohol (19) where this has been explained on the basis of formation of a diolefin-Rh species. In our system of allyl alcohol hydroformylation, the substrate inhibition observed is likely to be a result of some side reactions between allyl alcohol and the active catalytic species. The formation of a species of the type shown below by chelation of the Rh by the -OH group is also possible. This is, however, purely speculative as there are no reports on the formation of such species:



RATE MODEL

In order to develop a suitable rate equation representing the intrinsic kinetics of hydroformylation of allyl alcohol, it was first essential to ensure that the rate data obtained are in the kinetically controlled regime. The observation that agitation speed has no effect on the rate indicates the ab-

TABLE 4
Models Examined to Fit the Data on Allyl Alcohol Hydroformylation

Serial number	Rate model	Temp (°C)	k	K_B	K_D	m	n	ϕ_{\min}
1	2	3	4	5	6	7	8	9
1	$\frac{k(A^*)^{1.523}B^*CD}{(1 + K_B B^*)^3(1 + K_D D)^2}$	60	5.618×10^{13}	1.160×10^4	5.115×10^2			2.96×10^{-17}
		70	2.649×10^{14}	1.111×10^4	7.479×10^2			6.85×10^{-15}
		80	4.418×10^{14}	8.703×10^3	9.116×10^2			9.96×10^{-15}
2	$\frac{k(A^*)^{1.523}B^*CD}{(1 + K_B B^*)^m(1 + K_D D)^n}$	60	5.477×10^{13}	1.099×10^4	5.705×10^2	3.083	1.845	3.96×10^{-17}
		70	2.095×10^{14}	5.004×10^3	8.193×10^2	4.031	1.912	2.117×10^{-14}
		80	2.262×10^{14}	2.201×10^3	2.779×10^2	7.36	3.773	3.035×10^{-18}
3	$\frac{k(A^*)^{1.523}B^*CD}{(1 + K_B B^* + K_D D)^m}$	60	8.986×10^{14}	3.732×10^4	8.430×10^2			7.098×10^{-16}
		70	5.061×10^{15}	2.545×10^4	8.060×10^2			5.732×10^{-13}
		80	1.864×10^{14}	1.867×10^3	6.638×10^1			6.280×10^{-15}
4	$\frac{k(A^*)^{1.523}B^*CD}{[1 + (K_B B^* + K_D D)^2 B^*]}$	60	5.823×10^{12}	1.173×10^6	3.86×10^4			1.080×10^{-15}
		70	1.722×10^{13}	1.050×10^6	3.99×10^4			3.10×10^{-15}
		80	5.316×10^{13}	8.923×10^5	4.13×10^4			3.82×10^{-13}

Note. $A^* = P_H \times H_A$, $B^* = P_{CO} \times H_B$, C = concentration of catalyst, D = concentration of allyl alcohol.

sence of mass transfer resistance. There are practically no detailed reports published on the kinetic modeling of hydroformylation reactions. The observed dependency of the rate on different parameters indicates that the hydroformylation of allyl alcohol is first order with respect to catalyst concentration and 1.5th order with respect to dissolved H_2 concentration. The rate versus allyl alcohol concentration showed a complex dependence with a negative order in a certain range. In order to fit the rate data, several rate equations were examined. The rate parameters were evaluated using an optimization procedure. The values of the rate parameters evaluated for each model are presented in Table 4 along with ϕ_{\min} , the minimized sum of the squares of the difference between the observed and predicted rates. From the values of ϕ_{\min} and the predictability of the rate models, the following rate equation was found to represent the rate data satisfactorily,

$$R = \frac{k(A^*)^{1.523}B^*CD}{(1 + K_B B^*)^3(1 + K_D D)^2}, \quad (4)$$

where k is the intrinsic rate constant (in $\text{cm}^{10.569} \text{mol}^{-4.5}$), A^* and B^* are the concentrations of H_2 and CO in ethanol at the gas-liquid interphase (in mol cm^{-3}), respec-

tively, and C and D represent the concentrations of the catalyst and allyl alcohol (in mol cm^{-3}), respectively. The rate parameters for Eq. (4) at 60 to 80°C are presented in Table 5. The average deviation in the predicted and observed rates was found to be in the range of $\pm 9\%$. The Arrhenius plot showing the effect of temperature on the rate parameters is shown in Fig. 8 and 9 from which the activation energy was evaluated as 22.86 kcal mol^{-1} . The dependence of the rate parameters K_B and K_D on tem-

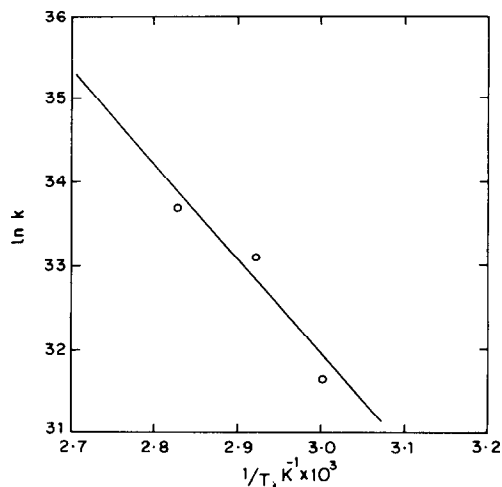
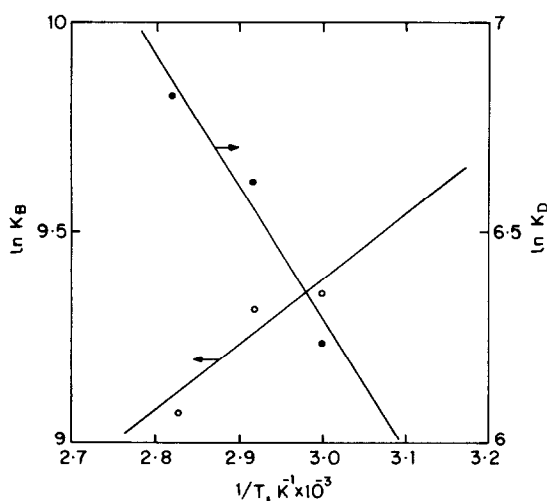


FIG. 8. Plot of $\ln k$ vs $1/T$.

FIG. 9. Plot of $\ln K_B$, $\ln K_D$ vs $1/T$.

perature (Table 5) show opposite trends; however, it is important to note that these parameters may not be representative of a single equilibrium reaction step and are in fact lumped parameters describing observed overall trends. Therefore, no specific conclusions can be drawn from the temperature dependence of K_B and K_D .

Since the mechanistic steps responsible for substrate inhibition with olefins are not well understood, it was not possible to propose a mechanistically meaningful model. However, even the empirical model proposed here could be useful for the purpose of engineering analysis and reactor design purposes.

CONCLUSIONS

The kinetics of the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyzed hydroformylation of allyl alcohol has

been investigated in a temperature range of 60–80°C. The trends observed were very complex. The rate versus P_{CO} and allyl alcohol concentrations passed through maxima showing substrate inhibited kinetics. The rate was found to be first order with respect to catalyst concentration. The dependence of the rate on P_{H} indicated the presence of a critical partial pressure of H_2 below which the reaction rates were very slow. The rate was found to be 1.5th order with P_{H} .

The following rate equation has been proposed based on the rate data and was found to fit the observed data satisfactorily:

$$R = \frac{k(A^*)^{1.523} B^* C D}{(1 + K_B B^*)^3 (1 + K_D D)^2}$$

The constants k , K_B , and K_D were evaluated. The activation energy was found to be 22.86 kcal mol⁻¹.

TABLE 5

Rate Parameters

Serial number	Temperature (°C)	k ($\text{cm}^{10.569} \text{mol}^{-4.5}$)	K_B ($\text{cm}^3 \text{mol}^{-1}$)	K_D ($\text{cm}^3 \text{mol}^{-1}$)
1	60	5.618×10^{13}	1.160×10^4	5.115×10^2
2	70	2.649×10^{14}	1.111×10^4	7.479×10^2
3	80	4.418×10^{14}	8.703×10^3	9.116×10^2

APPENDIX: NOMENCLATURE

- A^* Concentration of H_2 in ethanol at the gas–liquid interphase (mol cm^{-3})
 B^* Concentration of CO in ethanol at the gas–liquid interphase (mol cm^{-3})
 C Concentration of the catalyst (mol cm^{-3})

- D Concentration of allyl alcohol (mol cm^{-3})
- H_A Henry's law constant for the H_2 -ethanol system ($\text{mol cm}^{-3} \text{atm}^{-1}$)
- H_B Henry's law constant for the CO -ethanol system ($\text{mol cm}^{-3} \text{atm}^{-1}$)
- k Reaction rate constant ($\text{cm}^{10.569} \text{mol}^{-4.5}$)
- K_B Constant in Eq. (4) ($\text{cm}^3 \text{mol}^{-1}$)
- K_D Constant in Eq. (4) ($\text{cm}^3 \text{mol}^{-1}$)
- m Constant in Table 4
- n Constant in Table 4
- P_H Partial pressure of hydrogen (atm)
- P_{CO} Partial pressure of carbon monoxide (atm)
- R Rate of hydroformylation ($\text{mol cm}^{-3} \text{s}^{-1}$)
- T Reaction temperature ($^{\circ}\text{C}$)

REFERENCES

1. Kummer, R. (BASF) German Patent 2,401,533 (1975).
2. Smith, W. E. (General Electric) German Patent, 2,453,671 (1975).
3. Appleyard, C. J. S., and Gartshore, J. F. C., BIOS Report 367, No. 22 (1946).
4. Adkins H. and Krsek G., *J. Amer. Chem. Soc.* **70**, 383 (1948).
5. Adkins, H., and Krsek, G., *J. Amer. Chem. Soc.* **71**, 3051 (1949).
6. Falbe, J., Schulze-Steiner, H. J., and Korte, F., *Chem. Ber.* **98**, 886 (1965).
7. Brown, C. K., and Wilkinson, G., *J. Chem. Soc. A*, 2753 (1970).
8. Shimuzu, T. (Kuraray Co. Ltd.), German Patent 2,538,364 (1974).
9. Shimuzu, T., and Tamura, M. (Kuraray Co. Ltd.), Jap. Patent 7,868,709 (1978).
10. Matsumoto, M., Shimuzu, T., Moriya, S., Fuchigami, Y., Tsurumaru, H., and Tamura, M. (Kuraray Co. Ltd.), Jap. Patent 7,868,713 (1978), Jap. Patent 7,868,715 (1978), Jap. Patent 7,984,508 (1979).
11. Pittman, C. U., Jr., and Honnick, W. D., *J. Org. Chem.* **45**, 2132 (1980).
12. DeMunck, N. A., Notenboom, J. P. L., De Leur, J. E., and Scholten, J. J. F., *J. Mol. Catal.* **11**, 233 (1981).
13. Evans, D., Yagupsky, G., and Wilkinson, G., *J. Chem. Soc. A*, 2660 (1968).
14. Dake, S. B., and Chaudhari, R. V., *J. Chem. Eng. Data* **30**(4), 400 (1985).
15. Choudhary, V. R., Parande, M. G., and Brahme, P. H., *Ind. Eng. Chem. Fundam.* **21**(4), 473 (1982).
16. Pino, P., Piacenti, F., and Bianchi, M., in "Organic Synthesis via Metal Carbonyls" (I. Wender and P. Pino, Eds.), Vol. II. Books Demand UMI, New York, 1977.
17. Pino, P., *J. Organometal. Chem.* **200**, 223 (1980).
18. Evans, D., Osborne, J., and Wilkinson, G., *J. Chem. Soc. A*, 3133 (1968).
19. Wadkar, J. G., and Chaudhari, R. V., *J. Mol. Catal.* **22**, 103 (1983).