

Synthesis of Phenethyl Alcohol by Catalytic Hydrogenation of Styrene Oxide

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Abstract:

In the current work, phenethyl alcohol was synthesized by the hydrogenation of styrene oxide, which may be obtained by the oxidation of styrene. Conventional method of synthesis of phenethyl alcohol is by the Friedel–Crafts alkylation of benzene by using ethylene oxide and molar quantities of aluminum chloride. This method causes effluent disposal problems due to the stoichiometric use of aluminum chloride as the aluminum oxchloride formed in the process is normally not recycled. The hydrogenation of styrene oxide was conducted by using Raney nickel catalyst and process conditions were established. The yield of phenethyl alcohol obtained was 90.2% with 92% overall conversion of styrene oxide under suitable conditions. Styrene oxide was also synthesized in the laboratory.

Introduction

2-Phenylethyl alcohol (commonly known as phenethyl alcohol) is the main component of rose oils obtained from rose blossoms. It occurs in smaller quantities in neroli oil, ylang ylang oil, carnation oil, and geranium oil.¹ Phenylethyl alcohol is a colourless liquid with a mild and warm rose-honey-like odour having moderate to poor tenacity. It is one of the most widely used of all perfume chemicals.

Industrially phenethyl alcohol is synthesized by the following methods:²

(a) Friedel–Crafts alkylation of benzene using ethylene oxide and molar quantities of aluminum chloride; (b) the hydrogenation of styrene oxide, which is now preferred due to its environmental compatibility (Figure 1).

Friedel–Crafts alkylation causes effluent disposal problems due to the stoichiometric use of aluminium chloride as the aluminium oxchloride formed in the process is normally not amenable to offsite recycle. Furthermore, glass-lined reactors have to be used since aluminium chloride is highly corrosive. Another potential problem as reported by Bauer et al.² may be the difficulty in complete removal of aluminum chloride from the product with a view to ensuring its suitability for perfumery use. Also, in the light of safety norms imposed by statutory bodies, the availability of ethylene oxide to the small scale sector is no longer feasible, which has resulted in the decrease of phenethyl alcohol manufacturers in this sector. Thus, safety aspects and environmental problems imply that the method based on styrene oxide would be the obvious choice. Large number of patentees have used Pd/C or Raney nickel^{3,4} as catalyst

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(2) Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance & Flavour Materials*; New York, 1990.

PROCESS SCHEME

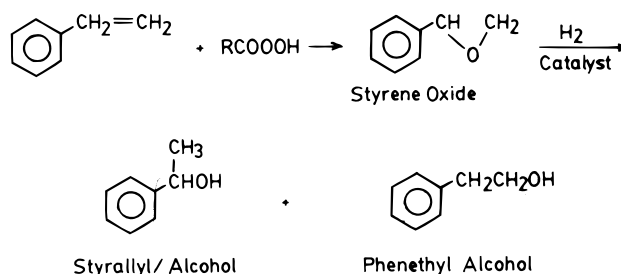


Figure 1. Hydrogenation of styrene oxide to phenethyl alcohol.

in the temperature range of 303–423 K. Both liquid-phase and vapour-phase hydrogenation are mentioned in the literature, but the majority of information pertains to liquid-phase hydrogenation. According to a typical patent, when styrene oxide was hydrogenated at low temperatures (313–323 K) using Raney nickel as catalyst, with 48% aqueous alkali at 20 atm of hydrogen, 99.3% selectivity of phenylethyl alcohol was obtained. At 343–423 K, 1-phenylethyl alcohol or styryl alcohol was claimed to be the major product.^{5–8} Other catalysts mentioned in the literature are Ni/Alumina,⁹ Ni–Cr,¹⁰ pentasil-type zeolite, or phosphate-doped with metal hydrogenation catalysts such as Pt, Ag, Ni, Co, Cu, Zn,¹¹ Pd/silica.¹² A patentee has claimed that the Raney nickel as catalyst could be reused.¹³ Though a large number of patents are available, the published information on the hydrogenation of styrene oxide to phenethyl alcohol is conspicuously absent.

In the current work, phenethyl alcohol was synthesized by the hydrogenation of styrene oxide by using catalysts such as Pd/C or Raney nickel. Styrene oxide was also synthesized by the epoxidation of styrene using an organic peracid, viz., peroxybenzoic acid.

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Table 1. Synthesis of Styrene Oxide

peroxybenzoic acid	= 30×10^{-3} kg, (0.2174×10^{-3} kg mol) in 230×10^{-6} m ³ chloroform
styrene	= 20×10^{-3} kg, 0.1923×10^{-3} kg mol
temperature	= 273 K
overall conversion of styrene	= 93%
% conversion to styrene oxide	= 77.8%
selectivity of styrene oxide	= 83.66%

Table 2. Effect of Type of Catalyst

time, s	catalyst			
	5% Pd/C		Raney nickel	
	% convn of styrene oxide	% select. of PEA ^b	% convn of styrene oxide	% select. of PEA
1200	96.7	97.8	17.2	100
1800	96.8	98.1	31.4	100
2700	97.4	98.1	40.6	98.7
3600	96.8	98.5	46.9	99.0

^a Conditions: styrene oxide, 5×10^{-3} kg, 0.04167×10^{-3} kg mol, 0.8333 kg mol m⁻³, catalyst loading, 0.2×10^{-3} kg, 4 kg m⁻³; solvent, methanol, 50×10^{-6} m³ (total volume); pressure, 15 atm; temperature, 301 K; speed of agitation, 1100 rpm. ^b PEA = phenethyl alcohol.

Experimental Section

Materials. Peroxybenzoic acid (prepared in the laboratory), styrene oxide (synthesized in the laboratory), methanol, benzoyl peroxide, sodium hydroxide, 30% aqueous hydrogen peroxide, chloroform (laboratory grade), and catalyst Raney nickel "F" type (from Kallin Industries) were used for the above study.

Synthesis of Styrene Oxide. A predetermined quantity of styrene was taken in the reactor equipped with a stirrer. The reactor temperature was brought down to 273 K by surrounding the reactor with ice. Preformed peroxybenzoic acid¹⁴ in chloroform was added, maintaining the temperature at 273 K. The addition was complete in 600 s. The reaction mixture was maintained at this temperature for 18×10^3 s or until all of the peracid disappeared, as observed iodometrically from time to time (Table 1). The benzoic acid was removed from the chloroform solution by shaking it with an excess of 10% sodium hydroxide solution. The traces of alkali was removed by washing with water, and the chloroform solution was dried with anhydrous sodium sulfate. Chloroform was distilled under vacuum, and the product was further purified by vacuum distillation.

Experimental Setup. The reaction was carried out in an Parr autoclave of capacity 100×10^{-6} m³.

Experimental Procedure. Predetermined quantities of styrene oxide, methanol, and catalyst were taken in the hastalloy autoclave of 100×10^{-6} m³ capacity. The autoclave was pressurized by hydrogen gas. At regular time intervals, samples were withdrawn for the estimation of product by gas chromatography (GC).

The column and conditions used were as follows: column, Carbowax, 2 m long; carrier gas rate, N₂, 0.138 MPa; FID;

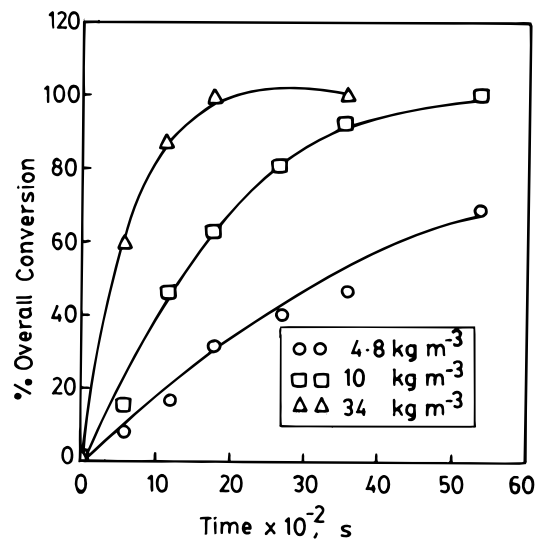


Figure 2. Effect of catalyst loading. Styrene oxide: 5×10^{-3} kg, 0.833 kg mol m⁻³. Pressure: 15 atm. Catalyst: Raney nickel. Temperature: 301 K. Solvent: methanol, 50×10^{-6} m³. Speed of agitation: 1100 rpm.

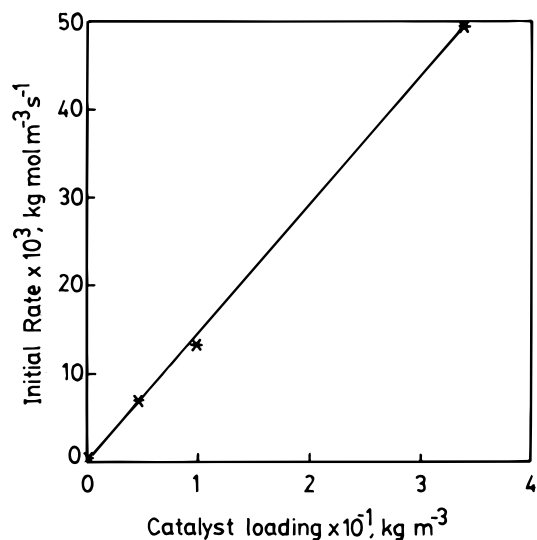


Figure 3. Effect of catalyst loading on initial rate.

oven temperature, 353 K, 60 s, isothermal, ramp 283 K min⁻¹ to 523 K; injector temperature, 523 K; detector temperature, 523 K.

Results and Discussion

Definitions. The terms conversion, selectivity, and yield have been defined.¹⁵

Synthesis of Phenethyl Alcohol. *Effect of Type of Catalyst.* Two catalysts, namely 5% Pd/C and Raney nickel "F" type, were selected for the study. Both of the catalysts selectively gave only phenethyl alcohol when the reaction temperature was 301 K. At this temperature, 5% Pd/C gave a selectivity of 97.8% with 96.7% conversion in 900 s, whereas that of Raney nickel gave 17% conversion in 1200 s with a selectivity of 100% of phenylethyl alcohol, indicating that 5% Pd/C was more active (Table 2). However, the

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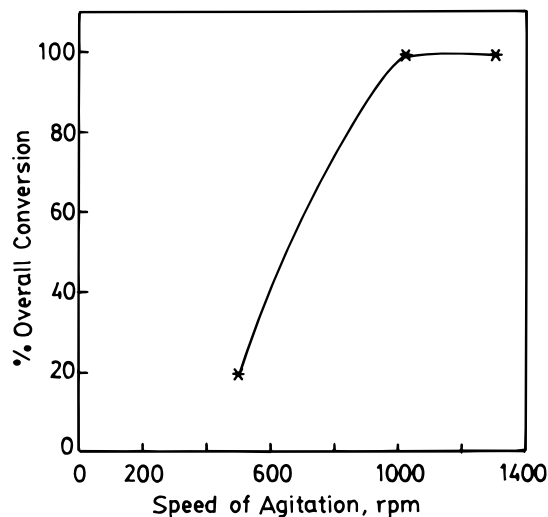


Figure 4. Effect of speed of agitation. Styrene oxide: 5×10^{-3} kg, $0.833 \text{ kg mol}^{-3}$. Pressure: 15 atm. Catalyst: Raney nickel. Temperature: 301 K. Solvent: methanol, $50 \times 10^{-6} \text{ m}^3$. Catalyst loading: 10 kg m^{-3} .

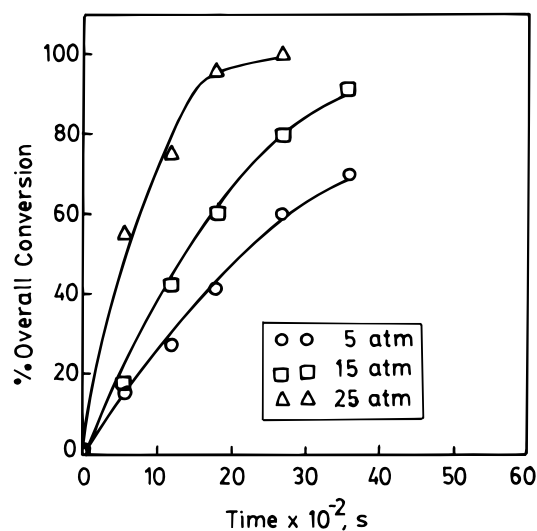


Figure 5. Effect of pressure. Styrene oxide: 5×10^{-3} kg, $0.833 \text{ kg mol}^{-3}$. Temperature: 310 K. Catalyst: Raney nickel. Solvent: methanol, $50 \times 10^{-6} \text{ m}^3$. Catalyst loading: 10 kg m^{-3} . Speed of agitation: 1100 rpm.

majority of this work was done with only Raney nickel catalyst since it is more cost-effective.

Effect of Catalyst Loading. When catalyst loading was increased from 4.8 to 34 kg m^{-3} of the reaction volume at 301 K under a hydrogen partial pressure of 15 atm and the initial concentration of styrene oxide was kept as 0.83 kg mol^{-3} of the reaction volume (Figure 2), as expected, the initial rate was found to increase with the catalyst loading (Figure 3).

Effect of Speed of Agitation. The effect of speed of agitation on the rate of the reaction was studied between 500 and 1300 rpm at 301 K and a hydrogen partial pressure of 15 atm using Raney nickel "F" type as catalyst at catalyst loading of 10 kg m^{-3} of reaction volume (Figure 4). Beyond 1025 rpm, the effect of speed of agitation was not significant, thereby indicating that the effect of external mass transfer was almost completely eliminated. Furthermore, the obser-

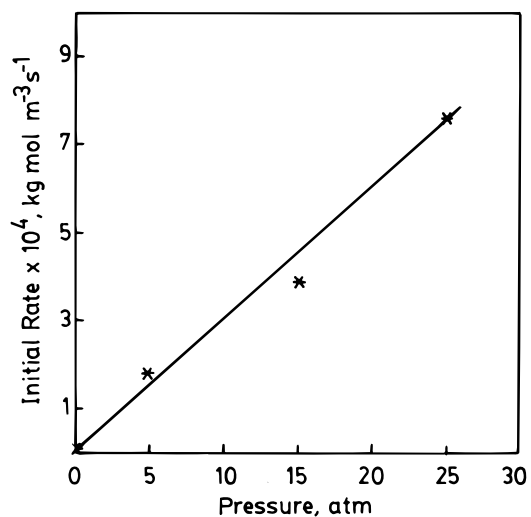


Figure 6. Effect of pressure on initial rate.

Table 3. Effect of Substrate Concentration

time, s	styrene oxide (kg mol^{-3})					
	0.4166		0.8333		1.25	
	% convn of SO ^b	% select. of PEA ^c	% convn of SO	% select. of PEA	% convn of SO	% select. of PEA
900	91.9	100	30	100	4.34	96
1800	99.4	98.9	60.4	100	8	100
3600	100	98.9	91.2	97.9	13.8	100

^a Conditions: catalyst, Raney nickel; catalyst loading, $0.5 \times 10^{-3} \text{ kg}$, 10 kg m^{-3} ; pressure, 15 atm; temperature, 301 K; speed of agitation, 1100 rpm. ^b SO = styrene oxide. ^c PEA = phenethyl alcohol.

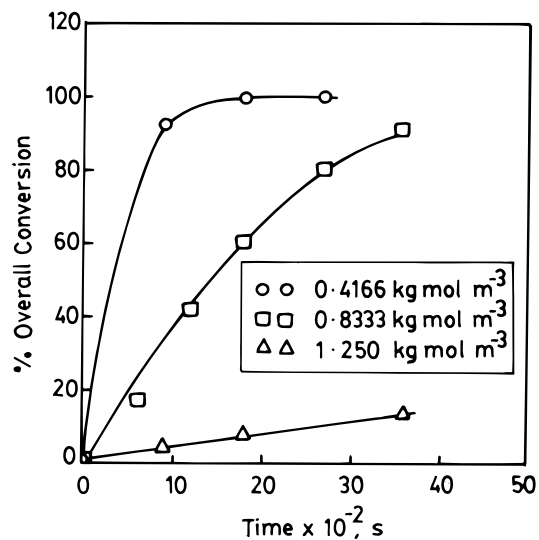


Figure 7. Effect of substrate concentration. Pressure: 15 atm. Catalyst: Raney nickel. Catalyst loading: $0.5 \times 10^{-3} \text{ kg m}^{-3}$. Temperature: 301 K. Solvent: methanol, $50 \times 10^{-6} \text{ m}^3$. Speed of agitation: 1100 rpm.

vation that the initial reaction rate was proportional to catalyst loading corroborated the finding that the process was kinetically controlled (Figure 3).

Effect of Pressure. When the pressure was increased from 5 to 15 atm, an increase in the overall conversion of styrene oxide was observed (Figure 5). The plot of initial rate against partial pressures of hydrogen was linear (Figure 6).

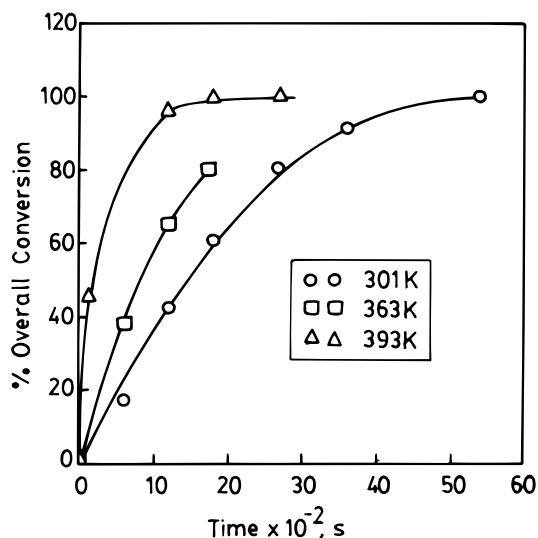


Figure 8. Effect of temperature. Styrene oxide: 5×10^{-3} kg, $0.833 \text{ kg mol m}^{-3}$. Pressure: 15 atm. Catalyst: Raney nickel. Catalyst loading: 10 kg m^{-3} . Solvent: methanol, $50 \times 10^{-6} \text{ m}^3$. Speed of agitation: 1100 rpm.

Effect of Substrate Concentration. Typical kinetic runs with different initial concentrations of substrate ranging from 0.4166 to $1.25 \text{ kg mol m}^{-3}$ are given in the Table 3 and Figure 7. There was a marked decrease in rate (% conversion) with increase in styrene oxide concentration. This is due to the strong adsorption of styrene oxide on the catalyst surface. As a result, deactivation of the catalyst is possible. It was not possible to correlate the rate by simple power law expression.

Effect of Temperature. In the range of 303–363 K, as expected, the reaction rate increased and there was no significant effect on the selectivity of the desired product (Figure 8). However, with additional increases in temperature, the selectivity with respect to the desired product decreased markedly, presumably due to enhanced formation of 1-phenylethyl alcohol (Figure 9).

Separation and Purification of the Product Mixture. The reaction mixture was filtered to recover the catalyst, and methanol was removed by distillation under vacuum. The colourless product had a purity of 97% and could be further purified by vacuum distillation.

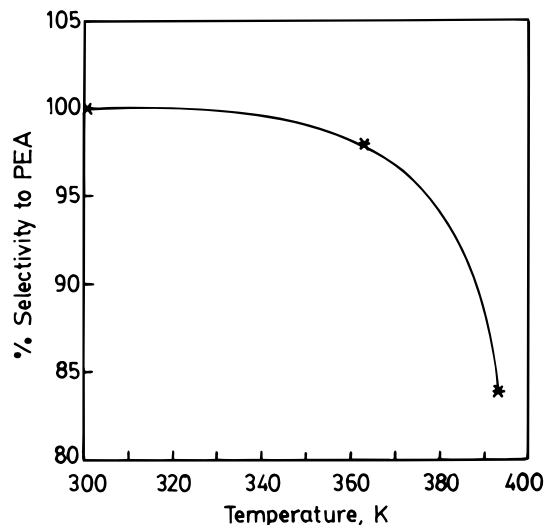


Figure 9. Effect of temperature on selectivity.

Conclusions

Under suitable reaction conditions [peroxybenzoic acid, $0.2174 \times 10^{-3} \text{ kmol}$; styrene, $0.2 \times 10^{-3} \text{ kg mol}$; solvent, chloroform, $230 \times 10^{-6} \text{ m}^{-6}$; temperature, 273 K; time, $18 \times 10^3 \text{ s}$], 77.8% conversion to and a selectivity of 83.6% of styrene oxide was obtained. Hydrogenation of styrene oxide using methanol as a solvent with both Raney nickel and Pd/C as catalyst gave selectively 2-phenethyl alcohol in almost 99% selectivity with almost insignificant amount of 1-phenylethyl alcohol, provided the temperature was maintained in the range of 301–363 K. A good quality product having an acceptable odour was obtained in this manner. Under suitable reaction conditions [styrene oxide, $0.8333 \text{ kg mol m}^{-3}$; catalyst, Raney nickel “F” type; catalyst loading, 10 kg m^{-3} reaction volume; solvent, methanol, $50 \times 10^{-6} \text{ m}^3$; hydrogen partial pressure, 15 atm; temperature, 301 K; speed of agitation, 1100 rpm], 92% overall conversion of with 98% selectivity towards 2-phenethyl alcohol was obtained in 3600 s.

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