CATALYTIC CONVERSION REACTION BETWEEN BIS-PHENOL A OR ITS DERIVATIVES WITH UNCONJUGATED FREE FATTY ACIDS

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"The effect of the reaction on the conversion of bisphenol A and its derivatives with unconjugated free fatty acids has been studied by the presence of one of the oxides of Group II elements, viz: MgO, CaO, SrO and BaO. The reaction was followed by determining the activity of samples withdrawn periodically from the reaction mixture. The working conditions of applying the alkali metal oxides as catalysts, have been discussed. The optimum conditions for completion of the reaction at the minimum time are given.

Previous work on the effect of CaO on the esterification process drew the attention to investigate the rest of Group II elements.

SUMMARY

The esterification reaction between bis (4-hydroxy phenyl) propane and unconjugated fatty acids has been catalyzed by the presence of one of the oxides of Group II elements, viz: MgO, CaO, SrO and BaO. The reaction was followed by determining the activity of samples withdrawn periodically from the reaction mixture. The working conditions of applying the alkali metal oxides as catalysts, have been discussed. The optimum conditions for completion of the reaction at the minimum time are given.

Previous work on the effect of CaO on the esterification process drew the attention to investigate the rest of Group II elements.
INTRODUCTION

Various catalysts were employed for the preparation of bisphenol A esters. These catalysts include Mg-MgO[1], alkaline metal hydroxides[2-5], organic amines[6] and H₂SO₄-H₂SO₄[7]. Many of these compounds were incorporated in the preparation of water-soluble vehicles for paints[8]. The aim of the present investigation is mainly concerned with studying the feasibility of applying the oxides of group II elements (MgO, CaO, SrO and BaO) to activate the esterification process of bisphenol A—[bis (3,5-dihydroxyphenyl) propane] or its derivatives with linseed oil fatty acids.

EXPERIMENTAL:

All chemicals and reagents were of the highest purity available. These were oleic acid, linseed oil fatty acids, potassium hydroxide, ethyl alcohol, benzene and phenol phthalein indicator.

Method of preparations[8]:

Fusion method:

A mixture of bisphenol A (0.1 mole; 22.8g), linseed oil fatty acids (0.2 mole; 56g) and the catalyst was heated at 383 K, 413 K and 443 K under continuous stirring and inert gas blanket. During heating aliquots samples were withdrawn periodically for acid value determinations. The catalysts investigated were MgO, CaO, SrO and BaO, at 0.02, 0.04 and 0.06 mole concentration.

The reaction was terminated when an acid value below 20 mg KOH was reached.

Calculation of the apparent energy of activation (Eₐ) was carried out using the conventional method[9], by applying the Arrhenius equation:

\[ \log \frac{K_2}{K_1} = \frac{E_a}{2.303 \ R \ \frac{T_2 - T_1}{T_2 \ T_1}} \]

where: \( K_1, K_2 \) the activation constants at temperatures \( T_1, T_2 \)
and \( R = 1.985 \) calories. Integration gives:
\[ \log K = \frac{-E_a}{2.303 R} \frac{1}{T} \]

where, \(K\) is the velocity constant, \(T\) is the absolute reaction temperature. Plotting \(\log K\) against \(1/T\) gives a straight line.

RESULTS AND DISCUSSION:

The esterification of bisphenol A and fatty acids is represented by the equation:

\[
\begin{align*}
\text{HO-} & \quad \text{C-} & \quad \text{OH + 2RCOOH} \\
\text{CH}_3 & \quad \text{CH}_3 & \\
\text{O} & \quad \text{R-C-O-} & \quad \text{C-} & \quad \text{O-C-} \\
\text{CH}_3 & \quad \text{CH}_3 & &
\end{align*}
\]

The effect of adding an alkaline earth metal oxide on the esterification reaction between linseed oil fatty acids and bisphenol A has been studied. The esterification reaction is of importance in the field of surface coating technology, in particular for water-soluble paints.

Trials were first performed using pure oleic acid and CaO as a catalyst at 441 K.\(^{10}\)
Table (1): Effect of CaO on the esterification process of bisphenol A with oleic acid at 44°C.

<table>
<thead>
<tr>
<th>Mole CaO</th>
<th>0.02</th>
<th>0.04</th>
<th>0.06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(hrs.)</td>
<td>Acid value</td>
<td>Acid value</td>
<td>Acid value</td>
</tr>
<tr>
<td>0.5</td>
<td>138</td>
<td>75</td>
<td>52</td>
</tr>
<tr>
<td>1.5</td>
<td>118</td>
<td>60</td>
<td>35</td>
</tr>
<tr>
<td>2.5</td>
<td>89</td>
<td>55</td>
<td>32</td>
</tr>
<tr>
<td>3.5</td>
<td>84</td>
<td>55</td>
<td>25</td>
</tr>
<tr>
<td>4.5</td>
<td>82</td>
<td>50</td>
<td>23</td>
</tr>
</tbody>
</table>

Table (1) shows the effect of CaO on the esterification process of bisphenol A with oleic acid.

Table (2) shows the effect of the alkaline earth metal oxide on the esterification yield of bisphenol A or its derivatives with linseed oil fatty acids. The procedure used to achieve the extent of esterification was the acid value determination method at different temperature and different concentration of the alkali metal oxide.[11]

The table is self explanatory and indicates that CaO is the most effective of the group in removing water from the reaction medium at a minimum time. This sequel is quite clear in spite that it agrees with the law of periodicity of the group. This may help in assessing that the reaction is not affected by the properties of the metal oxide added. In other words, the catalyzing effect of the metal oxide depends primarily on either the properties of the bisphenol A or those of the fatty acids. The comparison between the acid values in Table 1 and Table 2 at the same CaO concentration and at the same temperature indicates that CaO does not play any role with the acid but most probably its effect is connected with the bisphenol A. Moreover if the effect of the metal oxide is related to the fatty acid, there would be a saponification reaction occurring simultaneously with the esterification reaction. Such phenomenon does not observed except in case of MgO. The results of magnesium oxide(Table 2) reveal
that the mixture is more acidic i.e., a release of hydrogen ions takes place. This may be due to a substitution reaction between hydrolysable hydrogen of the bisphenol A and magnesium oxide. The ionic character of MgO (10) dictates the correctness of this interpretation. Moreover, the comparison between the acid values in the presence and absence of MgO indicates insignificant improvement of the reaction.

Order of the reaction:

Figures 1, 2, 3 and 4 shows the sequence of conversion of the acid value as a function of time taking into consideration that the standard acid value is 220. Figure 5 shows that the order of the reaction according to the graphical method (5) is zero order, a straight line is depicted, from which we can determine the reaction constant K can be obtained.

At normal condition, i.e., without addition of any of the ARMO the reaction may not be completed after 24 hrs where the acid value is nearly about 150 mg KOH. On the other side, the addition of CaO reduces the acid value to 23 mg KOH after 2.5 hrs.

The activation energy ($E_a$) calculated from Arrhenius equation for metal oxide at 0.06 mole are shown in Table (3)

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Temperature (K)</th>
<th>Time (hrs)</th>
<th>$E_a$ (joul/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>383-413</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>SrO</td>
<td>383-413</td>
<td>2</td>
<td>3.2</td>
</tr>
<tr>
<td>BaO</td>
<td>383-413</td>
<td>2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

In case of CaO, the activation energy $E_a$ was calculated from figure (6) and found to be 4.5 joul/mole.
CONCLUSIONS:

Raising the reaction temperature leads to a decrease in the conversion percentage in the case of MgO and increase in case of CaO, SrO and BaO. Increasing the catalyst concentration leads to an increase of the rate of conversion in all employed oxides and also increasing the reaction time leads to increase in the conversion percentages.

CaO is an excellent catalyst for the reaction at 0.06 mole concentration and 443 K. However, the activity of the other oxides employed can be arranged in the order BaO>MgO>CaO.

REFERENCES:


FIGURE CAPTIONS:

Figure 1: The conversion percentage in presence of fatty acids and bisphenol A in the presence of 0.06 mole at 443 K; (1) MgO, (2) CaO, (3) SrO and (4) without catalyst and BaO at 443 K.

Figure 2: The conversion percentage in presence of (1) 0.02(2), 0.04 and (3) 0.06 mole CaO at 383 K.

Figure 3: The conversion percentage in presence of (1) 0.02(2), 0.04 and (3) 0.06 mole CaO at 413 K.

Figure 4: The conversion percentage in presence of (1) 0.02, (2) 0.04 and (3) 0.06 mole CaO at 443 K.

Figure 6: Log Rate versus 1/T at different concentrations of CaO (0.02, 0.04 and 0.06 mole) at 383, 413 and 443 K.

Figure 5: Measurements of the order of the reaction of alkaline earth x versus t at 0.04 mole catalyst at 443 K.