Chapter 5

Hydroformylation of Vinyl Acetate Monomer As a Potential Route for the Synthesis of Hydroxy Propionic Acids

Hydroformylation of Vinyl acetate monomer (VAM) using homogeneous Co$_2$(CO)$_8$ as a catalyst followed by oxidation of the products, 2-acetoxy propanal (2-ACPAL) and 3-acetoxy propanal (3-ACPAL), which after hydrolysis gives 2- and 3-hydroxy propionic acids (HPA) has been studied as an alternative route for the synthesis of 2- and 3-hydroxy propionic acids. The feasibility of the VAM hydroformylation route for hydroxypropionic acids has been demonstrated, and a detailed study has been reported on the key hydroformylation step. The role of the catalyst, solvents and the effect of reaction conditions on the reaction rate and regioselectivity of the products have been investigated. Using Co$_2$(CO)$_8$ as a catalyst, ~98% selectivity to acetoxy propanals (ACPALs) has been achieved. A possible mechanism to explain the variation in regio-selectivity with Co$_2$(CO)$_8$ as catalyst has also been discussed. Kinetics of the hydroformylation step has been investigated and a rate equation proposed. The second step in the proposed route, i.e. oxidation of ACPALs to acetoxy propionic acids (ACPAs), has been studied using supported cobalt catalyst and molecular oxygen as the oxidant in a non-acidic medium with >95% conversion of ACPALs and >98% selectivity to ACPAs. Kinetics of the liquid phase oxidation of 2-ACPAL has been investigated and a rate equation proposed. The third step in the proposed route is hydrolysis of ACPAs to hydroxy propionic acids (HPAs) has been studied using solid acid catalysts, the best performance for the hydrolysis step with >90% selectivity to HPAs was observed. This study would be valuable in developing a new environmentally benign route for HPAs synthesis.
5.1. Introduction

2-hydroxy propionic acid (2-HPA) and 3-hydroxy propionic acid (3-HPA) known for almost 2000 years have been produced for only a century on an industrial scale\(^1\). 2-HPA, more popularly known as lactic acid, is important commercially in baking industry, cheese industry, pharmaceutical industry, cosmetic industry and shows assorted applications in dying wool and to make plasticizers for resin.\(^2\) 2-HPA has become increasingly important especially in the polymer industry and as a preservative and stabilizer in fat reduced food products. Polylactide polymers have recently been synthesized from 2-HPA, for their further application in the synthesis of biodegradable polymers, which has been the first among the commercial applications of 2-HPA in the manufacture of this important class of polymers. 3-HPA has a wide range of applications in polymer industry for the synthesis of different acrylic polymers, acrylic esters, polyesters and in food industry.\(^3,4\)

There are two commercial methods for the production of 2-HPA, a) fermentation of molasses, and b) Hydrocyanation of acetaldehyde followed by the hydrolysis of cyanohydrin produced. Both commercial processes produce racemic 2-HPA, of which the resolution is carried out separately since only L-2-HPA is useful in polylactide synthesis. Fermentation of molasses is the preferred and most common route, owing to cheap availability of molasses from sugar production. The fermentation is achieved on industrial scale in stirred tank bioreactors with low productivities. 2-HPA is separated from the lactate salts by addition of sulfuric acid and subsequent separation of the emerging gypsum. The gypsum has no further use and is an environmental threat to dispose off. Hydrocyanation of acetaldehyde and the subsequent hydrolysis of the cyanohydrin employ toxic HCN for cyanohydration and the corrosive sulfuric acid for hydrolysis, which eventually leads to generation of stoichiometric amounts of salts. Thus, a need for a clean, atom efficient and environmentally compatible alternative route exists even today for the synthesis of 2-HPA. The current 3-HPA synthesis involves the biocatalytic route starting from glycerol or glucose, which also suffers from low reaction rates, high dilution and high process cost.

A novel catalytic route starting from vinyl acetate (which is industrially produced in large volumes from ethylene) has been proposed for 2-HPA. The first report describing
2-HPA synthesis by a three steps route via VAM appeared in 1978, in which VAM was hydroformyolated to yield 2-acetoxy propanal using Rh(COD)(PPh₃)₂ as a catalyst at 373K and 3.33 MPa synthesis gas pressure. The intermediate aldehyde was then oxidized using cobalt or manganese catalysts with 0.2 MPa air pressure to yield 2-acetoxy propionic acid (2-ACP) that was hydrolyzed to 2-HPA in 75% yield using acidic catalysts such as TsOH or H₂SO₄. The major drawback in this is the use of acetic acid as a solvent in hydroformylation and the oxidation steps, which reduces the chemo-selectivity of 2-ACP in hydroformylation step besides being corrosive. In another report, hydrocarbonylation of VAM to yield 2-ACP using Pd-complex catalysts (373-473K, 0.6-6.9 MPa CO) was reported using [(allyl)PdCl₂]₂ or Pd(OAc)₂/ PPh₃ as a catalyst to achieve 96% conversion and 67% selectivity along with VAM hydrolysis products such as acetaldehyde and acetic acid. During hydrocarbonylation reaction, hydrolysis of VAM is a predominant side reaction especially at higher ligand (PPh₃/Pd ratio > 20) and water concentrations (> 0.9 wt%). A process for dl-2-HPA via alkoxycarbonylation of VAM to achieve methyl-2-acetoxypropionate using Pd, Rh and Ni catalysts at 373K and 6.9 MPa CO pressure; PdCl₂(PPh₃)₂ being the most effective catalyst, giving the maximum yield (81.6%) of methyl-2-acetoxypropionate, whereas Rh and Ni catalysts were less active for alkoxycarbonylation. Methoxycarbonylation of VAM to yield methyl-2-acetoxypropionate in 62% yield with very low catalytic activity using palladium catalysts in presence of a base such as pyridine or pyridine derivatives was reported at severe operating conditions (373-423K, 15-25 MPa), but the route from carbonylation of VAM has major drawbacks like low selectivity, difficulty in catalyst-product separation, and requirement of severe reaction conditions.

Boroley et al have reported hydroformylation of VAM using Co₂(CO)₈ as catalyst with high chemo selectivity to aldehydes. ~ 50% selectivity to normal aldehyde was achieved, where as previous literature report claim < 95 % regioselectivity to branch aldehyde using Rh as catalyst. Thus, the hydroformylation of VAM followed by oxidation of corresponding products provide an economic and environmentally benign catalytic route for the synthesis of precursors (2- and 3-ACPAs), which can be easily converted to 2-and 3- HPAs by hydrolysis, but clearly requires further improvement in the catalyst performance in all the three steps and environmental compatibility. Specific
literature on the understanding of parameters influencing the performance of these steps is also limited demanding further efforts to innovate new catalysts and optimize reaction conditions.

Hydroformylation of VAM is the key step in the synthesis of HPAs. The literature on hydroformylation of VAM shows that, the $\text{Co}_2(\text{CO})_8$ catalyzed hydroformylation of VAM gives lower catalytic activity and also poor selectivity to ACPALs due to severe reaction conditions (373-423K, 15-25 MPa). However, cobalt catalysts are economical compared to the rhodium catalysts, and therefore, the $\text{Co}_2(\text{CO})_8$ catalyzed VAM hydroformylation deserves a detailed investigation of the catalysis and reaction kinetics, which was the motivation of the present work.

In this chapter, a detailed study on the three-step hydroformylation-oxidation-hydrolysis route for the synthesis of 2- and 3- HPAs (Scheme 5.1) is investigated. Based on the results of these studies, a detailed kinetic analysis of the hydroformylation step is presented and a rate equation is proposed. In the second step, mixture of 2-and 3-HPAs was oxidized to 2- and 3-ACPAs with high yields using Co/C carbon as catalyst and air as an oxidant. In the third step, hydrolysis of the ACPAs was carried out using solid acid catalyst at mild reaction condition in high yields to 2- and 3-HPA. This study would be valuable in developing an environmentally benign route for the synthesis of HPAs.

5.2. Experimental

5.2.1. Materials

Cobalt (II) acetate, Cobalt (II) chloride, $\text{Co(CH}_3\text{COO)}_2\cdot4\text{H}_2\text{O}$, and $\text{RhCl}_3\cdot\text{xH}_2\text{O}$; the ligands- phosphine, diphosphine, acetylacetonate (acac) etc were procured from Aldrich, USA or Fluka, Switzerland and used without further purification. The solvents toluene, chlorobenzene, MEK, NMP, ethyl acetate, methanol, ethanol, DMF were procured from SD Fine Chemicals, India or E-Merck-India and used after fresh distillation, drying and argon flushing. CO of 99.9 % purity (Matheson, USA) and $\text{H}_2$ of 99 % purity (Industrial Oxygen Company, India) were used as received without further purification. $\text{Co}_2(\text{CO})_8$ (Dicobalt octacarbonyl) was prepared in the laboratory by high pressure-high temperature technique described in section 5.2.4. Synthesis gas mixture with a CO:$\text{H}_2$ ratio of 1 was prepared in a reservoir and used for hydroformylation reactions.
5.2.2. General Experimental Procedure

All the hydroformylation reactions were carried out in a 50 ml Parr Autoclave made of stainless steel material (SS-316; maximum pressure capacity of 20.7 MPa at 548 K), having gas inlet, outlet, intermediate sampling valve, temperature controlled heating (±1 K) and variable agitation speed (0 - 33.3 Hz). As a safety precaution, a rupture disc (gold faced), which can withstand a maximum pressure of 20.7 MPa, was attached to the reactor. For experiments with ≤ 7 MPa pressure, gas was fed through a constant pressure regulator attached to the synthesis gas reservoir while for high pressure experiments, the reactor pressure was maintained by intermittent gas supply from the synthesis gas reservoir (at 1:1 ration of CO:H2), after every drop of ~ 0.2 MPa reactor pressure. Synthesis gas reservoir was always maintained at a minimum 1.5 MPa higher than the reactor pressure. The reaction set-up used in the present study is shown in Figure 5.1. Ice water-cooled condensers were used for intermediate sampling. For Co2(CO)8-catalyzed hydroformylation, maintaining synthesis gas atmosphere is very critical due to instability of Co2(CO)8 at lower pressures.6 In typical cobalt catalyzed hydroformylation experiment, the known quantities of the substrate, catalyst, and the solvent were charged into the autoclave. The contents were immediately flushed thrice with synthesis gas. The reactor was pressurized to ~2 MPa synthesis gas, the solution was saturated by keeping agitation speed of ~16.6 Hz for 2-3 minutes and then heating was started at a constant ~1.66 Hz stirring. After attaining the desired temperature, the synthesis gas was made up to the required pressure from the reservoir and the reaction was initiated by increasing the agitation speed to 20 Hz. The pressure drop in the reservoir vessel was recorded by means of a pressure transducer (precision ± 0.0067 MPa) as a function of time. Intermediate liquid samples were also taken at regular intervals of time. Unless otherwise mentioned, all the reactions were run till the synthesis gas absorption nearly stopped. The autoclave was thoroughly cooled to <293 K, synthesis gas was vented off, the reactor was flushed thrice with nitrogen and the reaction mixture removed. After every reaction, the reactor was cleaned thoroughly and a wash with 10 % HNO3 was given to ensure the total removal of the metal particles. For solvent screening study, the VAM concentration and the total volume of the charge were kept constant. The analysis of the liquid samples was
carried out using GC to examine the product distribution pattern quantitatively. Details of GC analysis are given in the following section.

Figure 5.1. A schematic of the reactor setup for hydroformylation of VAM

5.2.3. Catalyst Recycle Procedure

After completion of a typical hydroformylation reaction, 10 ml of distilled water was added to the reactor through the intermediate addition device at 1.4MPa pressure under continuous agitation. The contents were further stirred under pressure for 15 minutes. After this, the gas was vented off. The reactor contents consisted of two distinctly separate layers- an aqueous layer and an organic layer. The organic phase consisting of the catalyst was recycled and the aqueous phase containing products were analyzed for the quantification of products. VAM was freshly added for the recycle experiments.

5.2.4. Synthesis of Co$_2$(CO)$_8$

The synthesis of Co$_2$(CO)$_8$ was carried out in a 50 ml Parr Autoclave made of Hastelloy C-276, (Rating -maximum pressure 20.7 MPa at 548K) having facilities for gas inlet, outlet, intermediate sampling, temperature controlled heating and variable agitation
speed (0–33.3 Hz). As a safety precaution, a rupture disc (gold faced), with a capacity to withstand a maximum pressure of 20.7 MPa was fitted to the reactor.

Generally, the pressures required for Co₂(CO)₈ synthesis are in the range of 15.2–16.6 MPa at temperatures in the range of 463–473K. In view of the non-availability of gas-cylinders of such high pressures, we used a different technique to boost up the pressure. After charging the cobalt precursor (CoCl₂·6H₂O), and solvent to the reactor, the reactor was chilled down to 0-3 °C. At this low temperature, the reactor was pressurized to ~ 11.2 MPa with synthesis gas at a constant agitation of 20 Hz. The reactor was allowed to attain the room temperature and then heated to the desired temperature at constant stirring of 8 Hz. The reaction was started by increasing the stirring speed to 20 Hz. Due to large temperature gradient of ~ 463K, while attaining the temperature of 468K, the pressure increased to ~ 16.5 MPa. Even at this temperature and pressure, an induction period of ~ 20-40 minutes was observed. The induction period was found to vary with the CO:H₂ ratio of the synthesis gas. All the reactions were conducted till the gas absorption stopped. After cooling the reactor to ~ 280-285K, it was depressurized slowly, flushed thrice with argon and the liquid contents were poured into a 100 ml beaker. The black particles obtained (if any) were weighed and discarded. The solvent was removed by purging argon through the reaction crude following which, shining dark-red crystals of Co₂(CO)₈ were obtained. These were immediately transferred into a high-pressure container under CO atmosphere. The Infra-red analysis (Figure 5.2) of the Co₂(CO)₈ prepared was found to be consistent with the reported spectra with a characteristic absorption band at 1857 cm⁻¹ (ν CO). Co₂(CO)₈ is a red-violet colored, highly unstable compound soluble in organic solvents. Under ambient conditions, it decomposes to Co₄(CO)₁₂ and higher nuclearity clusters of Co. At slightly higher temperatures (~ 305K), it releases CO almost instantaneously. It has been reported⁷ have reported that decomposition of Co₂(CO)₈ is an inverse second order with respect to CO concentration. Thus, to avoid decomposition of Co₂(CO)₈ to Co₄(CO)₁₂ (which is a irreversible reaction) it must be stored under positive CO pressures and at low temperatures (~ 273K).
5.2.5. Preparation of 3-acetoxy Propanal (3-ACPAL)

3-ACPAL required for analysis was prepared according to a procedure described by Ballard and co-workers. Glacial acetic acid and acrolein in a mole ratio of 4.5:1 were mixed and heated in a glass-lined reactor for four hours at 402K. The mixture was then subjected to fractional distillation.

3-ACPAL is highly unstable and decomposes rapidly to acrolein and acetic acid. Acrolein, being an $\alpha, \beta$-unsaturated aldehyde where a double bond and a carbonyl group are in conjugation, is more stable and so 3-ACPAL shows a tendency to decompose. So purification of 3-ACPAL through distillation was futile, as the purity of the distillate didn’t exceed 80%. Attempts to purify 3-ACPAL with column chromatography were also unsuccessful as it was decomposed on TLC plate as well as on the silica in a column. Therefore, the ~80% pure 3-ACPAL was used as a standard by subtracting the quantities of acrolein and acetic acid with the help of pre-calibration of acrolein and acetic acid.

5.2.6. Preparation of 2-acetoxy Propanal (2-ACPAL)

2-ACPAL was prepared by hydroformylation of VAM using the conventional Rh(CO)$_2$(acac) as catalyst and PPh$_3$ as ligand. The hydroformylation of VAM gave high regioselectivity (>98%) to 2-ACPAL. This reaction was carried out in a stainless steel Parr autoclave of 2-liter capacity, at 5.5MPa syngas pressure and at 373 K for 6 hours.
The product was separated by using vacuum distillation and nitrogen purging to get pure 2-ACPAL. The analysis was carried out using GC and found to get 97.3% purity of 2-ACPAL, which was then taken for the further studies.

5.2.7. Oxidation Experiments

Oxidation of ACPALs was carried out in a 50 ml jacketed glass reactor equipped with gas inlet sparger, condenser, thermo well and sampling port. Desired amounts of reaction mixture and catalyst were added to the reactor. The stirring was provided by using an overhead stirrer equipped with digital indicator for stirring speed measurement. A constant reaction temperature was maintained using a thermostat. The typical glass reactor setup used for the reaction is as shown in the Figure 5.3.

![Figure 5.3. A schematic of reaction set-up for oxidation experiments](image)

(1) Jacketed glass reactor (2) Sampling port (3) Gas Spurger (4) Overhead stirrer (5) Condenser
5.2.8. Hydrolysis Experiments

Hydrolysis of ACPAs was carried out in a 50 ml jacketed glass reactor equipped with thermo well, condenser, sampling port. The stirring was done by using magnetic stirrer as shown in the Figure 5.4. Desired amounts of ACPAs, water, and catalyst were added to the reactor and stirred at 353K for required time using a magnetic stirrer.

![Diagram of reaction set-up for hydrolysis experiments](image)

(1) jacketed glass reactor (2) Sampling port (3) Condenser (4) Magnetic stirrer (5) Magnetic needle

**Figure 5.4.** A schematic of reaction set-up for hydrolysis experiments

5.2.9. Analytical Methods

IR spectra were obtained using a Bio-rad FTS 175C spectrometer in transmission mode using KBr pellets as well as liquid cells. GC-MS analysis was carried out for identification of products on an Agilent GC of 6890N series equipped with 5973N Mass Selective Detector. Liquid reaction samples were analyzed on a Hewlett Packard 6890 Series GC controlled by the HP-Chemstation software and equipped with an auto sampler unit, by using a HP-1 capillary column (30 m x 30 μm x 0.25 μm film thickness with a stationary phase of polymethyl siloxane). The quantitative analysis was obtained by
constructing calibration curve in the range of concentrations studied. The conversion, chemo- and regio-selectivities of aldehydes and alcohols were calculated using the following formulae; and the results are discussed in terms of conversion, selectivity, turn over number (TON), turn over frequency (TOF), which are calculated as given below.

\[
Conversion, \% = \left( \frac{\text{Initial concentration of VAM} - \text{Final concentration of VAM}}{\text{Initial concentration of VAM}} \right) \times 100
\]

\[
Selectivity, \% = \frac{\text{Number of moles a product formed}}{\text{Number of moles VAM converted}} \times 100
\]

\[
TON = \frac{\text{Number of moles of hydroformylation products formed}}{\text{Number of moles of catalyst}}
\]

\[
TOF, (\text{hr}^{-1}) = \frac{\text{Number of moles of hydroformylation products formed}}{\text{Number of moles of catalyst} \times \text{time in hours}}
\]

5.3. Results and Discussion

Hydroformylation-oxidation-hydrolysis route to HPAs involves the following reaction steps (Scheme 5.1): (1) Hydroformylation of VAM to the regio-isomers 2-ACPAL and 3-ACPAL, (2) Oxidation of the mixture of 2- and 3-ACPAL to 2- and 3-ACPAL respectively, using molecular oxygen as the oxidant. (3) Hydrolysis of mixture of 2-and 3-ACPA to 2-and 3-HPA respectively. Tailoring the regioselectivity in hydroformylation step is the most important issue, and hence, hydroformylation step in this route is the key step, since the regioselectivity obtained in this step decides the overall yields of the 2- and 3-HPAs at the end of the process.
The important objectives of the work presented in this chapter are:

1. Evaluation of hydroformylation-oxidation-hydrolysis as an alternative route for selective synthesis of racemic 2- and 3-HPA.
2. Hydroformylation of VAM; Co$_2$(CO)$_8$ as catalyst for achieving high regioselectivity to linear-aldehyde (3-ACPAL) and detailed kinetic investigation of VAM hydroformylation as the key step in the present study.
3. Screening of catalysts and optimization of reaction conditions for the oxidation of 2- and 3-ACPAL for achieving high yields of corresponding carboxylic acids. Also the detailed kinetic investigation of oxidation of 2-ACPAL to 2-HPA using molecular oxygen as oxidant.
4. Screening of catalysts and optimization of reaction conditions for the hydrolysis of 2- and 3-ACPA for achieving high yields of corresponding carboxylic acids.

These objectives have been achieved in the present study with detailed experimentation, and the results obtained are presented below in three separate sections Hydroformylation of VAM, oxidation of ACPALs and hydrolysis of ACPAs.

5.3.1 Hydroformylation Experiments
5.3.1.1 Preliminary Experiments

The hydroformylation of VAM was studied as the key step in the synthesis of HPAs with the focus on understanding the activity of Co$_2$(CO)$_8$ catalyst, selectivity to ACPALs and reaction kinetics. It was essential to assess product distribution and material
balance in a few initial experiments. A typical concentration-time profile for VAM hydroformylation at 393K temperature and 5.51 MPa pressure of synthesis gas is as shown in Figure 5.5. Almost complete conversion of VAM was achieved in 3 hours and the material balance of CO or H₂ and VAM consumed was in good agreement with total amount of products formed. In the range of the conditions investigated, the major products formed were 2- and 3-ACPALS, while byproducts like acrolein and acetic acid were found in trace quantity (<2% on the basis of VAM consumed).

![Figure 5.5. Concentration time profile of hydroformylation of VAM](image)

**Reaction Conditions:** Co₂(CO)₈, 3.3X 10⁻⁴ kmol/m³; VAM, 1.02 kmol/m³; temperature, 393K; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, Toluene; up to 2.5 X 10⁻² m³ total volume

5.3.1.1.1 Effect of Synthesis Gas Pressure

The effect of synthesis gas pressure on the rate of hydroformylation of VAM was studied at a constant VAM concentration of 1.05 kmol/m³ and a Co₂(CO)₈ concentration of 5 X 10⁻⁴ kmol/m³ at the temperature of 393K. The results are shown in Figure 5.6. The conversion of VAM was found to increase with increase in total pressure of synthesis gas. An increase in the total synthesis gas pressure is expected to increase the effective concentration of the active catalytic species, i.e. HCo(CO)₄, thereby increasing the rate of...
hydroformylation. The n/iso ratio was found to increase marginally with increase in total pressure.

![Graph showing conversion and n/iso ratio vs pressure](image)

**Figure 5.6.** Effect synthesis gas pressure on conversion of VAM and selectivity to aldehydes

**Reaction Conditions:** \( \text{Co}_2(\text{CO})_8, 3.3 \times 10^{-4} \text{ kmol/m}^3; \text{VAM, 1.05 kmol/m}^3; \) temperature, 393K; agitation speed, 16.6 Hz; Solvent, Toluene; up to \( 2.5 \times 10^2 \text{ m}^3 \) total volume

### 5.3.1.1.2 Effect of Temperature

The effect of temperature on the \( \text{Co}_2(\text{CO})_8 \) catalyzed hydroformylation of VAM was investigated in the range of 353-393K by keeping other parameters constant. The rate of reaction was found to increase with temperature, up to 373K. Beyond this temperature, the reaction was found to proceed rapidly till the first 20 minutes of reaction time, and then stopped abruptly, and the absorption of synthesis gas ceased completely. A probable reason for the decomposition of the catalyst at higher temperature is the rate of absorption of synthesis gas for reaction being more than the rate of dissolution of synthesis gas into the reaction medium, thus causing the reaction to go into mass transfer limitation, thereby starving the sensitive \( \text{Co}_2(\text{CO})_8 \) catalyst of CO. The reaction was very slow at 353K. When the reactions were carried out for longer time, formation of byproducts was
observed. Also, 3-ACPAL was decomposed to some extent, forming acetic acid and acrolein, thus leading to lower n/iso ratio. Acetic acid formed in the reaction at 353K, deactivated the catalyst by precipitating pink colored Co(OAc)$_2$.

From the temperature effect experiments, the optimum range of temperatures was found to be 373 to 393K. It was observed that at 393K temperature, 50.1 % conversion of VAM with 96.2 % selectivity to aldehydes was obtained with an n/iso ratio of 0.85 (Table 5.1; entry 5).

Table 5.1. Hydroformylation of VAM: Effect of Temperature

<table>
<thead>
<tr>
<th>Sr</th>
<th>Reaction Time Min</th>
<th>Temp, K</th>
<th>Conversion %</th>
<th>Rate X 10$^{-4}$ kmol/m$^3$/s</th>
<th>Selectivity, %</th>
<th>n/iso ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>353</td>
<td>13.9</td>
<td>0.39</td>
<td>90.3</td>
<td>9.7</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>363</td>
<td>25.3</td>
<td>0.72</td>
<td>92.1</td>
<td>7.9</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>373</td>
<td>43.4</td>
<td>1.23</td>
<td>95.2</td>
<td>4.8</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>383</td>
<td>50.2</td>
<td>1.42</td>
<td>95.9</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>393</td>
<td>56.9</td>
<td>1.61</td>
<td>96.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Reaction Conditions: Co$_2$(CO)$_8$, 2.5X 10$^{-4}$ kmol/m$^3$; VAM, 1.05 kmol/m$^3$; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, Toluene; up to 2.5 X 10$^{-2}$ m$^3$ total volume

5.3.1.1.3 Screening of Solvents

It is well known that solvent plays a very important role in tailoring activity and selectivity in hydroformylation reaction. Cobalt catalyzed hydroformylation of VAM is a sensitive reaction, and shows considerable change in the activity-selectivity of the reaction on slight variation in the catalyst environment. With the aim to study the effect of solvents on hydroformylation of VAM, screening of halogenated and non-halogenated solvents was carried out. The results are presented in the Table 5.2.

The screening of solvents was carried out by keeping all reaction parameters constant. No reaction occurred in coordinating solvents such as dimethyl formamide, dimethyl acetamide, and acetonitrile. The final solution after these reactions was purple or green instead of usual saffron-red, which may be because of the coordination of the solvents with cobalt, forbidding the possibility of formation of the active hydrido carbonyl species. When the reaction was carried out in neat VAM, (solvent-less
conditions) (entry 1 Table 5.2), no reaction was observed. The reaction was very slow and could not proceed beyond 30 to 35% of VAM conversion (entry 2 and 3). When the reactions were carried out in hexane and cyclohexane, which are most commonly used solvents for the hydroformylation of olefins, the chemo-selectivity to aldehydes was >90%; but the regio-selectivity to 3-ACPAL was low. The solvents toluene and benzene were found to be effective for hydroformylation of VAM, in terms of activity as well as selectivity. In case of hydroformylation of VAM using toluene as solvent, >88% conversion of VAM and the selectivity to 2-ACPAL and 3-ACPAL was found to be 54.2 and 45.8 % respectively (entry 5), making the aldehyde selectivity 100%. Similar results were observed with benzene as solvent (entry 4). Halogenated solvents resulted in high reaction rates and high regioselectivity to 3-ACPAL (entries 6, 7), however, halogenated solvents are not preferred, especially for synthesis of bulk commodities, due to corrosion problems and environmental reasons. Thus from the screening of the solvents it is observed that toluene is the best solvent with high rates and high selectivity to 3-ACPAL.

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Solvents</th>
<th>Conversion , %</th>
<th>Rate X 10^{-4}, kmol/m^3/s</th>
<th>Aldehyde Selectivity, %</th>
<th>n/iso ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2-ACPAL</td>
<td>3-ACPAL</td>
</tr>
<tr>
<td>1</td>
<td>VAM</td>
<td>0</td>
<td>0.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Hexane</td>
<td>28.3</td>
<td>0.80</td>
<td>70.1</td>
<td>29.9</td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexane</td>
<td>32.4</td>
<td>0.92</td>
<td>72.4</td>
<td>27.6</td>
</tr>
<tr>
<td>4</td>
<td>Benzene</td>
<td>86.4</td>
<td>2.45</td>
<td>52.1</td>
<td>47.9</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>88.2</td>
<td>2.50</td>
<td>54.2</td>
<td>45.8</td>
</tr>
<tr>
<td>6</td>
<td>MCB</td>
<td>96.1</td>
<td>2.72</td>
<td>47.6</td>
<td>52.4</td>
</tr>
<tr>
<td>7</td>
<td>DCB</td>
<td>97.5</td>
<td>2.76</td>
<td>48.3</td>
<td>51.7</td>
</tr>
</tbody>
</table>

**Reaction Conditions:** Co_2(CO)_8, 3.3X 10^{-4} kmol/m^3; VAM, 1.05 kmol/m^3; temperature, 393K; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, up to 2.5 X 10^{-2} m^3 total volume
5.3.1.1.4. Catalyst Recycle Study

The high solubility of product ACPALs in water was helpful for effective separation of cobalt catalyst from the organic reaction mixture. The general method employed for catalyst separation was addition of water to the organic mixture and extracting out the ACPALs and unreacted VAM into the aqueous phase by stirring under synthesis gas pressure of 1.37 MPa. Synthesis gas pressure was found to be essential to save the catalyst from formation of cobalt-aqua complex. The catalyst was recycled 5 times without loss of activity. The result of the catalyst recycle study is as shown in the Figure 5.7. Thus, the catalyst recycles and catalyst product separation was established.

![Figure 5.7. Hydroformylation of VAM: Study of catalyst recycle](image)

**Figure 5.7.** Hydroformylation of VAM: Study of catalyst recycle

**Reaction Conditions:** Co$_2$(CO)$_8$, 3.3X $10^{-4}$ kmol/m$^3$; VAM, 1.05 kmol/m$^3$; temperature, 393K; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, Toluene; up to 2.5 X $10^{-2}$ m$^3$ total volume
5.4. Kinetics of Hydroformylation of VAM

A detailed kinetic investigation has been carried out for the Co$_2$(CO)$_8$ catalyzed hydroformylation of VAM in this chapter. There is no previous report on the intrinsic kinetics of hydroformylation of VAM using Co$_2$(CO)$_8$ as a catalyst. The knowledge of kinetics and development of rate equations is also important in understanding the mechanistic features of complex catalytic reactions. Such a study would be useful considering the industrial importance of this reaction in synthesis of HPAs. The effect of Co$_2$(CO)$_8$ concentration, VAM concentration and partial pressures of CO and H$_2$ on initial rate of hydroformylation of VAM has been investigated in the temperature range of 373 - 393K.

5.4.1. Evaluation of Kinetic Regime

5.4.1.1. Effect of Agitation Speed

For the study of intrinsic kinetics, it is essential that the reaction operate in the kinetic regime and not under the condition where mass transfer is controlling. For that purpose, the effect of agitation speed on the rate of reaction was studied. The results are presented in Figure 5.8. The rate was found to be independent of the agitation speed beyond 13.33 Hz, which clearly indicates that the reaction is in kinetic regime. Therefore, all the reactions for kinetic studies were carried out at an agitation speed of 20 Hz to ensure that the reaction occurred in the kinetic regime.
3.0 ~— 2.0 " O 2.0

0.0 10.0 15.0 20.0 25.0

Agitation Speed, Hz

Initial rate X 10^4, kmol/m^3/s

Figure 5.8. A plot of rate of hydroformylation of VAM vs. agitation speed

Reaction Conditions: Co_2(CO)_8, 3.3X 10^{-4} kmol/m^3; VAM, 1.05 kmol/m^3; temperature, 393K; synthesis gas, 5.51 MPa; Solvent, Toluene; up to 2.5 X 10^{-2} m^3 total volume

5.4.1.2 Solubility of H_2 and CO in Solvent

For interpretation of kinetic data, knowledge of the concentration of the gaseous reactants in the reaction medium is essential. The solubility of CO and H_2 in toluene was determined experimentally at 373, 383 and 393K, by using a method due to Chaudhari and coworkers.\(^{10}\) The solubility of H_2 and CO is measured in 6.0 x 10^{-4} m^3 capacity stirred autoclave supplied by Parr Instrument Company, USA, designed for 25 MPa pressure. The equipment was provided with automatic temperature control and a pressure recording system. A pressure transducer having a precession of ± 1 kPa was used to measure the autoclave pressure.

In a typical experiment for the measurement of solubility of H_2 and CO, a known volume of solvent was introduced into the autoclave and the contents were heated to a desired temperature. After a steady temperature reading was attained, the void space in the reactor was carefully flushed with a solute gas and pressurised to the level required. The contents were then stirred for about ten minutes to equilibrate the liquid phase with the solute gas. The change in the pressure in the autoclave was recorded on-line as a
function of time till it remained constant, indicating saturation of the liquid phase. From
the initial and final pressure readings, the solubility was calculated in mole fraction as

\[ X_a = \frac{(P_i - P_f) V_g M_s}{RT V_L \rho_s} \quad 5.1 \]

Where, \( X_a \) represents the mole fraction of the solute gas in the liquid phase at the
partial pressure of the solute gas prevailing at \( P_f \), \( P_i \) and \( P_f \) are the initial and final
pressure readings in the autoclave, \( V_g \) and \( V_L \) are the volumes of the gas and liquid
phases, respectively, \( R \) is the gas constant, \( T \) is the temperature, \( M_s \) is the molecular
weight of the solvent and \( \rho_s \) is the molar density of the liquid. The Henry’s law constant,
\( H \) was calculated as

\[ H = \frac{P_f}{X_a} \quad 5.2 \]

The results are presented as Henry’s law constant in Table 5.3

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>( H_A ) for ( H_2 ) kmol/ m(^3)/MPa</th>
<th>( H_A ) for CO kmol/ m(^3)/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>22.25</td>
<td>10.22</td>
</tr>
<tr>
<td>363</td>
<td>23.50</td>
<td>10.60</td>
</tr>
<tr>
<td>353</td>
<td>24.60</td>
<td>10.90</td>
</tr>
</tbody>
</table>

5.4.1.3 Mass Transfer Effects

The analysis of overall rate of reaction for two-phase (gas-liquid) catalytic
reactions is given by Ramachandran et al\(^{11} \). The following criteria described by
Ramachandran and Chaudhari\(^{20} \) were used to check the significance of various mass-
transfer effects.
5.4.1.3.1 Gas-liquid Mass Transfer Effect

The significance of gas-liquid mass transfer resistance was analyzed by comparing the initial rate of reaction and maximum possible rate of gas-liquid mass transfer. The gas-liquid mass transfer resistance is negligible if a factor $\alpha_i$, defined as follows, is less than 0.1 for the experimental conditions used.

\[
\alpha_{i,A} = \frac{R_{\exp}}{k_i a_b C_{A,aq}} 
\]

\[
\alpha_{i,B} = \frac{R_{\exp}}{k_i a_b C_{B,aq}}
\]

Where, $R_{\exp}$ is the observed rate of hydroformylation (kmol/m$^3$), $k_i a_b$ the gas-liquid mass transfer coefficient and $C_A$ and $C_B$ represent the saturation solubility of reacting gases i.e. H$_2$ and CO in equilibrium with the gas phase concentration at the reaction temperature (kmol/m$^3$). The gas-liquid mass transfer coefficient ($k_i a_b$) used in above equations was estimated by using a correlation (Equation 5.3) proposed by Chaudhari and coworkers$^{12}$ for a reactor similar to that used in this work for agitation speed of 1200 rpm.

\[
k_i a_b = 1.48 \times 10^{-3} (N)^{2.18} \times (V_g / V_L)^{1.88} \times (d_1 / d_r)^{2.1} \times (h_1 / h_2)^{1.16}
\]

The terms involved in above equation are described in Table-5.4 along with the respective values obtained from the reactor and charge used in the present case.
Table 5.5. Parameters used for $k_{LB}$ calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_g$</td>
<td>Gas volume (m$^3$)</td>
<td>$4.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>$N$</td>
<td>Agitation Speed (Hz)</td>
<td>20</td>
</tr>
<tr>
<td>$V_L$</td>
<td>Liquid volume (m$^3$)</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>$d_1$</td>
<td>Impeller diameter (m)</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$d_T$</td>
<td>Tank diameter (m)</td>
<td>$4.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>$h_1$</td>
<td>Height of the impeller from the bottom (m)</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$h_2$</td>
<td>Liquid height (m)</td>
<td>$2.1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

The $k_{LB}$ value for 1200 rpm (20 Hz) was evaluated as 0.22 s$^{-1}$.

The equilibrium solubilities for the gases given in Table 5.3 were used. The factor $\alpha_I$ was calculated (taking $R_{exp}$ as $2.02 \times 10^{-4}$ i.e. highest) for both hydrogen and carbon monoxide and found to be $2.17 \times 10^{-2}$ and $9.79 \times 10^{-3}$, respectively. Since the values of $\alpha_I$ are very much less than 0.1 for both the gaseous reactants, gas-liquid mass transfer resistance can be assumed to be negligible.

5.4.2 Initial Rate Data

The kinetics of the hydroformylation of VAM using $\text{CO}_2(\text{CO})_8$ as catalyst was investigated in the range of conditions shown in Table 5.6 as per the procedure described earlier.
Table 5.6. Range of conditions used for the kinetic studies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration (kmol/m$^3$)</td>
<td>2.5x10^{-5}-1x10^{-5}</td>
</tr>
<tr>
<td>Concentration of VAM (kmol/m$^3$)</td>
<td>0.51-3.05</td>
</tr>
<tr>
<td>Partial pressure of hydrogen (MPa)</td>
<td>1.04-2.07</td>
</tr>
<tr>
<td>Partial pressure of carbon monoxide (MPa)</td>
<td>0.34-2.74</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>373-393</td>
</tr>
<tr>
<td>Solvent</td>
<td>Toluene</td>
</tr>
<tr>
<td>Agitation speed (Hz)</td>
<td>16.6-20.0</td>
</tr>
<tr>
<td>Reaction volume (m$^3$)</td>
<td>2.5 x 10^{-5}</td>
</tr>
</tbody>
</table>

The initial rates of hydroformylation were calculated from the plot of aldehyde formation as a function of time. Under the conditions chosen for the kinetic study, no side reactions were found to occur and hence, these data would be representative of the overall hydroformylation of VAM to the corresponding aldehydes. An induction was observed during the reaction. Hence for the calculation of the rate, the data was corrected for the induction period. The results showing the dependence of the rates on different parameters and a kinetic model based on these data are discussed in the following sections.

5.4.2.1 Effect of Co$_2$(CO)$_8$ Concentration

The effect of Co$_2$(CO)$_8$ concentration on the rate of hydroformylation of VAM was studied in the temperature range of 373-393K, VAM concentration of 1.05 kmol/m$^3$ and a total pressure of CO+H$_2$ = 5.51 MPa (CO:H$_2$ = 1). The results are shown in Figure 5.9. The rate was found to be linearly dependent on the Co$_2$(CO)$_8$ concentration, indicating a first order kinetics. An increase in concentration of Co$_2$(CO)$_8$ causes an increase in the effective concentration of active catalyst, hydrido cobalt carbonyl species, as seen from the mechanism (scheme 5.2), thereby increasing the rate of reaction, and hence a first order dependence is observed.
Figure 5.9. A plot of Initial rate vs. catalyst concentration in hydroformylation of VAM

Reaction Conditions: VAM, 1.05 kmol/m$^3$; temperature, 373-393K; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, Toluene; up to 2.5 X 10$^{-2}$ m$^3$ total volume

5.4.2.2 Effect of VAM Concentration

The effect of VAM concentration on the rate of hydroformylation of VAM was investigated in the temperature range of 373-393K. The plot of rate vs. VAM concentration was found to have a linear dependence on VAM in the initial concentration range and at higher substrate concentration; it becomes independent of VAM concentration as shown in Figure 5.10. This could be due to the formation of diolefinic species in equilibrium. Such observation has been reported in kinetics of hydroformylation of olefins using homogeneous catalysts$^{13}$ as well as heterogeneous$^{14}$ and biphasic$^{15}$ catalysts.
Figure 5.10. A plot of Initial rate vs. VAM concentration effect in the hydroformylation of VAM

**Reaction Conditions:** Co$_2$(CO)$_8$, 2.3X $10^{-4}$ kmol/m$^3$; temperature, 373-393K; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, Toluene; up to 2.5 X $10^{-2}$ m$^3$ total volume

5.4.2.3 Effect of Partial Pressure of Hydrogen

The effect of partial pressure of H$_2$ on the rate of hydroformylation of VAM was investigated at a constant CO partial pressure of 2.75 MPa and the results are shown in Figure 5.11. The rate of reaction was found to have a first order dependence on $P_{H2}$. As shown in the mechanism, hydrogen preliminarily converts the catalytically inactive Co$_2$(CO)$_8$ into HCo(CO)$_4$ which consequently is converted to HCo(CO)$_3$. Also, the alkyl cobalt tri carbonyl species is converted into the aldehydes due to hydrogen. Therefore, it is evident that increase in partial pressure of hydrogen should increase rate of reaction. Hence, with increasing pressure of hydrogen, the rate enhancement is observed.
**Figure 5.11.** A plot of rate vs. $P_{\text{H}_2}$ for the hydroformylation of VAM

**Reaction Conditions:** Co$_2$(CO)$_8$, $2.3 \times 10^{-4}$ kmol/m$^3$; VAM, 1.05 kmol/m$^3$; temperature, 393K; agitation speed, 16.6 Hz, Solvent, Toluene; up to $2.5 \times 10^{-2}$ m$^3$ total volume

**5.4.2.4 Effect of Partial Pressure of Carbon monoxide**

The effect of $P_{\text{CO}}$ on the rate of hydroformylation of VAM was studied keeping a constant $H_2$ partial pressure of 2.75 MPa; the results are shown in Figure 5.12. A plot of rate vs. CO partial pressure passes through maximum. In the initial pressure range, the rate was found to be the first order with $P_{\text{CO}}$ and inversely dependent on $P_{\text{CO}}$ at higher CO pressures. The observed negative effect of $P_{\text{CO}}$ can be readily explained from the proposed mechanism where the CO concentration affects the equilibrium between the 16 electron HCo(CO)$_3$ species and the 18 electron HCo(CO)$_4$ species. At very low $P_{\text{CO}}$, positive effect is observed because of the requirement of certain minimum $P_{\text{CO}}$ for the CO-insertion step. After reaching that minimum $P_{\text{CO}}$ concentration, any further rise in $P_{\text{CO}}$ helps maintaining the HCo(CO)$_4$ species in preference to the HCo(CO)$_3$ species, and thereby prohibits olefin insertion.
Figure 5.12. A plot of rate vs. $P_{CO}$ for the hydroformylation of VAM.

**Reaction Conditions:** $CO_2(CO)_8$, $2.3 \times 10^4$ kmol/m$^3$; VAM, $1.05$ kmol/m$^3$; temperature, 373-393K; agitation speed, 16.6 Hz, synthesis gas, 5.51 MPa; Solvent, Toluene; up to $2.5 \times 10^2$ m$^3$ total volume

5.4.3 Kinetic Models

For the purpose of development of rate models, an empirical approach was followed. Prior to discrimination of rate equations, the rate data was analyzed for the importance of mass transfer resistances. The effect of agitation speed on the rate was investigated at the highest catalyst concentration and at the highest temperature. The rate was found to be independent of the agitation speed, and hence the data were representative of the true kinetics of the reaction. Also the analysis of initial rate data according to the criteria laid down by Ramachandran and Chaudhari$^{20}$ confirmed that the gas–liquid ($a_{g}$) mass transfer resistance was negligible. The initial rate data were hence used to evaluate the intrinsic kinetic parameters.

In order to fit the observed rate data, several rate equations were examined using a nonlinear regression analysis. The results on the kinetic parameters estimated for the
different models are presented in Table 5.6. For this purpose, an optimization program based on Marquardt’s method\textsuperscript{16} was used. The objective function was chosen as follows;

$$\phi = \sum_{i=1}^{n} [R_{Ai} - R'_{Ai}]^2$$

Where, $\phi$ is the objective function to be minimized ($\Phi_{\text{min}}$) representing the sum of the squares of the difference between the observed and predicted rates, $n$ is the number of experimental data, $R_{Ai}$ and $R'_{Ai}$ represent experimental and predicted rates, respectively. The values of rate parameters and $\Phi_{\text{min}}$, are presented in Table 5.7.

**Table 5.7.** Rate models examine to fit the data on VAM hydroformylation

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Rate Model</th>
<th>T (K)</th>
<th>$k_1$</th>
<th>$K_2$</th>
<th>$K_3$</th>
<th>$\Phi_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$r = \frac{k_1A^*B^<em>CD}{(1 + K_2D)(1 + K_3B^</em>)^2}$</td>
<td>343</td>
<td>3.14x10^{-3}</td>
<td>3.95</td>
<td>9.58x10^{-1}</td>
<td>8.76x10^{-12}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>5.92x10^{-3}</td>
<td>4.97</td>
<td>9.46x10^{-1}</td>
<td>3.60x10^{-11}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>363</td>
<td>1.16x10^{-2}</td>
<td>5.90</td>
<td>9.24x10^{-1}</td>
<td>1.54x10^{-10}</td>
</tr>
<tr>
<td>2</td>
<td>$r = \frac{k_1A^*B^<em>CD}{(1 + K_2D)(1 + K_3B^</em>)}$</td>
<td>343</td>
<td>1.43x10^{-3}</td>
<td>1.76x10^{-1}</td>
<td>2.95</td>
<td>8.12x10^{-12}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>3.27x10^{-4}</td>
<td>4.90x10^{-8}</td>
<td>9.17x10^{-4}</td>
<td>1.20x10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>363</td>
<td>4.49</td>
<td>3.40x10^{-4}</td>
<td>1.82x10^{-2}</td>
<td>5.24x10^{-9}</td>
</tr>
<tr>
<td>3</td>
<td>$r = \frac{k_1A^*B^<em>CD}{(1 + K_2D)(1 + K_3B^</em>)^2}$</td>
<td>343</td>
<td>1.51x10^{-2}</td>
<td>7.23x10^{-1}</td>
<td>2.64</td>
<td>1.13x10^{-11}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>2.88x10^{-2}</td>
<td>7.35x10^{-1}</td>
<td>2.61</td>
<td>4.60x10^{-11}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>363</td>
<td>5.17x10^{-1}</td>
<td>6.95x10^{-2}</td>
<td>2.52</td>
<td>2.06x10^{-10}</td>
</tr>
<tr>
<td>4</td>
<td>$r = \frac{k_1A^*B^<em>CD}{(1 + K_2D)(1 + K_3B^</em>)}$</td>
<td>343</td>
<td>3.42x10^{-3}</td>
<td>3.98</td>
<td>2.72</td>
<td>9.78x10^{-12}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>6.29x10^{-3}</td>
<td>3.93</td>
<td>2.64</td>
<td>4.00x10^{-11}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>363</td>
<td>5.67x10^{-2}</td>
<td>3.91</td>
<td>3.65x10^{-3}</td>
<td>2.31x10^{-9}</td>
</tr>
<tr>
<td>5</td>
<td>$r = \frac{k_1A^*B^<em>CD}{(1 + K_2D)(1 + K_3B^</em>)^2}$</td>
<td>343</td>
<td>2.52x10^{-3}</td>
<td>1.90</td>
<td>5.84x10^{-1}</td>
<td>9.57x10^{-12}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>353</td>
<td>1.26x10^{-1}</td>
<td>3.82x10^{-3}</td>
<td>-1.47x10^{-4}</td>
<td>6.08x10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>363</td>
<td>9.42x10^{-3}</td>
<td>1.91</td>
<td>5.62x10^{-1}</td>
<td>1.68x10^{-10}</td>
</tr>
</tbody>
</table>

Where, $A$ and $B$ represent the concentrations of $\text{H}_2$ and $\text{CO}$ in toluene at the gas-liquid interface (kmol/m$^3$) respectively. $C$ and $D$ are the concentrations of the catalyst and VAM (kmol/m$^3$), respectively.

The discrimination of rate models was done based on the thermodynamic criteria, activation energy and the $\Phi_{\text{min}}$ values. The rate models II and III were rejected based on
the thermodynamic criteria of inconsistency of equilibrium constant and high activation energy. Model V has rate parameters less than zero (−ve) and hence rejected. In the remaining two models (I and IV), the model IV was rejected based on the higher $\Phi_{\text{min}}$ values than model I. Therefore, model I (Equation 5.8) was considered to be the best model for representing the kinetics of hydroformylation of VAM using Co$_2$(CO)$_8$ as catalyst.

$$r = \frac{k_1A*B*CD}{(1+K_2D)(1+K_3B*)}$$  \hspace{1cm} 5.7

Where, $k$ is the intrinsic rate constant (m$^9$/kmol$^7$/s), $A$ and $B$ represent the concentrations of H$_2$ and CO in toluene at the gas-liquid interface (kmol/m$^3$) respectively. $C$ and $D$ are the concentrations of the catalyst and VAM (kmol/m$^3$), respectively. The rate parameters for Equation 5.8 for all the temperature are presented in Table 5.6 (entry 1). A comparison of the experimental rates with the rates predicted by Equation 5.7 is shown in Figure 5.13, which shows a reasonably good fit of the data. The average deviation in the predicted and observed rates was found to be in the range of ± 3 %. The Arrhenius plot showing the effect of temperature on the rate parameters is shown in Figure 5.14, from which the activation energy was evaluated as 67.94 kJ/mol. The dependence of the rate parameters $K_2$ and $K_3$ on temperature 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.
**Figure 5.13.** Comparison of experimental rates and rates predicted using model I

**Figure 5.14.** Temperature dependence of rate constant

### 5.5 Mechanism of Hydroformylation of VAM

Hydroformylation is one of the most well explored carbonylation reactions in terms of mechanistic aspects. Earlier studies in the cobalt catalyzed hydroformylation of VAM in our laboratory have shown that there is no considerable effect of ligands in
enhancing the rate of reaction, rather, the phosphine ligands cause decomposition of VAM; while a few nitrogen containing ligands actually cause rate retardation and cause undesirable side reactions. Thus, there is no actual role of ligands in the mechanism of cobalt-catalyzed VAM hydroformylation. Although cobalt is one of the earliest discovered hydroformylation catalyst, there has been some debate in the activation of hydrogen by cobalt. The most accepted way of activation is shown below (5.8).

\[
\text{Co}_2\text{(CO)}_8 + \text{H}_2 \rightarrow 2 \text{HCo(CO)}_4 \quad 5.8
\]

On the basis of kinetic data, two other activation paths have been postulated, one involving a dinuclear olefin complex (Equation 5.9) and the other a dinuclear-dihydrido olefin complex (Equation 5.10).

\[
\text{Co}_2\text{(CO)}_7(\text{CH}_2=\text{CH}_2) + \text{H}_2 \rightarrow \text{Co}_2\text{(CO)}_6 + \text{CH}_3\text{CH}_2\text{CHO} \quad 5.9
\]

\[
\text{Co}_2\text{(CO)}_8 + \text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{H}_2\text{Co}_2\text{(CO)}_7(\text{CH}_2\text{CH}_2) + \text{CO} \quad 5.10
\]

\[
\text{H}_2\text{Co}_2\text{(CO)}_7(\text{CH}_2\text{CH}_2) + 2\text{CO} \rightarrow \text{Co}_2\text{(CO)}_8 + \text{CCH}_2\text{CHOH} \quad 5.11
\]

These possibilities were ruled out because in the hydroformylation of ethylene with a D$_2$/H$_2$ (1/1) gas mixture propanal-$d_1$ is the primary product. Activation of H$_2$ by a coordinatively unsaturated acyl-cobalt tricarbonyl has also been proposed. We believe that the activation of hydrogen in the unmodified cobalt catalyzed VAM hydroformylation takes place in dual manner, where the primary activation of H$_2$ is as shown in equation 5.9, which gives rise to the highly unstable 18 electron HCo(CO)$_4$, which reversibly forms the catalytically active 16 electron HCo(CO)$_3$, as can be seen in Scheme 5.2. Further, the acyl-cobalt tricarbonyl again activates H$_2$ to yield a molecule of aldehyde in a manner postulated by Heck and Breslov, giving back the HCo(CO)$_3$.

The parametric effects and the effects of concentrations of the catalyst and VAM comply well with the mechanism shown in Scheme 5.2.
Scheme 5.2. Mechanism of hydroformylation of VAM

5.6 Liquid Phase Oxidation of Acetoxy Propanals

Liquid phase oxidation of aldehydes to carboxylic acid is one of the most common reactions in organic synthesis. Despite the growing awareness about green chemistry, synthetic industry still makes use of environmentally unacceptable reagents like K₂Cr₂O₇, KMnO₄, nitric acid, bromine etc. for several such oxidations, which yield value-added products, which are commodity or fine chemicals.²³ Extensive work has been done to develop metal-based catalyst system and inorganic or organic promoters for the efficient oxidation of aldehydes using the more acceptable ‘green’ oxidants like H₂O₂,
TBHP etc in acidic solvents. In the modern chemical industry, the liquid-phase oxidation of aldehydes by molecular oxygen is a very attractive process from an economic and environmental point of view. Several literature references quote oxidation of aldehydes to carboxylic acids using molecular oxygen as oxidant in acidic solvents like acetic acid, peracetic acid, butyric acid etc. The use of such acidic solvents implies corrosion and safety hazards, besides the generation of salts, which usually have to be land filled.

Scanty literature is available on the oxidation of ACPALs to ACPAs. These acids on hydrolysis yield the corresponding HPAs, which have wide range of applications in food, pharmaceutical, and polymer industry. Oxidation of 2-ACPAL has been reported by Tinkar and coworkers in acidic solvents like acetic acid with salts of cobalt and manganese as catalysts, in the presence of molecular oxygen as the oxidant. The use of soluble catalysts, which leads to separation problems, and the corrosive acidic solvents, are major shortcomings of this process. Besides this, the isolation and purification of the products are the major issues, mainly because of the applications of the products are in food and pharmaceutical industry.

In this chapter, the detailed study on oxidation of the mixture of 2- and 3-ACPAL has been investigated in a non-acidic solvent like methyl ethyl ketone (MEK), using molecular oxygen as oxidant and 1% Co/C as catalyst with high yield of 2- and 3-HPA. To assess the activity of the Co/C catalyst, a few other catalysts were also screened using the same experimental conditions. The effect of different parameters on conversion of aldehyde and selectivity to corresponding carboxylic acids was investigated to optimize the reaction conditions and parameters. Moreover, to get the detailed understanding of the liquid phase oxidation of ACPALs, oxidation of 2-ACPAL was carried out separately. The kinetics of the 2-ACPAL was carried out using the 1%Co/C as catalyst and air as oxidant in the temperature range of 303 - 343K. The material balance and reproducibility of the experiments was confirmed, by taking a few experiments in which the amounts of 2-ACPAL consumed and the products formed were compared for experiments at high conversions of 2-ACPAL.
5.6.1 Oxidation of ACPALs: Screening of Catalysts

Numerous supported transition metal catalysts were screened for liquid phase oxidation of mixtures of 2- and 3- ACPAL to 2 and 3-HPA, the results are presented in Table 5.8. To study the non catalytic oxidation of ACPALs, reaction was carried out without catalyst by purging molecular oxygen as oxidant, but the reaction could not proceed much (entry 1). Among the catalysts screened, 1%Co/C was found to give highest activity and selectivity to corresponding carboxylic acids (entry 7), the other catalysts screened were Ru/C, Pd/C, Pt/C, Fe/C, Cu/C etc (entry 2 - 6 ). Ru/C was also found to give good activity (entry 6).

Table 5.8. Liquid phase oxidation ACPALs: Screening of catalyst

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Catalyst</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Non catalytic</td>
<td>1.86</td>
<td>3.96</td>
</tr>
<tr>
<td>2</td>
<td>1% Fe/C</td>
<td>6.30</td>
<td>9.63</td>
</tr>
<tr>
<td>3</td>
<td>1% Cu/C</td>
<td>9.23</td>
<td>10.11</td>
</tr>
<tr>
<td>4</td>
<td>1% Pd/C</td>
<td>12.82</td>
<td>15.69</td>
</tr>
<tr>
<td>5</td>
<td>1% Pt/C</td>
<td>10.29</td>
<td>13.36</td>
</tr>
<tr>
<td>6</td>
<td>1% Ru/C</td>
<td>14.96</td>
<td>17.90</td>
</tr>
<tr>
<td>7</td>
<td>1% Co/C</td>
<td>25.30</td>
<td>33.87</td>
</tr>
</tbody>
</table>

Reaction Conditions: ACPALs, 2.05 kmol/m³ (2:3 ACPAL 54:46); ACPALs: Catalyst, 1000:1; temperature, 333K; Agitation speed, 16.6 Hz; Solvent, MEK; Total volume, up to 2.5 X 10⁻³ m³

5.6.2 Screening of Solvents

For the oxidation of aldehydes, several acidic as well as non-acidic solvents were screened and the results are shown in Table 5.9. Among the non-acidic solvents screened methyl ethyl ketone (MEK) was found to give the highest activity and selectivity. Acidic solvents like butyric acid and acidic acid were found to give higher rates than MEK. The reason for not selecting acidic solvents for further detailed study was because they are highly corrosive in nature. MEK was chosen as solvent as it offers advantages as easier separation by distillation, high rate of reaction and non-corrosive in nature.
Table 5.9. Liquid phase oxidation ACPALs: Screening of solvents

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Solvents</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 ACPAL 3 ACPAL</td>
<td>2-ACPA 3-ACPA</td>
</tr>
<tr>
<td>1</td>
<td>Toluene</td>
<td>2.80</td>
<td>5.23</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexane</td>
<td>4.90</td>
<td>7.63</td>
</tr>
<tr>
<td>3</td>
<td>Dichloromethane</td>
<td>7.60</td>
<td>10.60</td>
</tr>
<tr>
<td>4</td>
<td>MEK</td>
<td>25.60</td>
<td>35.92</td>
</tr>
<tr>
<td>5</td>
<td>Acetic acid</td>
<td>39.30</td>
<td>57.20</td>
</tr>
<tr>
<td>6</td>
<td>Propionic acid</td>
<td>33.10</td>
<td>46.59</td>
</tr>
<tr>
<td>7</td>
<td>Butyric acid</td>
<td>32.60</td>
<td>47.90</td>
</tr>
<tr>
<td>8</td>
<td>Isobutyric acid</td>
<td>33.62</td>
<td>44.93</td>
</tr>
</tbody>
</table>

**Reaction Conditions:** ACPALS, 2.05 kmol/m³ (2:3ACPAL,54:46); ACPALS : Catalyst 1% Co/C, 1000:1; temperature, 333K; Agitation speed, 16.6 Hz; Oxygen flow rate, 30 ml/min; Solvent, MEK ; Total volume, up to 2.5 X 10⁻⁵ m³

### 5.7 Liquid Phase Oxidation of 2-ACPAL

The liquid phase oxidation of 2-ACPAL was investigated in detail to understand the catalysis and kinetics involved, using 1%Co/C as a catalyst and air as the oxidant, in the temperature range of 303 to 343K. From the screening of catalysts for ACPALs, it was observed that Co/C gives highest activity and selectivity for the oxidation of ACPALs. Based on these results, further studies were carried out. The effect of Co loading in Co/C was studied: Marginal difference was observed in the activity of 1%Co/C, 3%Co/C and 5% Co/C (entry 1-3). So for the detailed investigation, 1% Co/C was chosen as catalyst. The effect of catalyst concentration was studied and results are presented in Table 5.10. 2-ACPAL conversion increases with increase in catalyst concentration (entry 4-6). To study the effect of temperature, the reactions were carried out in the temperature range of 303 - 343K (entry 7-9). It was observed that the rate of reaction increase with increase in temperature and without affecting the selectivity to 2-ACPA.
Table 5.10. Liquid phase oxidation 2-ACPAL: Preliminary experiments

<table>
<thead>
<tr>
<th>Sr</th>
<th>Catalyst</th>
<th>Cobalt concentration X $10^5$, kmol/m$^3$</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
<th>T.O.N.</th>
<th>T.O.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td></td>
<td>0.4</td>
<td>92.1</td>
<td>10.2</td>
<td>20.3</td>
</tr>
<tr>
<td>1</td>
<td>1% Co/C</td>
<td>0.85</td>
<td>38.9</td>
<td>98.9</td>
<td>988.0</td>
<td>1976.0</td>
</tr>
<tr>
<td>2</td>
<td>3% Co/C</td>
<td>0.85</td>
<td>40.1</td>
<td>98.6</td>
<td>1017.9</td>
<td>2035.9</td>
</tr>
<tr>
<td>3</td>
<td>5% Co/C</td>
<td>0.85</td>
<td>38.1</td>
<td>97.9</td>
<td>967.2</td>
<td>1934.3</td>
</tr>
<tr>
<td>4</td>
<td>1% Co/C</td>
<td>0.34</td>
<td>20.1</td>
<td>97.7</td>
<td>510.7</td>
<td>1021.5</td>
</tr>
<tr>
<td>5</td>
<td>1% Co/C</td>
<td>1.70</td>
<td>56.9</td>
<td>99.6</td>
<td>1444.4</td>
<td>2888.8</td>
</tr>
<tr>
<td>6</td>
<td>1% Co/C</td>
<td>2.55</td>
<td>68.2</td>
<td>96.3</td>
<td>1732.0</td>
<td>3464.0</td>
</tr>
<tr>
<td>7</td>
<td>303</td>
<td>0.85</td>
<td>15.9</td>
<td>95.9</td>
<td>404.4</td>
<td>808.8</td>
</tr>
<tr>
<td>8</td>
<td>313</td>
<td>0.85</td>
<td>23.6</td>
<td>99.3</td>
<td>599.8</td>
<td>1199.7</td>
</tr>
<tr>
<td>9</td>
<td>323</td>
<td>0.85</td>
<td>30.3</td>
<td>98.7</td>
<td>769.2</td>
<td>1538.3</td>
</tr>
<tr>
<td>10</td>
<td>333</td>
<td>0.85</td>
<td>38.9</td>
<td>98.9</td>
<td>988.0</td>
<td>1976.0</td>
</tr>
<tr>
<td>11</td>
<td>343</td>
<td>0.85</td>
<td>60.6</td>
<td>94.2</td>
<td>1538.3</td>
<td>3076.6</td>
</tr>
</tbody>
</table>

**Reaction Conditions:** 2-ACPAL, 1.4 kmol/m$^3$; ACPALs: catalyst: 100:1; 3 kg/m$^3$; temperature, 333K; Agitation speed, 16.6 Hz; Reaction time, 0.5 hours; Oxygen flow rate, 30 ml/min; Solvent, MEK; Total volume, up to $5.5 \times 10^5$ m$^3$

5.7.1. Kinetics of Liquid Phase Oxidation of 2-ACPAL

Kinetics of liquid phase oxidation of 2-ACPAL has been investigated using 1%Co/C as catalyst and molecular oxygen as oxidant. In none of the previous studies, detailed investigation of intrinsic kinetics of liquid phase oxidation of 2-ACPAL has been reported. Considering the industrial importance of this reaction in synthesis of HPAs, such a study would be useful. The effect of catalyst concentration, 2-ACPAL concentration and oxygen partial pressure on initial rate of oxidation of 2-ACPAL has been investigated in the temperature range of 293-343K. The material balance and reproducibility of the experiments were confirmed for kinetic study. For this purpose, few experiments were carried out in which the amount of 2-ACPAL consumed, and 2-ACPA formed were compared for the experiments with high conversion of 2-ACPAL. The typical concentration time profile of oxidation of 2-ACPAL is as show in the Figure 5.15.
Figure 5.15. Concentration time profile for oxidation of 2-ACPAL

Reaction Conditions: 2-ACPAL, 1.4 kmol/m$^3$; 1% Co/C, 3 kg/m$^3$; temperature, 333K; Agitation speed, 16.6 Hz; Oxygen flow rate, 30 ml/min; Solvent, MEK; Total volume, up to 5.5 X 10$^{-5}$ m$^3$

5.7.2 Evaluation of Kinetic Regime

5.7.2.1 Effect of Agitation Speed

For the investigation of kinetics, it is essential that the reaction should operate in kinetic regime and not under the condition where mass transfer is controlling. For that purpose, the effect of agitation speed on the rate of reaction was studied and the results are presented in Figure 5.16. The rate was found to be independent of the agitation speed beyond 1000 (16.6 Hz) rpm, which clearly indicates that the reaction is in kinetic regime. Therefore, all the reactions for kinetic studies were carried out at an agitation speed of 1200 rpm (20 Hz) to ensure that the reaction occurred in the kinetic regime. This observation of agitation speed was also supported by criteria’s given in chapter-2. The value of $\alpha_{gl}$, $\alpha_{ls}$ and $\phi_{exp}$, which are defined as the ratios of the observed rates to the maximum rates of gas-liquid, liquid-solid and intraparticle mass transfer rates was found
to be $\alpha_l = 5.32 \times 10^{-4}$ $\alpha_{15} = 0.031$ $\varphi_{exp} = 1.89 \times 10^{-3}$ respectively, which are less than 1, implies the reaction is in kinetic regime.

![Graph](image)

**Figure 5.16.** Effect of agitation speed on the rate of oxidation of 2-ACPAL.

**Reaction Conditions:** 2-ACPAL, 1.4 kmol/m$^3$; 1% Co/C, 3 kg/m$^3$; temperature, 333K; Oxygen flow rate, 30 ml/min; Solvent, MEK; Total volume, up to 5.5 X 10$^{-5}$ m$^3$

**5.7.2.2 Effect of Oxygen Flow Rate**

To study the effect of oxygen flow rate on the rate of the oxidation, reaction was studied in the range of oxygen flow rate 10 – 70 ml/min. There was a marked improvement in the rate of reaction when the flow rate is very less but it was observed that there is no effect of oxygen flow rate on the rate of reaction in the studied range. The results are as shown in the Figure 5.17.
Figure 5.17. Effect Oxygen Flow rate on rate of 2-ACPAL oxidation

**Reaction Conditions:** 2-ACPAL, 1.4 kmol/m$^3$; 1% Co/C, 3 kg/m$^3$; temperature, 333K; Agitation speed, 16.6 Hz; Solvent, MEK; Total volume, up to 5.5 X 10$^{-5}$ m$^3$

5.7.3. Initial Rate Data

The kinetics of the liquid phase oxidation of 2-ACPAL using 1%Co/C as catalyst and molecular oxygen as oxidant was investigated in the range of conditions shown in Table 5.11.

**Table 5.11. Range of conditions used for the kinetic studies**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration (kg/m$^3$)</td>
<td>2.5x10$^{-5}$-1x10$^{-5}$</td>
</tr>
<tr>
<td>Concentration of 2-ACPAL (kmol/m$^3$)</td>
<td>0.51-3.05</td>
</tr>
<tr>
<td>O$_2$ concentration (kmol/m$^3$)</td>
<td>0.5-5</td>
</tr>
<tr>
<td>Temperature, (K)</td>
<td>303-333</td>
</tr>
<tr>
<td>Solvent</td>
<td>MEK</td>
</tr>
<tr>
<td>Reaction volume (m$^3$)</td>
<td>5.0 x 10$^{-5}$</td>
</tr>
</tbody>
</table>
The initial rates of oxidation of 2-ACPAL were calculated from the plot of 2-ACPA formed as a function of time. Under the conditions chosen for the kinetic study, no side reactions were found to occur and hence, these data would be representative of the overall oxidation of 2-ACPAL to 2-ACPA. The results showing the dependence of the rates on different parameters and a kinetic model based on these data are discussed in the following sections.

5.7.3.1 Effect of Catalyst Concentration

The effect of catalyst concentration, on the rate of oxidation of 2-ACPAL was studied in the temperature range of 303-333K. The results are shown in Figure 5.18. The rate was found to be linearly dependent on the 1% Co/C loading, indicating a first order kinetics.

![Graph showing the effect of catalyst concentration on rate of 2-ACPAL oxidation.](image)

**Figure 5.18.** Effect of catalyst concentration on rate of 2-ACPAL oxidation

**Reaction Conditions:** 2-ACPAL, 1.4 kmol/m$^3$; temperature, 303-333K; Agitation speed, 16.6 Hz; Oxygen flow rate, 30 ml/min; Solvent, MEK; Total volume, up to 5.0 X 10$^{-5}$ m$^3$
5.7.3.2 Effect of 2-ACPAL Concentration

The effect of 2-ACPAL concentration on the rate of oxidation of 2-ACPAL was investigated in the temperature range of 303-333K and the results are shown in the Figure 5.19. The plot of rate vs. 2-ACPAL concentration was found to have a linear dependence on 2-ACPAL in the initial concentration range and at higher substrate concentration; it becomes independent of the substrate concentration.

![Figure 5.19. Effect of 2-ACPAL concentration on rate of 2-ACPAL oxidation](image)

**Reaction Conditions:** 1% Co/C, 3 kg/m³; temperature, 303-333K; Agitation speed, 16.6 Hz; Oxygen flow rate, 30 ml/min; Solvent, MEK; Total volume, up to 5.0 X 10⁻⁵ m³

5.7.3.3 Effect of Oxygen Partial Pressure

The oxygen partial pressure was varied in order to study its effect on rate of the reaction in the temperature range of 293-323K. It was observed that there was marginal increase in the rate of the reaction initially but it was independent of oxygen partial pressure at higher partial pressure of oxygen. The results are as shown in the Figure 5.20.
2.5 -

Figure 5.20. Effect of $P_{O_2}$ on rate of 2-ACPAL oxidation

**Reaction Conditions:** 2-ACPAL, 1.4 kmol/m$^3$; 1% Co/C, 3 kg/m$^3$; temperature, 303-333K; Agitation speed, 16.6 Hz; Oxygen flow rate, 30 ml/min; Solvent, MEK; Total volume, up to 5.0 X 10$^{-5}$ m$^3$

5.7.4. Kinetic Models

For the purpose of development of rate models, an empirical approach was followed as described in the section 5.4.3. Prior to discrimination of rate equations, the rate data were analyzed for the importance of mass transfer resistances. The effect of agitation speed on the rate was investigated at the highest catalyst concentration and at highest temperature. The rate was found to be independent of the agitation speed, and hence the data were representative of the true kinetics of the reaction. Also the gas–liquid ($a_{gl}$), gas-liquid-solid ($a_{gls}$), mass transfer resistance were found to be negligible.
Table 5.12. Rate models examine to fit the data on liquid phase oxidation of 2-ACPAL

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Rate Model</th>
<th>T (K)</th>
<th>(k_1)</th>
<th>(K_2)</th>
<th>(K_3)</th>
<th>(\Phi_{\min})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(r = \frac{k_{EFG^<em>}}{(1 + K_2E)(1 + K_3G^</em>)})</td>
<td>303</td>
<td>3.14\times10^{-3}</td>
<td>3.95</td>
<td>9.58\times10^{-1}</td>
<td>8.76\times10^{-10}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
<td>5.92\times10^{-3}</td>
<td>4.97</td>
<td>9.46\times10^{-1}</td>
<td>3.60\times10^{-10}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>1.16\times10^{-2}</td>
<td>5.90</td>
<td>9.24\times10^{-1}</td>
<td>1.54\times10^{-10}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>1.91\times10^{-2}</td>
<td>7.90</td>
<td>8.12\times10^{-1}</td>
<td>1.54\times10^{-10}</td>
</tr>
<tr>
<td>2</td>
<td>(r = \frac{k_{EFG^<em>}}{(1 + K_2E)(1 + K_3G^</em>)^2})</td>
<td>303</td>
<td>1.43\times10^{-3}</td>
<td>1.76\times10^{-1}</td>
<td>2.95</td>
<td>8.12\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
<td>3.27\times10^{-4}</td>
<td>4.90\times10^{-8}</td>
<td>9.17\times10^{-4}</td>
<td>1.20\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>4.49</td>
<td>3.40\times10^{-4}</td>
<td>1.82\times10^{-2}</td>
<td>5.24\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>5.67\times10^{2}</td>
<td>3.82\times10^{3}</td>
<td>3.65\times10^{5}</td>
<td>2.06\times10^{-9}</td>
</tr>
<tr>
<td>3</td>
<td>(r = \frac{k_{EFG^<em>}}{(1 + K_2E)^2(1 + K_3G^</em>)})</td>
<td>303</td>
<td>1.51\times10^{-2}</td>
<td>7.23\times10^{-1}</td>
<td>2.64</td>
<td>1.13\times10^{-8}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
<td>2.88\times10^{-2}</td>
<td>7.35\times10^{-1}</td>
<td>2.61</td>
<td>4.60\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>5.17\times10^{-1}</td>
<td>6.95\times10^{2}</td>
<td>2.52</td>
<td>2.06\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>9.42\times10^{-3}</td>
<td>1.91</td>
<td>5.62\times10^{-1}</td>
<td>2.31\times10^{-7}</td>
</tr>
<tr>
<td>4</td>
<td>(r = \frac{k_{EFG^<em>}}{(1 + K_2E)^2(1 + K_3G^</em>)^2})</td>
<td>303</td>
<td>3.42\times10^{-3}</td>
<td>3.98</td>
<td>2.72</td>
<td>9.78\times10^{-10}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
<td>6.29\times10^{-3}</td>
<td>3.93</td>
<td>2.64</td>
<td>4.00\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>5.67\times10^{2}</td>
<td>3.91</td>
<td>3.65\times10^{5}</td>
<td>2.31\times10^{-7}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>3.14\times10^{-3}</td>
<td>3.95</td>
<td>9.58\times10^{-1}</td>
<td>1.54\times10^{-10}</td>
</tr>
<tr>
<td>5</td>
<td>(r = \frac{k_{EFG^<em>}}{(1 + K_2E)^2(1 + K_3G^</em>)^2})</td>
<td>303</td>
<td>2.52\times10^{-3}</td>
<td>1.90</td>
<td>5.84\times10^{-1}</td>
<td>9.57\times10^{-9}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
<td>1.26\times10^{3}</td>
<td>3.82</td>
<td>1.47\times10^{1}</td>
<td>6.08\times10^{-8}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>9.42\times10^{-3}</td>
<td>1.91</td>
<td>5.62\times10^{-1}</td>
<td>1.68\times10^{-8}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>3.27\times10^{4}</td>
<td>4.90\times10^{8}</td>
<td>9.17\times10^{-4}</td>
<td>1.13\times10^{-8}</td>
</tr>
</tbody>
</table>

Where, \(G\) represent the concentrations of \(O_2\) in MEK at the gas-liquid interface (kmol/m\(^3\)) respectively. \(E\) and \(F\) are the concentrations of the 2-ACPAL (kmol/m\(^3\)), and catalyst (kg/m\(^3\)), respectively.

The discrimination of rate models was done based on the thermodynamic criteria, activation energy and the \(\Phi_{\min}\) values. The rate models II and III were rejected based on
the thermodynamic criteria of inconsistency of equilibrium constant and high activation energy. In models I, IV and V, the model IV and V were discriminated based on the higher \( \Phi_{\text{min}} \) values than model I. Therefore, model I (Equation 5.12) was considered the best model for representing the kinetics of liquid phase oxidation of 2-ACPAL using 1%Co/C catalyst.

\[
  r = \frac{k,EFG^*}{(1 + K_2E)(1 + K_3G^*)}
\]

Where, \( k \) is the intrinsic rate constant (m\(^3\)/kmol\(^3\)/s), \( G \) represent the concentrations of O\(_2\) in MEK at the gas-liquid interface (kmol/m\(^3\)). E and F are the concentrations of the 2-ACPAL (kmol/m\(^3\)), and catalyst (kg/m\(^3\)), respectively. The rate parameters for Equation 4.12 for all the temperature are presented in Table 5.12 (entry 1). A comparison of the experimental rates with the rates predicted by Equation 5.22 is shown in Figure 5.21, which shows a reasonably good fit of the data. The average deviation in the predicted and observed rates was found to be in the range of \( \pm 4\% \). The Arrhenius plot showing the effect of temperature on the rate parameters is shown in Figure 5.22, from which the activation energy was evaluated as 68.9 kJ/mol. The dependence of the rate parameters \( K_2 \) and \( K_3 \) on temperature show similar 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.

![Figure 5.21. Comparison of experimental rates and rates predicted using model I](image)

Figure 5.21. Comparison of experimental rates and rates predicted using model I
5.8 Hydrolysis of Acetoxy Propionic Acids

Conventional reagent based hydrolysis requires corrosive mineral acids or bases. In view of the environmental hazards and waste generation from these reagents, they are considered as a last choice from process point of view. Many solid acids like zeolites, oxides, mixed oxides including heteropoly acids, ion-exchanged resins and phosphates etc. are environmentally benign and effective substitutes for such reagents. Cation exchange resin catalysts have been used for several years in several reactions including hydrolysis / esterification reactions. Ion exchange material may be broadly defined as an insoluble matrix containing labile ions capable of exchanging with ions in the surrounding medium without major physical change in its structure. Typical cation exchange resin catalysts are sulphonic acids fixed to a polymer carrier, such as polystyrene cross-linked with divinylbenzene (DVB). Several such resins are commercially available, which include Amberlyst resins (e.g. Amberlyst-15, Amberlite IR-120 etc.) In the present study, to complete the synthesis of HPAs via VAM hydroformylation, Amberlite IR-120 resin was found to be the best hydrolysis catalyst.
For hydrolysis experiments, 2-ACPA obtained at the end of oxidation reaction was concentrated by distilling off toluene, and then isolated in mixture form by distillation of the two acids under high vacuum, at low temperature (273K). Hydrolysis of the mixture of acids was carried out at 343K to obtain the respective 2-HPA (Lactic acid), as shown in Scheme 5.3. Water was used as a solvent for the hydrolysis of acids and results are presented in Table 5.13. The solid acid catalysts screened included Zr-P, Filtrol-24, sulphated Zirconia, Amberlite IR 120. (entry 1-4). Amberlite IR-120 resin was found to give highest activity for the hydrolysis of the ACPAs (entry 3). The reactions were carried out at 343K for 300 minutes in a batch mode. Acetic acid in the stoichiometric amount of the 2-HPA formed during the reaction, which helps to proceeds in the reaction in forward reaction. Similarly, mixture of 2-ACPA and 3-ACPA was hydrolyzed under the similar conditions (entry 6) and found to give selectively 2-HPA (Lactic acid). Amberlite IR-120 resin was filtered out and recycled for reaction without loss of activity (entry 5).
Table 5.13. Hydrolysis of ACPAs

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Catalyst</th>
<th>Type of acidity (B or L)</th>
<th>CE C, meq/g</th>
<th>Surface Area, m²/g</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zr-P</td>
<td>B and L</td>
<td>ND</td>
<td>120</td>
<td>22.9</td>
<td>90.3</td>
</tr>
<tr>
<td>2</td>
<td>Filtrol-24</td>
<td>Mainly B</td>
<td>0.3</td>
<td>350</td>
<td>35.6</td>
<td>88.5</td>
</tr>
<tr>
<td>3</td>
<td>sulphated Zirconia</td>
<td>Mainly B</td>
<td>ND</td>
<td>100</td>
<td>40.2</td>
<td>92.6</td>
</tr>
<tr>
<td>4</td>
<td>Amberlite IR 120</td>
<td>Mainly B</td>
<td>4.9</td>
<td>55</td>
<td>90.5</td>
<td>95.1</td>
</tr>
<tr>
<td>5*</td>
<td>Amberlite IR 120</td>
<td>Mainly B</td>
<td>4.9</td>
<td>55</td>
<td>85.9</td>
<td>96.3</td>
</tr>
<tr>
<td>6</td>
<td>Amberlite IR 120</td>
<td>Mainly B</td>
<td>4.9</td>
<td>55</td>
<td>88.6</td>
<td>97.8 96.4</td>
</tr>
</tbody>
</table>

B- Brønsted; L-Lewis; CEC- Cation Exchange Capacity

Reaction Conditions: ACPA, 2.05 kmol/m³ (2:3-ACPA, 54:46); Catalyst, 0.1g; temperature, 343K; Agitation speed, 12 Hz; Solvent, water; Total volume, up to 2.5X 10⁵ m³

5.9. Conclusions

The VAM hydroformylation-oxidation-hydrolysis route for the synthesis of 2 and 3-HPA is an excellent alternative for the conventional multistep synthesis procedure. A detailed investigation of this route has been carried out in this chapter. Unlike the conventional Rh catalyst, the cobalt carbonyl catalyst yield the linear aldehyde isomers along with the branched aldehyde. The kinetics of CO₂CO₈ catalyzed VAM hydroformylation step has been carried out with the objective of exploring the key step in synthesis of HPAs. Kinetic study of hydroformylation of VAM revealed that the reaction was first order with respect to catalyst, and H₂ concentration. The rate versus partial pressure of CO and VAM showed a substrate-inhibited kinetics at higher CO partial pressure. Activation energies for VAM hydroformylation was evaluated as 84.6 kcal/mol.

The oxidation of aldehyde formed in the hydroformylation step has been carried out with the heterogeneous Co/C catalyst and the reusability of the same has been
established by recycle experiments. The detailed parametric and kinetic investigation of oxidation step has been carried out with 2-ACPAL as substrate and air as oxidant. The kinetic of oxidation of 2-ACPAL revealed that the reaction was first order with respect to catalyst concentration and 2-ACPAL and oxygen partial pressure shows first order dependence in the initial concentration range, becomes independent at higher concentrations. Both the aldehydes 2- and 3-ACPALs has found to give corresponding acetoxy propionic acids with excellent selectivity at mild reaction conditions.

The acetoxy propionic acid thus obtained were hydrolyzed to corresponding HPAs with different solid acid catalyst including Zirconia and its derivatives and cation exchange resins with –SO3H groups. The cation exchange resin having bronsted acidic sites were found to be the best with satisfactory reusability, while Lewis acidic zirconia derivatives has been found to be less effective in terms of ACPAs conversion.

The three step involved i.e. VAM hydroformylation- oxidation-hydrolysis were investigated in detail and reaction conditions optimized in order to achieved high conversion of corresponding reactants and selectivity to the desired products in each of the step.
Nomenclature

A  Concentration of hydrogen, kmol/m³
B  Concentration of carbon monoxide, kmol/m³
C  Concentration of catalyst, kmol/m³
D  Concentration of camphene, kmol/m³
H  Henry constant defined by equation 4.4
E  Concentration of ACPAL, kmol/m³
F  Concentration of Catalyst, kg/l/m³
G* Concentration of oxygen, kg/l/m³
k₁, k₂ Intrinsic rate constants, m³/kmol
k₂ Constant in Eq. 4.9 m³/kmol
Pf  Final pressure MPa
Pi  Initial pressure MPa
R  Universal gas constant, kJ/kmol/K
r  Rate of hydroformylation, kmol/m³/s.
R'₁, R₂  Experimental rates, kmol/m³/s
Rₐ, Rₐ  Predicted rates, kmol/m³/s
Rᵣ Reaction rate for the hydroformylation step (kmol/m³/s)
t  Reaction time, h.
T  Temperature, K
V_g  Gas volume, m³
V_L  Total liquid volume, m³
Xₐ  Solubility of gas of the solute gas at pressure P_f, kmol/m³/MPa
Φ  Parameter defined by Eq-5.6
References

1. F.E. Paulic, Catal. Rev. 6 (1972) 49