CHAPTER 3
ALKYLATION OF ANILINE WITH
\textit{n}-PROPANOL AND ISOPROPANOL OVER
ZEOLITE

3.1 Introduction

Alkylation of aniline is industrially important as the major products of this reaction form the basic raw materials for the synthesis of organic chemicals and intermediates involved in the pharmaceutical, agrochemical, and dye industries (1,2). The liquid phase Friedel-Crafts alkylation of arenes using Lewis acid catalysts (AlCl$_3$, FeCl$_3$, BF$_3$), although industrially important, suffers from such drawbacks as corrosivity, toxicity, the need for work-up of the reaction mixture, and effluent pollution. This makes it desirable to replace these homogeneous catalysts for alkylation reactions by heterogeneous catalysts. Gas phase alkylation is also a preferable option since it offers advantages in the field of process technology, such as utilisation of reaction heat (3-5). The most important selective gas phase alkylation of oligocyclic arenes is the methylation of naphthalenes (6).

A 90% selectivity at 20% conversion is achieved at $460^\circ$C using the heterogeneous zeolite catalyst, HZSM-5.

3.1.1 Alkylation of aromatics with olefins

Alkylation reactions of benzene, toluene and phenol by olefins have been reported on Y and ZSM-5 zeolites. The reactions have been studied in the liquid phase (7,8) as well as the vapour phase (9-13). Alkylation of
benzene with propene to produce cumene with 84-94% selectivity is a well known zeolite catalysed reaction (9). Becker et al (10) studied benzene alkylation with ethene and propene on H-mordenite between 100°C and 420°C. The rate of reaction was found to be maximal around 400°C. The selectivity for monoalkylated products in this reaction decreased with an increase in temperature. Reaction of toluene with ethene over HZSM-5 zeolite gave an isomeric mixture of ethyltoluenes in which the meta- isomer was the major product (11). Kaeding (12) investigated the effect of crystal size in alkylation of ethylbenzene with ethene on HZSM-5 between 250 and 400°C. Conversion of ethylbenzenes was higher on smaller crystals. However, the selectivity for p-diethylbenzene formation was higher on larger crystals. In the shape-selective alkylation of biphenyl with propene on SAPO-11 catalyst (13), the observation was made that the low catalytic activity of SAPO-11 was on account of its weak acid strength and the availability of fewer active sites.

3.1.2 Vapour-phase alkylation of aromatics with alcohols

Alkylation of benzene with ethanol over zeolites gives ethylbenzenes (14). The reaction has been investigated under various conditions of temperature, contact time, etc. The maximum yield of ethylbenzene (70%) was obtained under the following standard conditions: temperature 450°C; rate of flow of benzene, 42g per hour; rate of flow of ethanol, 12g per hour. The molar ratio of benzene to ethanol used was 1.8. Alkylation of benzene with isopropanol over zeolites such as HZSM-12 (15), H/EU-1 (16).
H-mordenite and LaHY (17) have been reported. However, large-pore silica zeolites such as HZSM-12 was found to be more effective catalysts for this reaction. Isopropylation of benzene over rare-earth exchanged zeolite-Y has also been reported (18). It was concluded that selectivity and stability of zeolites HY, LaHY and CeHY were dependant on their acidic and structural properties, and that the acidity of the zeolite-Y increased with the extent of the rare-earth exchange.

Alkylation of toluene with methanol is one of the methods used to obtain xylene (19, 20). The corresponding ethylation reaction has also been reported on HZSM-5 at temperatures between 250 and 500°C; the selectivity towards ethyltoluenes was found to decrease with increase in temperature (21). It has been reported that the alkylation of phenol with methanol over zeolites gives both O-alkylated and C-alkylated products, with the O-alkylated products being relatively dominant (22, 23).

3.1.3 Vapour-phase alkylation of aniline with olefins and alcohols

The alkylation of aromatic amines over zeolites gives N-alkylated as well as C-alkylated products. An early study has been that of Chen et al (24), who reported the alkylation of aniline with methanol over ZSM-5 and other zeolites. The major products obtained were toluidine, N-methylaniline, and N-N-dimethylaniline. It was concluded that acid strength sites on the zeolite were necessary to promote the alkylation, although stability reasons demanded the coexistence of basic sites. Ione et al (25) have also reported the alkylation of aniline with methanol over ZSM-5 catalyst. Prasad and Rao
(26) have studied the alkylation of aniline with methanol over the silica-free microporous solid, AlPO₄-5. They report that the formation of N-methylaniline is favoured at low reaction temperatures and that this product is subsequently further alkylated to N-N'-dimethylaniline. Isomerization of the latter to give N-methyltoluidines was demonstrated to occur at high temperatures, and a carbo-cationic mechanism was proposed for this.

Dixon and Burgoyne (27) reported the alkylation of substituted anilines with isobutene over H-Y zeolite catalyst. N-alkylated and C-alkylated products were again obtained. The selectivity is reduced for arylamines having ortho substituents such as chloro or methyl groups. With increase in temperature N-alkylated, o-alkylated, p-alkylated anilines become the major products on alkylation of aniline with isobutene. The rearrangement of N-alkylanilines with homogeneous catalysts was reported by Hart and Kosak (28). On heating N-alkylarylamine hydrohalide, the alkyl group migrates predominantly to the p-position. Burgoyne and Dixon (29) have also reported that N-isopropylaniline on H-Y zeolite and γ-alumina catalysts at 250°C rearranged to give o- and p- isopropylanilines. N-isopropylaniline on dealkylation over H-Y zeolite and γ-alumina catalysts at 250°C gave aniline as the major product. Recently, the alkylation of aniline with ethanol using HZSM-5 zeolites containing different SiO₂/Al₂O₃ ratios has been studied (30). HZSM-5 with a SiO₂/Al₂O₃ ratio of 70 seems to have the requisite acid sites needed for optimum aniline alkylation activity and selectivity towards the products namely, N-ethylaniline and N-N'-diethylaniline. A preliminary report has also appeared on the alkylation of aniline with isopropanol over
Na, H and Ce forms of zeolites at different temperatures (31). A detailed investigation of the latter reaction was undertaken in this study using the two isomeric alcohols, isopropanol and \( n \)-propanol with a view to exploring differences in their reactivity patterns as well determining reaction conditions that influence product selectivities and yields.

3.2 Experimental

Na and Ce forms of Y- and ZSM-5 type zeolites were prepared by ion exchange as detailed in Chapter 2. Aniline, isopropanol and \( n \)-propanol were purified by distillation. All experiments were carried out in a fixed bed reactor, as described in Chapter 2. The catalyst was activated at 500\(^0\)C for 4hrs before use in each experiment. The yields of the products were analysed by gas chromatography and GC-MS, with comparison effected with authentic samples where relevant. Gas chromatographic analyses were performed with a Shimadzu GC-17AAF chromatograph equipped with a flame ionisation detector (FID) and 5m\( \times \) 0.22mm i.d. methyl silicone column. Samples of 1.0\(\mu\)L were injected using a Hamilton \# 801 microsyringe. Injector temperature (290.0\(^0\)C) was set to vaporise the sample instantaneously and render the sample homogeneous. The oven temperature was programmed from 30-220\(^0\)C at the rate of 10\(^0\)/min using nitrogen as carrier gas. For GC-MS analysis, the column used was 30m \( \times \) 0.22mm i.d 5\% phenylmethyl siloxane; temperature programming: 60-260\(^0\)C at the rate of 10\(^0\)/min using helium as carrier gas.
### 3.2.1 Characterisation of products

Table 3.1 GC-Mass spectral data\(^a\) of products obtained in the reaction between aniline and isopropanol over zeolite.

<table>
<thead>
<tr>
<th>Products</th>
<th>RT</th>
<th>( m/z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-isopropylaniline</td>
<td>9.6</td>
<td>( M^+ 135(100), 120(72), 92(51), 91(38), 77(53), 65(43), 51(32) )</td>
</tr>
<tr>
<td>( o )-isopropylaniline</td>
<td>10.6</td>
<td>( M^+ 135(25), 120(100), 93(14), 92(7), 77(18) 65(8) )</td>
</tr>
<tr>
<td>( p )-isopropylaniline</td>
<td>10.8</td>
<td>( M^+ 135(80), 120(100), 103(57), 77(65), 65(42) )</td>
</tr>
</tbody>
</table>

\(^a\)Column : 5% Phenylmethyl siloxane, 30m;
Carrier gas : He; Temp programming at \( 10^0/ \) min over the range 60-260\(^0\) C.
Detector : Mass Selective Detector;
\(^b\) Retention time in minutes; \(^c\) Relative intensity is given in parenthesis.
Table 3.2  GC-Mass spectral data\(^a\) of products obtained in the reaction between aniline and n-propanol over zeolite

<table>
<thead>
<tr>
<th>Products</th>
<th>(\text{RT})</th>
<th>(m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-n-propylaniline</td>
<td>10.4</td>
<td>(M^+ 135(27), 120(8), 106(100), 91(6), 77(32), 65(6), 51(12).)</td>
</tr>
<tr>
<td>o-n-propylaniline</td>
<td>10.7</td>
<td>(M^+ 135(43), 106(100), 91(7), 77(20), 65(5), 51(3).)</td>
</tr>
<tr>
<td>p-n-propylaniline</td>
<td>10.6</td>
<td>(M^+ 135(21), 106(100), 91(3), 77(9), 65(4), 51(3).)</td>
</tr>
</tbody>
</table>

\(^a\)Column : 5% Phenylmethyl siloxane, 30m;

Carrier gas: He; Temp Programming at 10\(^\circ\)/min over the range 60-260\(^\circ\)C.

Detector: Mass Selective Detector;

\(^b\) Retention time in GC;  \(^c\)Relative intensity is given in parenthesis,
3.3 Results

3.3.1 Alkylation of aniline with isopropanol

The products of the alkylation of aniline with isopropanol over zeolite are N-isopropylaniline, o-isopropylaniline, p-isopropylaniline and dialkylated anilines are shown in Scheme (3.1). As may be seen both C-alkylated and N-alkylated products are obtained.

Effect of flow rate

The liquid feed, which is a 1:3 molar mixture of aniline and isopropanol, was passed over the catalyst at different flow rates as recorded in Table (3.3). It was observed that the conversion of aniline was only 4.7% with a flow rate of 30mL/hr. However, with this flow rate a high selectivity of 92.2% for N-isopropylaniline was achieved. The conversion of aniline increased to 26% under a flow rate of 5mL/hr; but the selectivity for N-alkylation decreased to 54.8%. Thus a decrease in contact time (increased flow rate) results in decreased conversion of the aniline to alkylated products, but favours N-alkylation over C-alkylation.

Effect of catalyst

Results of the alkylation of aniline with isopropyl alcohol over Ce, H and Na forms of zeolite catalysts are given in Table (3.4). Under comparable conditions, Ce-Y zeolite is more active than the other catalysts. The conversion of aniline increased to 63.2 % at 450°C under a flow rate of 5mL/hr using 7g catalyst. Among the C-alkylated products, the major product obtained was the ortho- isomer.
Scheme. 3.1. Products obtained in the reaction of aniline with isopropanol over zeolite
3.3.2 *Alkylation of aniline with *n*-propanol.*

Alkylation of aniline with *n*-propanol over zeolite gave N-*n*-propylaniline, o-*n*-propylaniline, *p*-*n*-propylaniline, N-isopropylaniline, o-isopropylaniline, *p*-isopropylaniline are shown in scheme (3.2). The major product of the reaction was N-*n*-propylaniline.

\[
\begin{align*}
\text{NH}_2 & + \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{\text{Zeolite}} \text{NH-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 & + \text{NH}_2\text{-CH}\text{-CH(CH}_3\text{-CH}_2\text{-CH}_3 \\
\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 & + \text{CH}_3\text{-CH}\text{-CH(CH}_3\text{-CH}_2\text{-CH}_3
\end{align*}
\]

**Scheme. 3.2.** *Products obtained in the reaction of aniline with* 
*n*-propanol over zeolites
**Effect of catalyst**

Results of the alkylation of aniline with n-propanol over different types of zeolites are given in Table (3.5). Alkylation of aniline with n-propanol over Ce-Y type zeolite at 450°C under a flow rate of 5mL/hr gave the maximum conversion of aniline (83.2%). Increasing the quantity of the catalyst favoured higher conversions of aniline. For both the cation-exchanged Y- and ZSM-5 type zeolites, conversion of aniline increased in the order Ce>H>Na, attesting to the importance of acid sites on the catalyst for the success of the alkylation reaction.

**Effect of temperature**

The general trend for the alkylation reaction is that the conversion usually increases with increase in temperature and reaches a steady state at higher temperatures. The alkylation of aniline with n-propanol (1:3 mole) over Ce-Y zeolite (3g) at a flow rate of 10mL/hr was carried out at different temperatures 200-450°C (Table 3.5). The conversion of aniline increased as the temperature increased, but the selectivity for N-n-propylaniline decreased. At 200°C the conversion of aniline was 9.8 mole% but this increased to 52.3 mole % at 450°C

**Effect of flow rate**

Table (3.6) shows the effect of flow rates on formation and selectivity of the products. The reactions were carried out at 450°C under different flow rates. Conversion of aniline decreased with increase in rate of flow of the reagents over the catalyst. The selectivity of N-n-propylaniline decreased
with increase in contact time; under the flow rate of 40mL/hr the selectivity for N-alkylated product was 77.2%.

3.4 Discussion

The results of the reaction of aniline with isopropanol and n-propanol over zeolites are listed in Tables 3.3, 3.4, 3.5 and 3.6. Under comparable conditions, Ce-Y zeolites show greater activity than the other solid zeolite catalysts. It has been reported (32) that incorporation of Ce$^{3+}$ in zeolites by ion-exchange, as with other polyvalent cations, leads to a greater number of protonic acid sites on account of hydrolysis. Because of this, such polyvalent cation-exchanged zeolites are strongly acidic (see equations 1-3 below). The polyvalent cations cause stronger electrostatic fields compared to protons.

The trend obtained with ZSM-5 catalysts in the Na, H, and Ce forms (Tables 3.4 and 3.5) is also rather similar to that obtained with Y-type zeolites. Being a medium pore zeolite, ZSM-5 was expected to show differences in product distribution due to shape selectivity. However, this is not in evidence from the results. Conversions were generally higher with n-propanol than with isopropanol. The yield of N-isopropylaniline in the reaction between aniline and isopropanol was relatively lower than the corresponding yield of N-n-propylaniline obtained in the alkylation of aniline with n-propanol. This is probably on account of the greater thermal stability of N-n-propylaniline product over N-isopropylaniline.
Table 3.3  The effect of flow rate in the reaction between aniline and isopropanol over Ce-Y zeolite\textsuperscript{a}

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>Temp</th>
<th>Mole %</th>
<th>Mole % selectivity of products</th>
<th>Mole % yield of propene</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL/hr</td>
<td>°C</td>
<td></td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>26.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>350</td>
<td>23.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>350</td>
<td>20.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>350</td>
<td>6.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>350</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>350</td>
<td>4.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} aniline/ isopropanol mole ratio: 1/3 ; catalyst: 3g

\textsuperscript{b} selectivity = [mole % yield of product / mole% conversion of aniline] × 100

\textsuperscript{c} (1) = N-isopropylaniline  (2) = o-isopropylaniline

(3) = p-isopropylaniline  (4) = dialkylated product
Table 3.4  Alkylation of aniline with isopropanol a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Flow rate mL/hr</th>
<th>Temp  °C</th>
<th>Mole % conversion of aniline</th>
<th>Percentage selectivity of products (1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>Mole % yield of propene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-Y</td>
<td>10</td>
<td>350</td>
<td>28.3</td>
<td>67.0</td>
<td>24.0</td>
<td>5.3</td>
<td>3.7</td>
<td>12.9</td>
</tr>
<tr>
<td>H-Y</td>
<td>10</td>
<td>350</td>
<td>12.7</td>
<td>66.3</td>
<td>25.2</td>
<td>5.3</td>
<td>3.2</td>
<td>10.6</td>
</tr>
<tr>
<td>Na-Y</td>
<td>10</td>
<td>350</td>
<td>8.5</td>
<td>68.2</td>
<td>22.3</td>
<td>6.1</td>
<td>3.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Ce-ZSM-5</td>
<td>10</td>
<td>350</td>
<td>13.8</td>
<td>66.3</td>
<td>27.1</td>
<td>5.4</td>
<td>1.2</td>
<td>7.8</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>10</td>
<td>350</td>
<td>7.2</td>
<td>63.2</td>
<td>26.0</td>
<td>6.3</td>
<td>4.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Na-ZSM-5</td>
<td>10</td>
<td>350</td>
<td>5.3</td>
<td>72.0</td>
<td>4.2</td>
<td>2.5</td>
<td>1.3</td>
<td>8.8</td>
</tr>
<tr>
<td>*Ce-Y</td>
<td>5</td>
<td>450</td>
<td>63.2</td>
<td>60.7</td>
<td>29.4</td>
<td>6.8</td>
<td>3.1</td>
<td>21.3</td>
</tr>
</tbody>
</table>

a aniline/isopropanol mole ratio: 1/3 ;  
b catalyst :4g  
c selectivity = [mole% yield of product/mole% conversion of aniline] × 100  
d (1) = N-isopropylaniline  
(2) = o-isopropylaniline  
(3) = p-isopropylaniline  
(4) = dialkylated products.  
* Wt of catalyst = 7g.
Table 3.5  Alkylation of aniline with n-propanol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>Flow rate (mL/hr)</th>
<th>Mole % conversion of aniline</th>
<th>Percentage selectivity&lt;sup&gt;c,d&lt;/sup&gt; of products</th>
<th>Mole % yield of propene</th>
<th>Mole % yield of propene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-Y</td>
<td>200</td>
<td>10</td>
<td>9.8</td>
<td>(1) 72.0  (2) 7.0  (3) 3.0  (4) 8.0  (5) 7.0</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>250</td>
<td>10</td>
<td>15.6</td>
<td>(1) 70.0  (2) 6.4  (3) 4.4  (4) 11.2 (5) 5.2</td>
<td>2.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>300</td>
<td>10</td>
<td>24.3</td>
<td>(1) 66.9  (2) 7.7  (3) 5.2  (4) 10.3 (5) 6.6</td>
<td>3.3</td>
<td>5.9</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>350</td>
<td>10</td>
<td>36.6</td>
<td>(1) 64.6  (2) 8.8  (3) 6.1  (4) 8.5  (5) 8.4</td>
<td>3.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>400</td>
<td>10</td>
<td>41.5</td>
<td>(1) 63.3  (2) 9.4  (3) 7.3  (4) 7.4  (5) 9.2</td>
<td>3.4</td>
<td>8.1</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>450</td>
<td>10</td>
<td>52.3</td>
<td>(1) 58.0  (2) 13.0 (3) 7.0  (4) 8.4 (5) 13.0 (6) 0.6</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>Ce-Y</td>
<td>350</td>
<td>20</td>
<td>32.0</td>
<td>(1) 68.0  (2) 9.2  (3) 4.8  (4) 6.8  (5) 7.4</td>
<td>3.8</td>
<td>4.6</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>350</td>
<td>30</td>
<td>25.0</td>
<td>(1) 72.5  (2) 7.6  (3) 4.6  (4) 7.7  (5) 4.2</td>
<td>3.4</td>
<td>3.9</td>
</tr>
<tr>
<td>Ce-Y</td>
<td>350</td>
<td>40</td>
<td>14.5</td>
<td>(1) 77.2  (2) 4.3  (3) 3.4  (4) 8.6  (5) 3.7</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>H-Y</td>
<td>350</td>
<td>10</td>
<td>22.5</td>
<td>(1) 68.0  (2) 8.6  (3) 6.4  (4) 7.3  (5) 6.2</td>
<td>3.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Na-Y</td>
<td>350</td>
<td>10</td>
<td>14.2</td>
<td>(1) 67.3  (2) 7.8  (3) 5.8  (4) 10.2 (5) 6.3</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Ce-ZSM5</td>
<td>350</td>
<td>10</td>
<td>32.3</td>
<td>(1) 66.2  (2) 8.2  (3) 7.1  (4) 8.9 (5) 6.8</td>
<td>2.8</td>
<td>2.3</td>
</tr>
<tr>
<td>H-ZSM5</td>
<td>350</td>
<td>10</td>
<td>17.4</td>
<td>(1) 66.9  (2) 8.3  (3) 6.1  (4) 9.7  (5) 5.6</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Na-ZSM5</td>
<td>350</td>
<td>10</td>
<td>10.5</td>
<td>(1) 67.5  (2) 9.4  (3) 6.7  (4) 7.8 (5) 6.0</td>
<td>2.6</td>
<td>3.9</td>
</tr>
<tr>
<td>* Ce-Y</td>
<td>450</td>
<td>5</td>
<td>83.2</td>
<td>(1) 62.3  (2) 10.2 (3) 7.8  (4) 8.2 (5) 7.6</td>
<td>3.9</td>
<td>14.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> aniline/ n-propanol mole ratio : 1/3;  <sup>b</sup>catalyst : 4g
<sup>c</sup> selectivity = [mole % yield of product/ mole% conversion of aniline] × 100.
<sup>d</sup> (1) = N-n-propylaniline  (2)=α-n-propylaniline  (3)= p-n-propylaniline  
(4) = N-isopropylaniline  (5) = α-isopropylaniline  (6) = p-isopropylaniline.

* Wt of catalyst = 7g.
Table 3.6  Alkylation of aniline by n-propanol over Ce-Y zeolite\textsuperscript{a}:

Effect of flow rate

<table>
<thead>
<tr>
<th>Flow rate (mL/hr)</th>
<th>Temp (°C)</th>
<th>Catalyst</th>
<th>Mole %</th>
<th>Percentage selectivity of products\textsuperscript{b,c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>conv. of aniline</td>
</tr>
<tr>
<td>10</td>
<td>450</td>
<td>Ce-Y</td>
<td>52.3</td>
<td>55.0</td>
</tr>
<tr>
<td>20</td>
<td>450</td>
<td>Ce-Y</td>
<td>45.0</td>
<td>62.3</td>
</tr>
<tr>
<td>30</td>
<td>450</td>
<td>Ce-Y</td>
<td>41.7</td>
<td>66.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} aniline/n-propanol mole ratio: 1/3; catalyst: 3g

\textsuperscript{b} selectivity = \frac{\text{mole % yield of product}}{\text{mole% conversion of aniline}} \times 100.

\textsuperscript{c}(1) = N-n-propylaniline  (2) = \alpha-n-propylaniline  (3) = \rho-n-propylaniline

(4) = N-isopropylaniline  (5) = \alpha-isopropylaniline  (6) = \rho-isopropylaniline.
Experimental evidence as reported elsewhere indicates that N-isopropylaniline when contacted over zeolite at 300°C isomerises to the C-alkylated products, α-isopropylaniline and β-isopropylaniline, besides also suffering some dealkylation to aniline and propene (27,33).

For both the reactions with n-propanol and isopropanol, N-alkylated aniline was the principal product, but a significantly higher amount of the C-alkylated product was obtained using isopropanol. Propene formation in the reaction with n-propanol was much less than in the reaction with isopropanol, as expected of the behaviour of primary alcohols relative to secondary alcohols. Propene was suspected to be the alkylation agent which led to the C-alkylation products, via the isopropylcarbenium ion. Propene could conceivably arise from dehydration of the alcohol and/or the decomposition of N-alkylaniline. Since both these pathways appear to be more dominant with isopropanol, the relatively lower selectivity for C-alkylation observed when n-propanol was used could be rationalised in this light.

As may be seen from the data in Tables 3.3, 3.4 and 3.5 the formation of propene decreased upon increasing the flow rate of the reagents as well as upon decreasing the temperature. This is probably because at higher flow rates and lower temperatures, the occurrence of secondary reactions is lessened. It is to be noted that with both isopropanol and n-propanol, the conversion of aniline is also significantly less at higher flow rates and lower temperatures. When the flow rate is lowered in both cases, the selectivity for N-alkylation decreases while that of C-alkylation increases. This may be attributed to increased decomposition of N-propylaniline with prolonged
contact time and/or increased dehydration of propanol to propene with prolonged contact time.

For reactions with isopropanol and \( n \)-propanol, among the C-alkylated products, the ortho-isomer is formed in preference to the para-isomer. This kinetic preference for the ortho-alkylated product has been reported in the reaction of aniline with alkenes in the presence of a variety of acid catalysts such as \( \gamma \)-Al\(_2\)O\(_3\), H-Y zeolites, and the amorphous silica-alumina gel (13% Al\(_2\)O\(_3\)/87% SiO\(_2\)). It has been reported (34) that in the reaction of aniline with propene, the products formed were N-isopropylaniline, \( o \)- and \( p \)-isopropylanilines and dialkylated anilines. No \( n \)-propyl derivatives were obtained. In the present study with \( n \)-propanol, besides the \( n \)-propylated products, isopropylated products were also obtained.

The principal \( n \)-propylated products are N-\( n \)-propylaniline and the ortho-para isomers of C-\( n \)-propylaniline. A possible route for the formation of these products is via the Sn2 mechanism as shown in Scheme 3.3.

The C-alkylation involves the participation of canonical forms (1) & (2) that contribute to the resonance structure of the aniline molecule.

\[
\begin{align*}
\text{NH}_2 & \quad \leftrightarrow \quad +\text{NH}_2 \\
\text{1} & \quad \leftrightarrow \quad \text{2}
\end{align*}
\]

The isopropylated products are formed in relatively lower yields. The ratio of N-propylaniline to N-isopropylaniline is approximately 9:1 at 200\(^\circ\)C, but only marginally decreases to about 8:1 at 450\(^\circ\)C. The trend suggests that isomerization is not an exclusive pathway for the N-isopropyl product, and
marginally decreases to about 8:1 at 450°C. The trend suggests that isomerization is not an exclusive pathway for the N-isopropyl product, and

\[
\text{Scheme 3.3 } \text{Proposed } S_n2 \text{ mechanism for the alkylation of aniline}
\]

with \textit{n-propanol}

implies a possible decomposition of the N-\textit{n}-propylnilane particularly with increasing temperature.
The products of the decomposition, namely propene and aniline then react to give the N-isopropylaniline as well as the C-isopropylanilines, as has been demonstrated elsewhere (34). It is noted that the ortho/para ratio is somewhat higher here than for the C-n-propylated case. This is probably on account of the case of formation of the o-isopropylaniline via a [4+2] concerted addition of propene to anilinium ion (scheme 3.4).

Scheme 3.4 Mechanism for the formation of o-isopropylaniline
The *para*-isomer can conceivably arise from N-isopropylaniline via two pathways as has been pointed out by Burgoyne and Dixon (35) (see scheme 3.5). Of these, the transalkylation pathway was considered to be the primary low energy route.

![Chemical structure](image)

**Scheme 3.5.** Transalkylation of N-isopropylaniline (Ref. 35)

For the reaction of isopropanol with aniline the principal isopropylated products are N-isopropylaniline and the *ortho-para* isomers of C-isopropylaniline. A possible route for the formation of these products is via the *S*₂₂ mechanistic pathway as shown below (scheme 3.6).
**Scheme 3.6** mechanism of alkylation of aniline with isopropanol by

**SN2 route**

The thermal behaviour of N-\textit{n}-propylaniline (34) and N-isopropylaniline (33) over Ce-Y and HZSM-5 zeolites was studied in the vapour phase at
atmospheric pressure and 200-400°C. In both cases it was reported that aniline and propene were the major products formed by dealkylation of the N-substituted anilines. The other products were o- and p- isopropylanilines; no C-n-propyl derivatives were detected. The ortho- and para-isopropylanilines were formed by secondary reactions involving the products aniline and propene, facilitated by the catalyst (33). An S\textsubscript{N}1 pathway was proposed for the interaction. In the present study with isopropylalcohol, no n-propyl products were obtained. The complete absence of ortho- and para-n-propylanilines suggests that the ortho- and para-isopropylanilines were formed by the reaction between aniline and propene via a carbenium ion mechanism as indicated in schemes 3.3 and 3.6.

### 3.5 Conclusion

From the foregoing studies on the vapour-phase alkylation of aniline at atmospheric pressure using 3 molar equivalents of n-propanol and isopropanol over different catalysts, it is clear that Ce-exchanged Y zeolite was the most active. The conversion yields of aniline with either alcohol reactant were poor to moderate at 350°C under a flow rate of 10mL/hr using Ce, H, and Na forms of Y and ZSM-5 type zeolites. The ZSM-5 catalysts did not show any advantage in terms of reactivity or selectivity. Alkylation of aniline with isopropanol produces N-isopropylaniline (major product), as well as the ortho and para-isopropylanilines formed through S\textsubscript{N}1 as well as S\textsubscript{N}2 mechanisms. Alkylation of aniline by n-propanol over zeolites produced N-n-propylaniline (major product), ortho and para n-propylanilines
through the Sn2 mechanism, and N-isopropylaniline, o and p-isopropylanilines through Sn1 Mechanism. The selectivity of N-isopropylaniline was higher than that of the ortho and para-isopropylanilines when the reaction was performed at lower temperatures and under high flow rates. At higher temperatures, the occurrence of secondary reaction, that is, the alkylation of aniline with propene over the catalyst becomes relatively dominant and yields the ortho and para-isopropylanilines.