

CHAPTER VI

DISCUSSION AND CONCLUSIONS



6.1 General

At the beginning of this work, the author attempted to find a suitable method of studying the kinetics of the phenol-furfural reaction. Volumetric titration, viscometry and spectrophotometry were the three selected choices and the latter was found to be the most suitable.

To measure the rates of reaction by volumetric titration method, the method of Hugh R Rogers' furfural determination was used to determine the quantities of furfural at various times. According to this method, gram of furfural can be calculated using the equation

$$\text{Gram of furfural} = \frac{(\text{M. of } I_2 \times 10^{-2} \text{ M. of } S_2O_3^{2-} \times x) \times 0.024 \times 100}{\% \text{ furfural oxidized}}$$

where $x = \text{cm}^3$ of thiosulfate used, $10 = \text{cm}^3$ of iodine added and % furfural oxidized must be constant, not depending on the quantities of furfural used. Table 5.1.1.1 shows that % furfural oxidized decreases when milligram of furfural is increased. This is contradicted to the equation above. This contradiction led the author to further check the time allowance for the solution to stand before the titration of the excess iodine. According to Table 5.1.1.2, when 4 mg of furfural was used and the standing times were varied, volume of thiosulfate used in the titrations

was constant, i.e. percent furfural oxidized was unchanged. From both Tables 5.1.1.1 and 5.1.1.2, it is reasonable to conclude that the method of Hugh R Rogers' furfural determination can not be used in this work.

Since the phenol-furfural reaction is condensation polymerization, it was expected that viscometric method may be valid with the increase of viscosity of the reaction solution after mixing the reactants in the presence of a catalyst. Concentrated hydrochloric acid was used as the catalyst. Although there was a change in the colour of solution when the catalyst was present as shown in Tables 5.1.2.2.1 and 5.1.2.2.2, the observed efflux time of the reaction solution at temperatures of 30, 40 and 50°C remained constant even though it had been reacting for 20 hours as shown in Tables 5.1.2.4.1, 5.1.2.4.2, and 5.1.2.4.3. From this result, the viscometric method was rejected because of the insensitivity of viscosity with the concentration change of the reaction solution.

The method of spectrophotometry was then used in the kinetic study of the phenol-furfural reaction because, when phenol and furfural reacted with hydrochloric acid as catalyst, the color of the reaction solution changed from colourless to yellow or green, depending on whether the concentration of phenol or furfural was higher, and finally turned to deep brown or black. First of all, spectra of the reactants and product would be compared. From Figures 5.1.3.1, 5.1.3.2 and 5.1.3.3, there are real differences

in spectrum patterns of the reactants and product. It is noticeable that no visible absorbance was obtained from reactants while the product gave strong absorbance in the visible range, so there are two possible ways to study the kinetics by spectrophotometric method; visible spectrophotometry and ultra violet spectrophotometry. It was decided to choose the latter because the maximum wavelengths of the reactants and product are quite different.

Comparison of Figure 5.1.3.4 with Figures 5.1.3.2 and 5.1.3.3 shows that when a drop of concentrated hydrochloric acid was added to the dilute solution of each reactant, there was no change in the spectrum of phenol whilst absorbance at wavelength of 270 nm was lower and of 224 nm higher in the spectrum of furfural. This is because the active aldehyde group in furan ring is easily protonated.

Reproducibility was checked for phenol-furfural and furfural-conc.HCl systems as shown in Tables 5.1.3.1 and 5.1.3.2 respectively. The data for both systems indicated that even with standing in the reaction cell upto 180 minutes, the absorbances at various wavelengths remained unchanged so it appeared that the reaction did not occur during the first 180 minutes. Effect of hydrochloric acid on the phenol-furfural mixture was also studied spectrophotometrically. Figure 5.1.3.5 shows increasing in absorbance at wavelength of 271 nm and decreasing in absorbance at wavelength of 217 nm when concentrated hydrochloric acid was dropwise added to the mixture.

The phenol-furfural reaction was kinetically studied at 50°C by means of ultra violet absorbances at wavelengths of 217 and 271 nm. The kinetic data shown in Figure 5.1.3.6 and Table 5.1.3.3 indicates the unaltered absorbance of the reaction solution. This result seems to point that absorbances in the ultra violet region are not sensitive to the concentration of the reaction solution thus absorbance in the visible region was selected to follow the reaction rate. However, ultra violet absorbance measured in the previous work, is included together with visible absorbance in Figures 5.1.3.8 and 5.1.3.9. According to the figures, only changes in the visible absorbance were found so the ultra violet spectrophotometric method was given up and only visible spectrophotometry was used in this work.

6.2 Interpretation of the kinetic data

6.2.1 Temperature effect The experiment was carried out in two distinct ways, namely, with excess phenol and with excess furfural. Measurements were made at three different temperatures.

6.2.1.1 When excess phenol was present

In this case, the temperatures of 53°C , 50°C and 45°C were chosen. According to the graphs in Figure 5.2.9, only the reactions at 50°C and 53°C obey the zero order plot but not at 45°C . Based on Arrhenius law, activation energy was evaluated from the specific rate constants at 50°C and 53°C .

6.2.1.2 When excess furfural was present

The temperatures were set up at 55, 50 and 47°C in this case. The graphs in Figure 5.2.10 show the constancy of slopes at 55 and 50°C whilst at 47°C, it is smaller. Further observation of the figure above, a straight line is still obtainable even at 47°C so it may be said that the zero order plot is valid for all of the three temperatures.

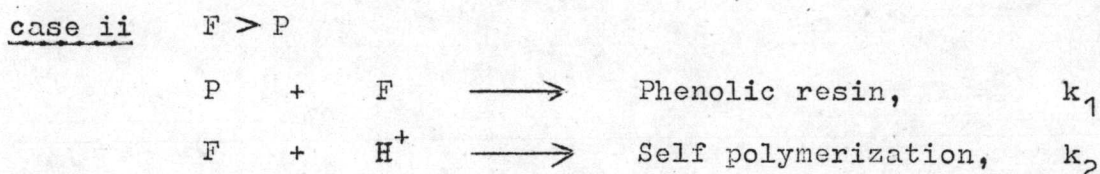
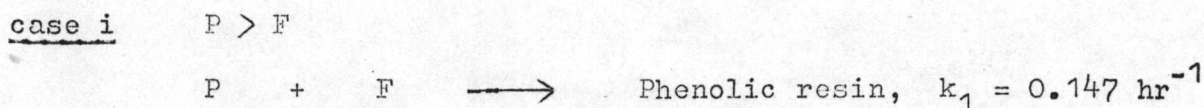
6.2.2 Catalyst effect This effect is shown in Figure 5.2.11 and Table 5.3.3 which can be interpreted that, when the amount of catalyst is increased, the rate constant of the reaction is also increased. In other words, the rate of the reaction increases with the amount of catalyst. Since the catalyst used in this work is hydrochloric acid, it is then suggested that the polymerization of phenol and furfural progresses rapidly when the concentration of the acid is high.

6.2.3 Concentration effect The following considerations seem to indicate that the mechanism of the reaction with excess furfural may be different from that with excess phenol.

Firstly, in the case of excess phenol in the reaction, the colour of the reaction solution changed from colourless to green and finally deep brown or black whilst in the case of excess furfural it changed from colourless to yellow and also finally deep brown or black. Secondly, as seen from Figure 5.2.1 to Figure 5.2.8, absorbance patterns were different and thirdly, which is the most significant, the value of rate constant at 50°C

in the case of excess furfural is higher than that with excess phenol.

Let P denotes phenol, F denotes furfural. Data from Tables 5.3.1 and 5.3.2 seem to suggest the following cases:

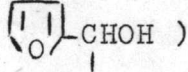


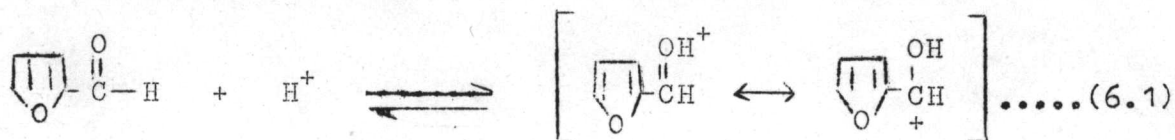
in which $k_1 + k_2 = 0.227 \text{ hr}^{-1}$

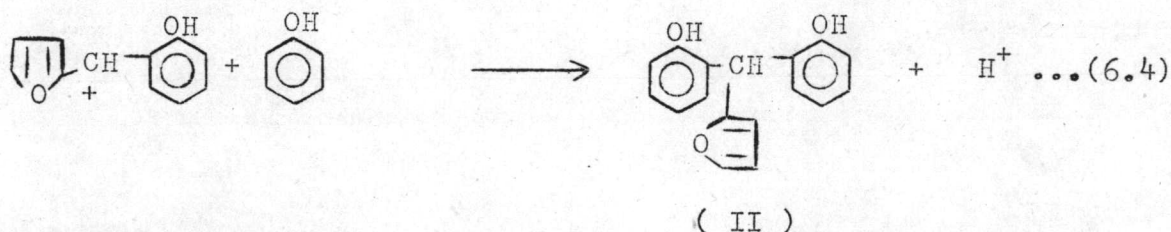
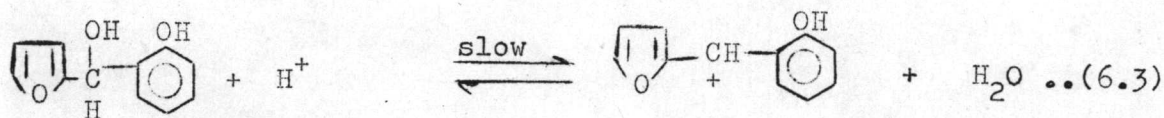
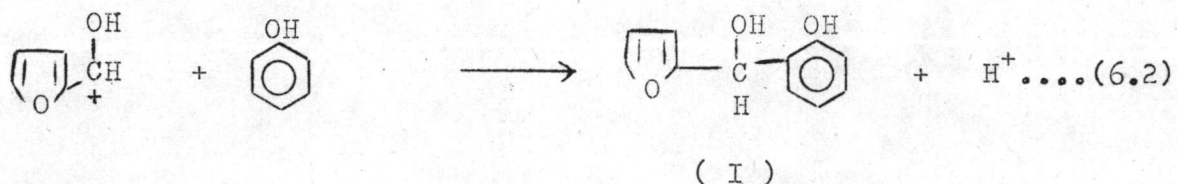
thus $k_2 = 0.080 \text{ hr}^{-1}$

6.3 Reaction mechanism The mechanism of the condensation

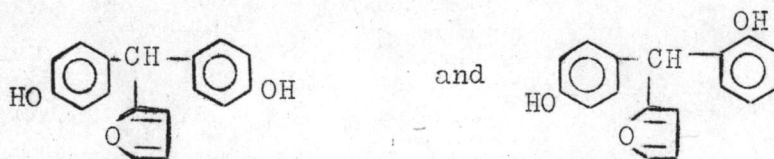
between phenol and furfural is still not entirely clear.⁽¹⁹⁾

Whatever the exact mechanism may be, the phenolic hydroxyl group activates the benzene ring so that a furyl methylol () group always enters the nucleus in positions ortho and para to the hydroxyl group. In the presence of an acid catalyst and with the excess amount of phenol, it is likely that the initial compound formed is a phenol alcohol (I) which, condenses instantly under the influence of the acid catalyst to yield dihydroxy diphenyl furan methane (II).

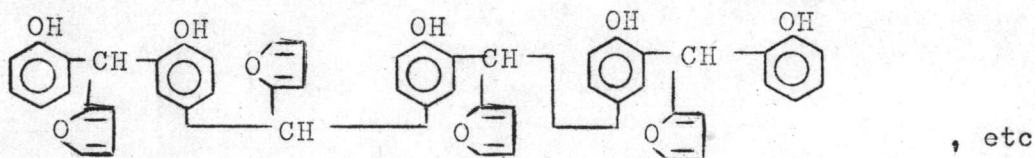




Structure of II shown in step 6.4 is one possible isomer, the other two possible isomers are

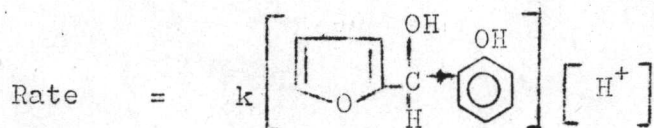


Continued reaction links more phenol groups together to form a novolac or permanently fusible type of hard, brittle resin with the structure



where ortho and para links occur at random.

According to the mechanism above, step 6.3 is rate determining step so that the rate of the reaction can be expressed as



in which k is the rate constant for step 6.3. Since H^+ is frequently constant, being regenerated in step 6.4, the expected kinetics is, hence, pseudo-first order with respect to the phenol alcohol (I). However, the reaction rate constant ($k [\text{H}^+]$ in this case) will be dependent on the hydrogen ion concentration in solution. The rate equation is verified by data in Table 5.3.3. It may be also said that the kinetics is zero order with respect to phenol or furfural. The high value, 8.01×10^4 joule mole⁻¹, of the activation energy confirms the slow reaction in step 6.3.

In the case of excess furfural, little kinetic information obtained in this work does not make it possible to propose the mechanism.