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# Kinetics and Process Parameter Studies in Catalytic Air Oxidation of Veratraldehyde to Veratric Acid

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## Abstract:

**Kinetics and different process parameters for the air oxidation of veratraldehyde to veratric acid were studied. At a temperature of 130 °C, air pressure of 1 MPa, cobalt acetate loading of 0.03 mol/L, and an initial concentration of 30% w/v of veratraldehyde, the reaction was found to be first order with respect to veratraldehyde. In 3 h at an aldehyde conversion level of 100%, as high as 99% selectivity was achieved.**

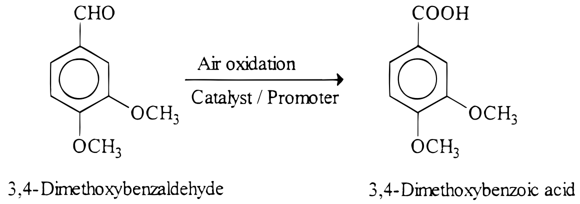
## Introduction

Veratric acid is an important organic intermediate with considerable industrial significance. Usually, a costly oxidizing agent like potassium permanganate is used to synthesize veratric acid by starting with veratraldehyde[1,2] or veratryl alcohol.[3] Veratraldehyde can be synthesized from vanillin,[4,5] dimethoxytoluene,[6] or veratryl alcohol.[7] The use of a cheaper oxidizing agent like air is worth considering for the oxidation of veratraldehyde to veratric acid, but there is absolutely no information regarding the process parameters and kinetics of this sort of air oxidation. Thus, in this study, (Scheme 1) an attempt has been made to find out the most suitable process conditions and the kinetics of this process.

## Experimental Section

**Material.** The reagents for analysis and the other chemicals used were of analytical reagent (A.R.) grades. Compressed air, used for oxidation, was supplied from an air compressor. A.R. grade cobalt acetate, manganese acetate, and lithium bromide were used as the catalyst and promoter. A technical grade of veratraldehyde was used in each reaction.

***Scheme 1.*** **Air oxidation of veratraldehyde**



**Experimental Procedure.** A predetermined amount of the catalyst, promoter, and reactant were mixed with solvent, and the solution was shaken thoroughly to make it homogeneous. The reactor was pressurized with air to the desired pressure. The reactor was then heated to the desired temperature, and the flow of air was started. After allowing the reaction to proceed for the predetermined period, the reactor was allowed to cool to room temperature, and the pressure was released. A complete diagram of the bubble column reactor is shown in Figure 1.

**Analytical.** The reaction mixture was filtered and distilled under vacuum to remove acetic acid and then diluted with water. The organic compounds were extracted in toluene. After being washed thoroughly with water the organic layer was taken for analysis.

**Estimation of Veratraldehyde.** The veratraldehyde was analyzed by using a calibrated method against standard samples by gas chromatography. A S.S. column of 2-m length packed with 10% SE-30 on chromosorb-W was used along with a FID detector. GC conditions were the following: $N_2$ carrier gas, 30 mL/min, detector and injector temperature, 300 °C, and oven temperature (isothermal), 235 °C.

**Estimation of Veratric Acid.** A measured volume of the organic extract was washed with sodium hydroxide to extract the veratric acid as sodium salts. The aqueous layer was neutralized with mineral acid to precipitate the acid.The latter was dried and weighed. The organic extract was directly titrated with standard sodium hydroxide to estimate the carboxylic acids when solvents other than acetic acid were used.

**Isolation.** After the stipulated reaction period, the solvent was removed by vacuum distillation, and then water was added to the residual mixture. Toluene was added to extract the organic substances. The toluene layer was washed with 15% sodium hydroxide solution to extract the veratric acid in the aqueous layer as the sodium salt. The free acid was precipitated from the aqueous solution by addition of 10% hydrochloric acid. The acid was then filtered, dried, and recrystallized from methanol to obtain 99.2% pure veratric acid.

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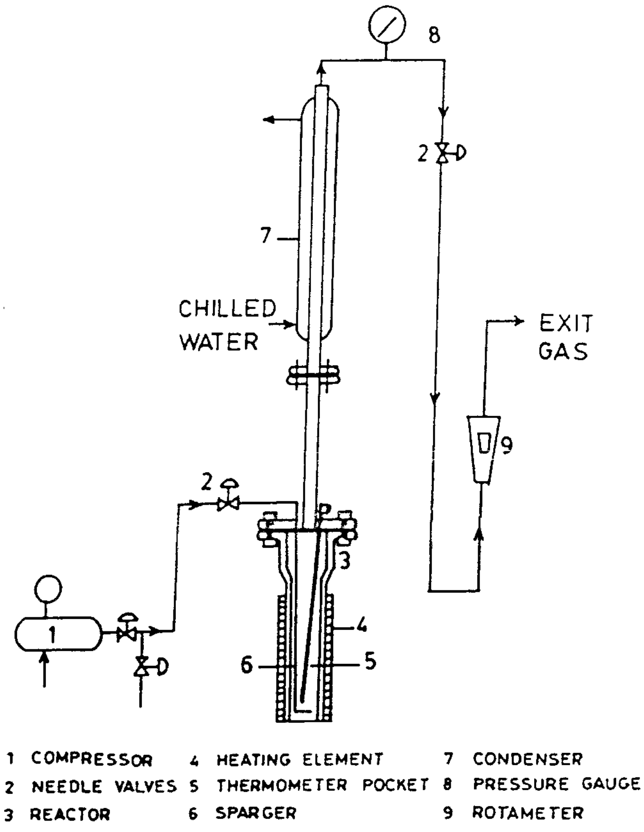


***Figure 1.*** **Experimental set up for the liquid-phase air oxidation of veratraldehyde to veratric acid.**

## Results and Discussions

In the present investigation, oxidation of veratraldehyde to veratric acid, a significant part of the work was carried out to study the parameters to establish the simplest kinetic interpretation from the process development and research point of view.

**Definitions.**

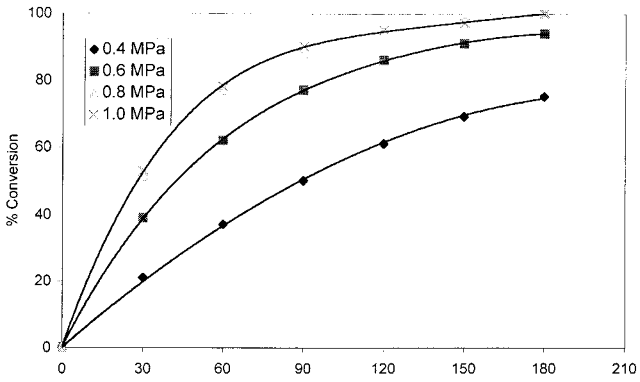
$$\% \text{ Conversion} = \frac{\text{Moles of veratraldehyde consumed}}{\text{Moles of veratraldehyde taken}} \times 100$$

$$\% \text{ Selectivity} = \frac{\text{Moles of veratraldehyde converted into veratric acid}}{\text{Total moles of veratraldehyde consumed}} \times 100$$

**Process Parameter Studies. Effect of Air Pressure.** In a liquid-phase oxidation by air, usually the reaction is carried out at a high pressure. Such a high pressure is required to keep reactants in liquid phase and to maintain sufficient partial pressure of oxygen.

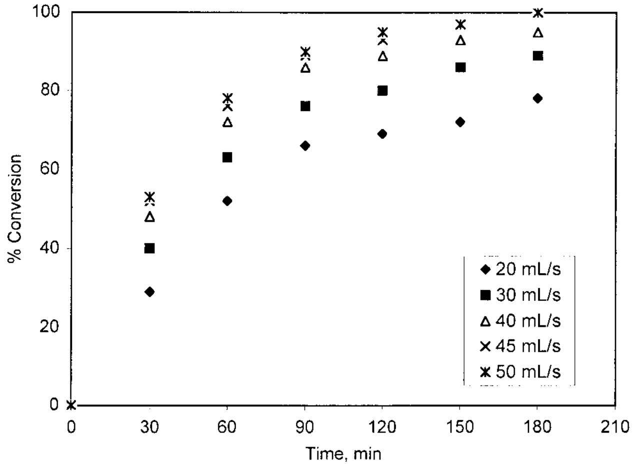
In this work, the pressure was varied from 0.4 to 1.0 MPa (Figure 2). At a pressure of 0.4 MPa, the rate of reaction was too slow. When pressure was increased to 0.8 MPa, a marked improvement in the rate of reaction was noticed. However, a further increase in pressure did not have any influence on the rate of reaction.

***Effect of Air-Flow Rate.*** The reactor employed in this investigation was a typical bubble column reactor where no mechanical agitator was provided for agitation. However, in such reactions adequate mixing can be attained if a significantly high linear superficial velocity of the gas is maintained. To ascertain whether mass transfer effects have been eliminated, air flow was varied from 20 mL/s to 50 mL/s (Figure 3); between 45 and 50 mL/s, there was no change in the conversion obtained (Table 1). Hence, in all of the subsequent runs air-flow rate was maintained at 50 mL/s.



Reaction conditions: Reactant concentration, 30% w/v; temperature, 130°C; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 2.*** **Effect of air pressure on the rate of reaction.**



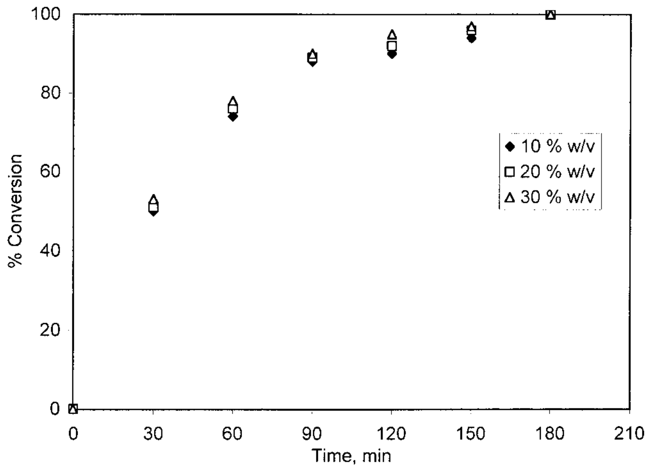
Reaction conditions: Reactant concentration, 30% w/v; temperature, 130°C; air pressure, 1 MPa; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 3.*** **Effect of air flow rate on the rate of oxidation.**

***Table 1.*** **Time vs conversion data for different air-flow rates**[a]

| time, min | % conversion at 20 mL/s air-flow rate | % conversion at 30 mL/s air-flow rate | % conversion at 40 mL/s air-flow rate | % conversion at 45 mL/s air-flow rate | % conversion at 50 mL/s air-flow rate |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 29 | 40 | 48 | 52 | 53 |
| 60 | 52 | 63 | 72 | 76 | 78 |
| 90 | 66 | 76 | 86 | 89 | 90 |
| 120 | 69 | 80 | 89 | 93 | 95 |
| 150 | 72 | 86 | 93 | 97 | 97 |
| 180 | 78 | 89 | 95 | 100 | 100 |

[a] *Reaction conditions*: veratraldehyde concentration, 30% w/v; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; air pressure, 1 MPa; temperature, 130 °C; solvent, acetic acid; total reaction volume, 300 mL.



Reaction conditions: Temperature, 130°C; air pressure, 1 MPa; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 4.*** **Effect of reactant concentration on the rate of reaction.**

***Table 2.*** **Time vs conversion data for different initial concentrations of veratraldehyde**[a]

| time, min | % conversion at 10 % w/v initial concentration of veratraldehyde | % conversion at 20 % w/v initial concentration of veratraldehyde | % conversion at 30 % w/v initial concentration of veratraldehyde |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 30 | 50 | 51 | 53 |
| 60 | 74 | 76 | 78 |
| 90 | 88 | 89 | 90 |
| 120 | 90 | 92 | 95 |
| 150 | 94 | 96 | 97 |
| 180 | 100 | 100 | 100 |

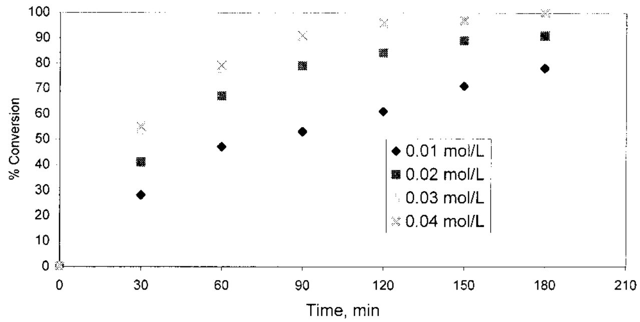
[a] *Reaction conditions*: temperature, 130 °C; air-flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; air pressure, 1 MPa; solvent, acetic acid; total reaction volume, 300 mL.

***Table 3.*** **Time vs conversion data for different cobalt acetate catalyst loading**[a]

| time, min | % conversion at 0.01 mol/L cobalt acetate loading | % conversion at 0.02 mol/L cobalt acetate loading | % conversion at 0.03 mol/L cobalt acetate loading | % conversion at 0.04 mol/L cobalt acetate loading |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 30 | 28 | 41 | 53 | 55 |
| 60 | 47 | 67 | 78 | 79 |
| 90 | 53 | 79 | 90 | 91 |
| 120 | 61 | 84 | 95 | 96 |
| 150 | 71 | 89 | 97 | 97 |
| 180 | 78 | 91 | 100 | 100 |

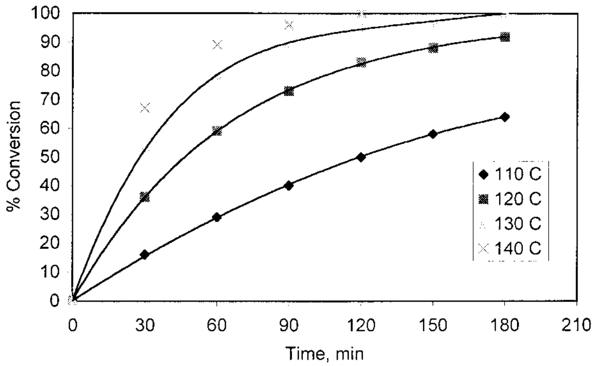
[a] *Reaction conditions*: veratraldehyde concentration, 30% w/v; air-flow rate, 50 mL/s; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; air pressure, 1 MPa; temperature, 130 °C; solvent, acetic acid; total reaction volume, 300 mL.

***Effect of Initial Reactant Concentration.*** The initial concentration of the aldehyde was varied from 10 to 30% w/v (Figure 4). It was observed that the effect of concentration had very little influence on the rate of oxidation of veratraldehyde (Table 2).



Reaction conditions: Reactant concentration, 30 % w/v; temperature, 130°C; air pressure, 1 MPa; air flow rate, 50 mL/s; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 5.*** **Effect of cobalt acetate loading on the rate of oxidation of veratraldehyde.**



Reaction conditions: Reactant concentration, 30 % w/v; air pressure, 1 MPa; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 6.*** **Effect of temperature on the rate of reaction.**

***Table 4.*** **Time vs conversion data for different temperatures**[a]

| time, min | % conversion at 110 °C | % conversion at 120 °C | % conversion at 130 °C | % conversion at 140 °C |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 30 | 16 | 36 | 53 | 67 |
| 60 | 29 | 59 | 78 | 89 |
| 90 | 40 | 73 | 90 | 96 |
| 120 | 50 | 83 | 95 | 100 |
| 150 | 58 | 88 | 97 | |
| 180 | 64 | 92 | 100 | |

[a] *Reaction conditions*: veratraldehyde concentration, 30% w/v; air-flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; air pressure, 1 MPa; solvent, acetic acid; total reaction volume, 300 mL.

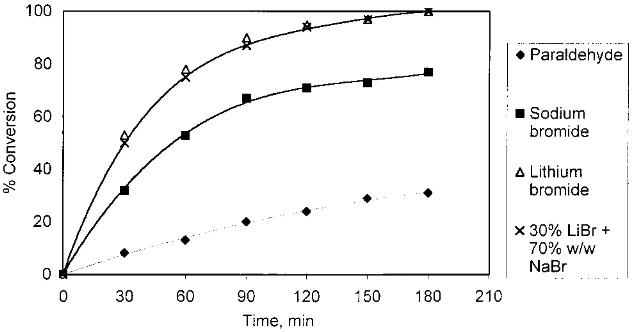
***Effect of Cobalt Acetate Loading on the Rate of Reaction.*** The reaction was studied for different cobalt acetate catalyst loading using manganese acetate as the cocatalyst (Table 3). It was observed that with an increase in cobalt acetate loading the conversion increased significantly but the conversion was almost leveled off beyond a catalyst loading of 0.03 mol/L (Figure 5).

***Effect of Temperature.*** The reaction temperature was varied from 110 to 140 °C (Figure 6). At 110 °C the rate of oxidation was very poor (Table 4). A temperature of 130 °C was found to be the best under the reaction conditions to

***Table 5.*** **Effect of temperature on conversion and selectivity**[a]

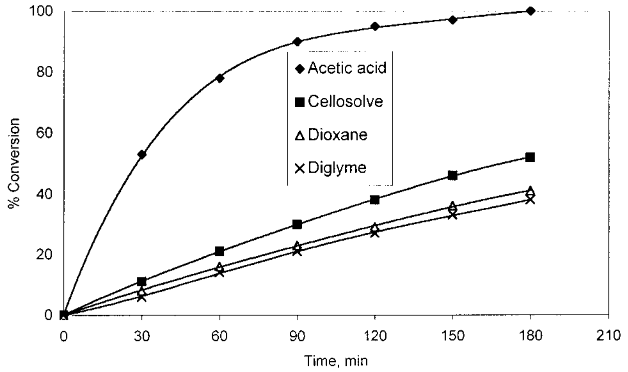
| temperature, °C | % conversion | % selectivity |
|---|---|---|
| 110 | 50 | 99 |
| 120 | 83 | 99 |
| 130 | 95 | 99 |
| 140 | 100 | 92 |

[a] *Reaction conditions*: veratraldehyde concentration, 30% w/v; air-flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; air pressure, 1 MPa; solvent, acetic acid; total reaction volume, 300 mL; reaction time, 2 h.



Reaction conditions: Reactant concentration, 30% w/v; temperature, 130OC; air pressure, 1 MPa; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; promoter, 0.005 mol/L; solvent, acetic acid; volume, 300 mL.

***Figure 7.*** **Effect of promoter on the rate of reaction.**



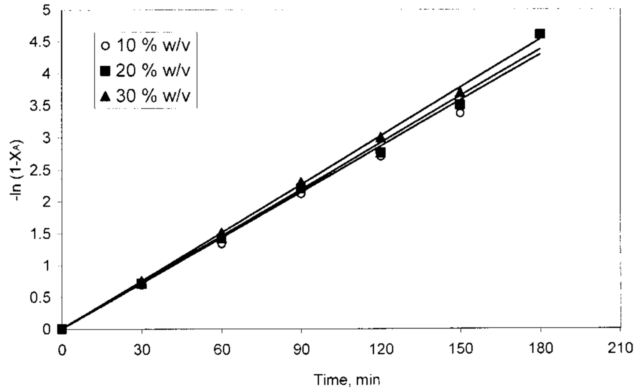
Reaction conditions: Reactant concentration, 30% w/v; temperature, 130°C; air pressure, 1 MPa; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; total reaction volume, 300 mL.

***Figure 8.*** **Effect of solvent on the conversion of veratraldehyde.**

achieve maximum conversion and selectivity to veratric acid (Table 5).

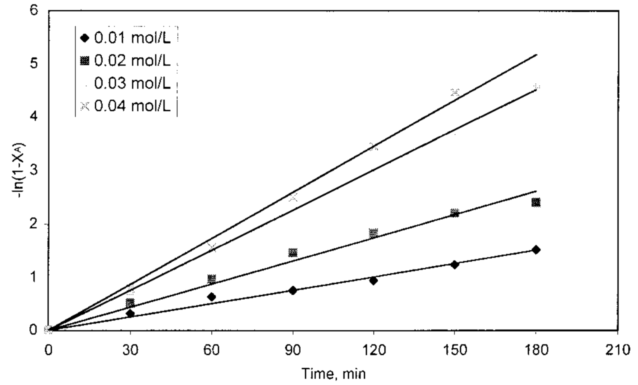
***Effect of Promoters.*** Different types of promoters like paraldehyde, sodium bromide, and lithium bromide were used. It was observed that under the reaction conditions, lithium bromide was found to be the best promoter (Figure 7). However, lithium bromide is costlier than sodium bromide; hence, 30−70% (w/w) a mixture of lithium bromide and sodium bromide proved to be the best to achieve a satisfactory reaction rate under the reaction conditions. A promoter concentration of 0.005 mol/L was used in each experiment.

***Effect of Solvent.*** The effect of different solvents on the rate of reaction was studied, and it was observed that when acetic acid was used as a solvent, the rate of reaction was most satisfactory (Figure 8). Water was also used as a solvent, but the rate of reaction was very slow and only 11% conversion was obtained in 3 h.



Reaction conditions: Temperature, 130°C; air pressure, 1 MPa; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 9.*** **$-\ln(1 - X_A)$ vs *t* at different initial veratraldehyde concentrations.**



Reaction conditions: Reactant concentration, 30% w/v; temperature, 130°C; air pressure, 1 MPa; air flow rate, 50 mL/s; lithium bromide, 0.005 mol/L; manganese acetate, 0.03 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 10.*** **$-\ln(1 - X_A)$ vs *t* at different cobalt acetate loading.**

**Kinetics.** The reactions were carried out at a high air-flow rate to eliminate mass transfer effects. There was absolutely no increase in the conversion level when air pressure was increased from 0.8 to 1.0 MPa. It indicates that the reaction is insensitive with a further increase in pressure. Thus, in the rate equation the pressure term can be considered as constant, and the simplest rate equation of this catalytic air oxidation can be written as

$$-\mathrm{d}C_A/\mathrm{d}t = kC_AWp_{\mathrm{air}} \tag{1}$$

or

$$-\ln(1 - X_A) = k_1t \tag{2}$$

Where, $X_A$ = moles of veratraldehyde consumed/moles of veratraldehyde taken, $W$ = g of catalyst taken, $t$ = time, $p_{\mathrm{air}}$ = partial pressure of air = 1 MPa = constant, $k_1 = kWp_{\mathrm{air}}$, and $k$ = rate constant.

Figure 9 shows that the reaction is first order with respect to a given initial veratraldehyde concentration at an air pressure of 10 atm, air-flow rate of 50 mL/s, and a cobalt acetate catalyst loading of 0.03 mol/L. The initial rates at different catalyst loading are found from the slopes of Figure 10. It is observed that (Figure 11) the initial rate increases

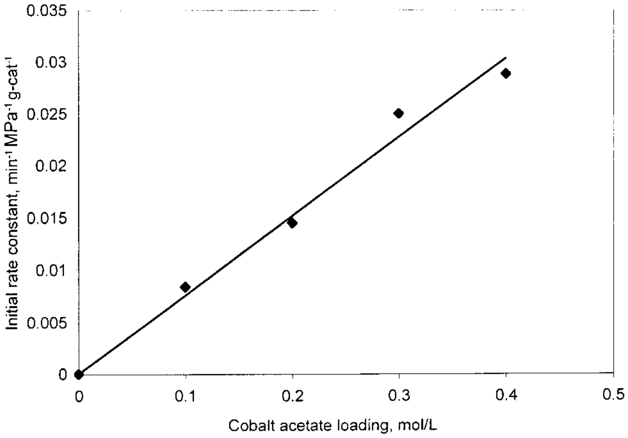
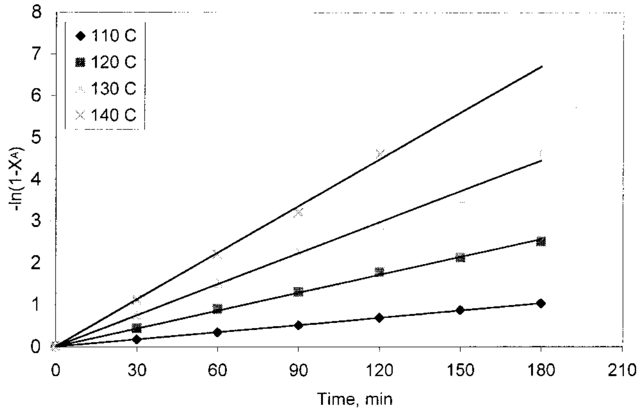


***Figure 11.*** **Initial rate at different cobalt acetate loading.**



Reaction conditions: Reactant concentration, 30% w/v; air pressure, 1 MPa; air flow rate, 50 mL/s; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; lithium bromide, 0.005 mol/L; solvent, acetic acid; total reaction volume, 300 mL.

***Figure 12.*** **$-\ln(1 - X_A)$ vs *t* at different temperatures.**

linearly with the increase in cobalt acetate loading. The diffusion is estimated to be unimportant due to the homogeneity of the reaction mixture and the conditions employed. Thus, the data represent the true kinetics of the process at a catalyst loading of 0.03 mol/L.

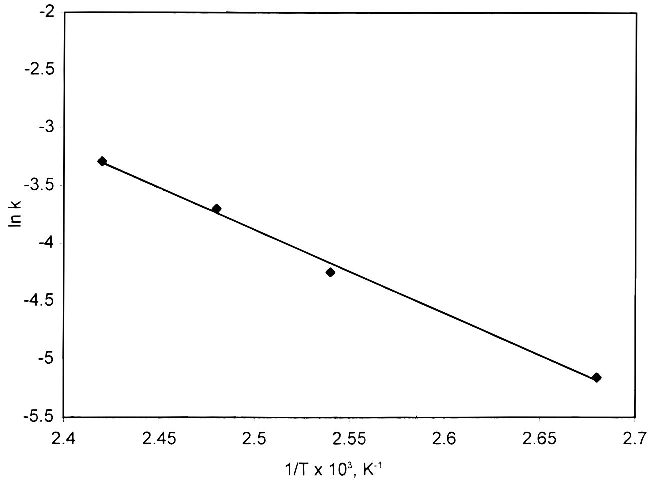


***Figure 13.*** **Arrhenius plot for the air oxidation of veratraldehyde.**

At different temperatures, $-\ln(1 - X_A)$ vs $t$ is plotted (Figure 12) and from the slopes, $k$ at different temperatures are found to be $4.3 \times 10^{-6}$, $1.07 \times 10^{-5}$, $1.87 \times 10^{-5}$, and $2.8 \times 10^{-5}$ $s^{-1}$ $MPa^{-1}$ g-$cat^{-1}$ under the reaction conditions. The energy of activation is found to be 60 kJ/mol from the slope of the Arrhenius plot (Figure 13).

## Conclusions

The air oxidation of veratraldehyde to veratric acid follows a first-order kinetic. The energy of activation was found to be 60 kJ/mol.

Under the best suitable reaction conditions (air-fow rate, 50 mL/s; air pressure, 1 MPa; cobalt acetate, 0.03 mol/L; manganese acetate, 0.03 mol/L; promoter, lithium bromide, 0.005 mol/L; temperature, 130 °C; time, 3 h.), veratric acid could be obtained with 99% selectivity at 100% overall conversion level of veratraldehyde.

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