Kinetic Study of the Alkylation of p-Cresol with Isobutylene to Produce BHT Stabilizer for Polymer Materials

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Received 14 September 1993; accepted 1 February 1994

ABSTRACT

The alkylation of p-cresol with isobutylene gas and oleum as a catalyst is studied at 75 °C in a semibatch reactor. Alkylation is carried out at isothermal conditions. For the study of the kinetic rate, a small amount of the crude products at different times during reaction is removed from the reactor and concentrations are determined by gas-liquid chromatography. Results indicate that the rate of reaction depends only on the volume of p-cresol, hence, is infinitely slow and the reaction of p-cresol with isobutylene at constant concentration of isobutylene is first order multiple series-parallel. The final equation obtained, which shows that the reaction is independent of reactor height, depends only on the pressure of isobutylene gas, Henry's law constant and duration of reaction.

Key Words
kinetic, semibatch reactor, alkylation, variable volume, multiple series-parallel reaction.

INTRODUCTION

Phenolic compounds are well known as antioxidants for polymeric materials [1-3]. BHT (butylated hydroxy toluene) antioxidant is used in petroleum products, jet fuels, rubbers, plastics, food products [4-6], medical and paramedical applications [7,8]. Alkylation of p-cresol is a process of considerable industrial importance [9]. Alkylation of aromatic compounds is a Friedel Crafts reaction [10] and industrial alkylation of p-cresol is usually carried out in a gas-liquid system using isobutylene gas as the alkylation agent [11-14]. In such a system, the transfer of material between the two phases plays an important role in the determination of the overall rate of reaction [15, 16]. The synthesis of BHT from p-cresol and isobutylene and the two phase alkylation of p-cresol by isobutylene gas in an isothermal semibatch reactor are reported and, for the first
time, data on the kinetic rate are presented.

EXPERIMENTAL

Materials
p-Cresol, isobutylene and oleum were purchased from Merck Chemical Company. p-Cresol was purified according to known procedures [17].

Reactor
In order to first gain insight into the kinetics regime, an ideal contactor [18] was employed and then a semibatch reactor consisting of a column of stainless steel 0.8 m high and a 0.2 m internal diameter equipped with a condenser and a mixer was utilized. Isothermal system was provided by circulating heat transfer oil at the correct temperature (75°C) through a jacket constructed around the reactor. The reactor was purged with isobutylene (including 10Kg p-cresol and 0.3Kg oleum) via the appropriate flow meter. The crude product from the reactor was transferred to a mixing tank containing 0.1 mole sodium hydroxide solution to be neutralized (Figure 1).

Analytical Technique
When steady state conditions were established, 6 samples at different times were removed (Table 1), and the reactions were maintained by closing the isobutylene gas valve. Immediately the crude product was neutralized with 0.1 mole sodium hydroxide solution and then washed with distilled water until washings were neutral. The washed solution, which included p-cresol, 2-tert
Table 1. Results of analyses of output product from reactor

<table>
<thead>
<tr>
<th>Pass time flow of isobutylene (hr)</th>
<th>0</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of p-cresol (mol/L)</td>
<td>9.25</td>
<td>4.96</td>
<td>3.63</td>
<td>2.7</td>
<td>1.59</td>
<td>0.95</td>
<td>0.98</td>
</tr>
<tr>
<td>Concentration of 2-tert butyl-p-cresol (mol/L)</td>
<td>0</td>
<td>3</td>
<td>3.55</td>
<td>4</td>
<td>3.9</td>
<td>2.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Concentration of 2,6-di tert butyl p-cresol (mol/L)</td>
<td>0</td>
<td>2.73</td>
<td>3.21</td>
<td>3.45</td>
<td>3.58</td>
<td>3.5</td>
<td>3.59</td>
</tr>
<tr>
<td>Xa (p-cresol)</td>
<td>0</td>
<td>0.3</td>
<td>0.43</td>
<td>0.53</td>
<td>0.67</td>
<td>0.77</td>
<td>0.87</td>
</tr>
</tbody>
</table>

butyl-p-cresol and 2,6-di-tert butyl-p-cresol (BHT) and a small amount of oligomers, was dried over anhydrous sodium sulphate and after distillation under vacuum pressure until removing oligomers, the final products were analyzed by gas-liquid chromatography. A gas-liquid chromatograph (Beckman GC 2160) was connected to a recorder and an integrator and a flame ionization detector was used. A 1.5 m stainless steel column packed with 10% SE 30 on PAW of 80-100 mesh was employed which gave good separation, working at 250 °C. Nitrogen was used as the carrier gas with a constant flow rate of 1 cm³/s.

RESULTS AND DISCUSSION

Results obtained from the ideal contactor show that the reaction depends only on the volume of p-cresol and is independent of interfacial surface, hence, reaction is infinitely slow. Multiple reactions which consist of steps- in-series and steps- in-parallel are called series-parallel reactions [15]. Reaction of p-cresol with isobutylene is series-parallel. The first product is 2-tert butyl-p-cresol and then 2,6-di-tert butyl-p-cresol is produced. The following assumptions were made:

- The total pressure in the gas phase is constant.
- Solubility of isobutylene in liquid phase is negligible.
- Henry’s Law is applicable.
- Rate of reaction via mass transfer is slow.

\[ \text{Isobutylene} \,(\text{b}) \text{Gas} + \text{p-cresol} \,(\text{a}) \text{Liquid} \rightarrow \text{Product} \]

It should be noted that each mole of isobutylene reacting in the liquid is replaced by one mole of fresh isobutylene from the gas stream. In a semi-batch operation where one fluid is continuously passed through a vessel containing a second fluid, we want to find the contact time needed for a given extent of reaction. Isobutylene bubbling through the reactor containing p-cresol at 75 °C is absorbed and reacts slowly with p-cresol. Agitation at 200 rpm is sufficient to keep compositions throughout the liquid uniform. With the passage of time the concentration of p-cresol will fall but the concentration of isobutylene will remain unchanged. This system is variable-volume and the general form for the rate of change of p-cresol is:

\[ r_s = \frac{dC_s}{dt} + \frac{C_s \, dV}{V \, dt} \] (1)

Figure 2 shows that change in volume with time varies linearly with conversion, or
$V = V_0 \left[1 - \varepsilon_a X_a \right]$  

Where $\varepsilon_a$ is the fractional change in volume between no conversion and complete conversion of p-cresol and $X_a$ is fractional conversion. The $\varepsilon_a$ of p-cresol at this condition is: 1.42. Noting that

$N_a = N_0 [1-X_a]$,  

we have on combining

$C_a = \frac{N_a}{V} = \frac{N_0 [1-X_a]}{V [1+\varepsilon_a X_a]} = C_0 \frac{1-X_a}{1+\varepsilon_a X_a}$  

$\frac{C_a}{C_0} = \frac{1-X_a}{1+\varepsilon_a X_a}$  

which is the relationship between conversion and concentration for variable-volume. Equation 5 written for p-cresol becomes:

$-r_a = \frac{C_0}{1+\varepsilon_a X_a} \frac{dX_a}{dt}$  

The kinetics are first order with respect to both p-cresol and isobutylene. We then have

$-r_a = -\frac{1}{V} \frac{dN_a}{dt} = K_1 C_b \left[C_a \right]$  

This equation is transformed into conversion units by combining it with equations 5 and 6. Thus,

$-r_a = \frac{C_0}{1+\varepsilon_a X_a} \frac{dX_a}{dt} = \frac{K_1 C_s [1-X_s]}{1+\varepsilon_s X_s}$  

Separating and integrating, we obtain:

$-\ln [1-X_s] = K_1 C_b t$  

or

$-\ln [1-X_s] = P_b K_1 t/H_b$  

$P_b$ is isobutylene pressure and $H_b$ is Henry's constant. For determination of the rate constant $K_1$, the crude products were removed 6 times from the reactor and were neutralized. After washing, drying and distilling they were analyzed by GLC (Table 1). Figure 3 shows the change of $\ln [1-X_s]$ with time for a consecutive first-order reaction.

CONCLUSIONS

Based on the results obtained in this investigation, it is evident that the reaction of isobutylene with p-cresol is a first order series-parallel with variable volume of the liquid phase at constant concentration of isobutylene gas. Equation 10 indicates that reactivity is independent of reactor height and depends on pressure of isobutylene gas and Henry's law constant and duration of reactions. At these conditions, per cent weight of BHT compared to total weight of crude products is 95%.
REFERENCES