CHAPTER-IV

STUDIES ON THE REACTION OF RESORCINOL WITH p-DIMETHYL-
AMINOBENZALDEHYDE IN THE SOLID STATE.
It is interesting to study the kinetics and mechanism of the analytically important colour reactions of organic compounds. In this way it is possible to improve the colour reactions and to modify them to meet a particular situation. The reaction of p-dimethylaminobenzaldehyde (p-DAB) with diphenylamine
dihydrochloride was therefore studied using the capillary technique of Prof. R. P. Rastogi. This technique is simple and can be used with considerable advantage for those reactions which show a significant increase in the coloured boundary. A quick screening by the capillary technique of 58 compounds which give coloured products with p-DAB showed that the movement of the coloured boundary is the fastest in the case of resorcinol (RSN). Therefore, it was decided to investigate the p-DAB-RSN reaction in the solid state by this technique.

A search of the literature shows that very little work has been done on the RSN – p-DAB reaction. Only one study has been reported in the solid state. F. G. Osipenko and I. G. Tishchenko found that RSN reacts with p-DAB in the solid state to give a light orange molecular compound. Mixtures containing different mole percentages of RSN were melted and then allowed to cool. The temperature at which solidification occurred was called the solidification temperature. A plot of the solidification temperature versus the mole percentage of RSN gave a maximum at 73°C and at a mole ratio of 1:1. Except these thermal
studies no kinetic, thermodynamic or I. R. studies were carried out. No studies were reported on this reaction in the presence of an acid in the solid state.

Relatively more work has been reported on this reaction in the solution state. R. M. Acheson and I. Turner\textsuperscript{4} reported that RSN and 2-methylresorcinol react with p-DAB in 2N HCl to give a deep red colour. After 10 minutes the solution became paler and a brown oil precipitated. Analysis of the product after purification showed that equimolar proportions of the reactants combined with the loss of some hydrogen. A free radical structure (I) of the purple compound was proposed.

The I. R. spectrum of the purified product was quite different from the superimposed spectra of the aldehyde and RSN and showed no absorption in the aldehyde carbonyl region. No independent proof for the presence of a free radical was given and its presence was inferred only from the circumstantial evidence that the purple resorcinol product in 2N sodium hydroxide absorbed only a little over half a mole of hydrogen using Raney nickel catalyst and gave a colourless solution with a benzenoid type of the ultra violet absorption spectrum suggesting that oxidation involving the loss of one hydrogen atom occurs. Hence Acheson\textsuperscript{4} proposed that the structure of the purple compounds (I and other resonance forms, or a complex of II and I) as shown in Scheme 6 may be analogous to that of quinhydrone.
Scheme 6 Structure of p-Dimethylamino-Benzaldehyde-Resorcinol Reaction Products Proposed by R.M. Acheson in the Solution State
S. A. Ismaiel and coworkers\textsuperscript{5} showed that if 1 ml of a solution containing 80 $\mu$g of RSN was mixed with 8 ml of 62.5\% $\text{H}_2\text{SO}_4$ and 1 ml of a 0.5\% p-DAB solution and heated on a waterbath for 15 minutes the colour developed showed maxima at 455 and 570 nm. The 570 nm maximum was used for determination of 40 - 140 $\mu$g of RSN per 25 ml of the solution. The nitrogen content of the coloured product corresponded to the p-DAB - RSN ratio 1:2. The same p-DAB - RSN ratio was proposed by Z. Bidlo and coworkers\textsuperscript{6} who determined 1-10 mg of RSN per litre in 96\% $\text{H}_2\text{SO}_4$.

The literature survey given above shows that the p-DAB - RSN reaction is useful in the determination of RSN in pharmaceutical products in solution and more study is needed to elucidate the chemistry of this reaction either in the solution or the solid state. The present work was therefore undertaken and some interesting results were obtained which are presented in this chapter.

**EXPERIMENTAL**

**Materials:** p-DAB (E.M.), RSN and potassium hydrogen sulphate (PHS) of BDH AnalaR were used. All other reagents were of analytical grade. In order to obtain a substance in definite particle size it was ground in the mortar and sized with standard sieves.
**Apparatus:** Graduated capillaries (3mm i.d.), Reid's apparatus, Cook's M400 Series Research Microscope, Hydraulic press, Perkin Elmer 621, Beckman DK - 2A, Bausch and Lomb Spectronic 600, Bausch and Lomb Spectronic 20, and Varian X-band Spectrometer were used for reaction kinetics, vapour pressure, Particle size measurements, Pellet preparation, Infrared, Ultra Violet, Reflectance, Spectra in Visible region and EPR studies.

**PROCEDURE**

i) **Kinetics:** The kinetics in the solid state was studied by the capillary method developed by R. P. Rastogi. The substance to be filled in the capillary was first passed through the sieves and particles of the desired mesh size were used. The packing of the capillary was done in a reproducible manner by applying as far as possible uniform pressure to the material in the capillary. The reactions were followed in an electrically controlled oven at the desired temperature. The coloured boundary at the (RSN) - (p-DAB) junction was yellow and that at the (RSN + PHS) - (p-DAB) junction was red-yellow. The red ring remained stationary at the junction and the yellow boundary moved towards the p-DAB column. The coloured boundary at the (RSN) - (p-DAB + PHS) junction was red. The red boundary moved towards the p-DAB column at much slower rate than that of the yellow boundary. The distance through which the coloured boundary moved was noted correct to ±0.01 cm and the reproduci-
bility of the kinetic data was found to be 80%. The studies were made at different temperatures and for particles of various sizes. For the kinetic data given in this chapter the particle size of PHS, RSN and p-DAB was 8.33 μ to 12.3 μ, 6.3 μ to 12.5 μ and 8.3 μ to 12.5 μ respectively. It was observed that only RSN diffused through the p-DAB or acidic p-DAB (p-DAB + PHS). The results are shown in figures 8 - 11. When log k is plotted against 1/T for these reactions straight lines were obtained. The results are given in figure 12. From the values of k at different temperatures, the values of the entropy of activation $\Delta S^*$, enthalpy of activation $\Delta H^*$, energy of activation E, and the free energy of activation $\Delta G^*$ were computed by assuming that the temperature dependence of k is according to the following equation

$$k = Qe^{-E/RT}$$  \hspace{1cm} (i)

where Q is the frequency factor, and E is the energy of activation. The results obtained are given in table V.

The velocity of the reaction was the same whether the reaction was performed in the visible light or in ultraviolet light or absolutely in the dark. Hence the role of $\lambda$ electrons is secondary in influencing the reaction kinetics. The kintics was carried out with particles of mesh sizes (i) less than 50 (ii) 50 - 100 (iii) 100 - 200 for RSN and p-DAB. The rate is the same in every case.
FIG. 8 KINETIC DATA FOR THE REACTION BETWEEN p-DAB AND RSN UNDER DIFFERENT CONDITIONS AT 65°C
FIG. 9 KINETIC DATA FOR THE LATERAL DIFFUSION REACTION
AND THE TEST OF $\xi^2 = kt$ FOR THE REACTION BETWEEN p-DAB AND RSN

$\Delta$ at 55 ± 1°C
$\Delta$ at 60 ± 1°C
● at 65 ± 1°C
○ at 70 ± 1°C
FIG. 10 KINETIC DATA FOR THE LATERAL DIFFUSION REACTION AND THE TEST OF $\xi^2 = kt$ FOR THE REACTION BETWEEN p-DAB AND (RSN+PHS)
FIG. 11 KINETIC DATA FOR THE LATERAL DIFFUSION REACTION AND THE TEST OF $\xi^2 = k t$ FOR THE REACTION BETWEEN RSN AND (p-DAB + PHS)
FIG. 12 DEPENDENCE OF REACTION RATE ON TEMPERATURE
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (± 1°C)</th>
<th>k_i (mm²/hr)</th>
<th>E (KCal/mole)</th>
<th>ΔH* (KCal/mole)</th>
<th>ΔG* (KCal/mole)</th>
<th>ΔS* (Cal/mole/degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I  p-DAB-RSN</td>
<td>55</td>
<td>1.50</td>
<td></td>
<td>56.8</td>
<td>19.3</td>
<td>114.2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5.60</td>
<td>57.5</td>
<td>56.8</td>
<td>18.7</td>
<td>114.2</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>12.30</td>
<td></td>
<td>56.8</td>
<td>18.5</td>
<td>112.8</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>79.60</td>
<td></td>
<td>56.8</td>
<td>17.5</td>
<td>114.9</td>
</tr>
<tr>
<td>II p-DAB-(RSN+PHS)</td>
<td>55</td>
<td>1.20</td>
<td></td>
<td>58.5</td>
<td>19.4</td>
<td>118.9</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.10</td>
<td>59.1</td>
<td>58.5</td>
<td>18.9</td>
<td>120.2</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>12.20</td>
<td></td>
<td>58.5</td>
<td>18.5</td>
<td>117.6</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>86.60</td>
<td></td>
<td>58.5</td>
<td>17.4</td>
<td>119.5</td>
</tr>
<tr>
<td>III (p-DAB+PHS)-RSN</td>
<td>55</td>
<td>0.10</td>
<td></td>
<td>37.7</td>
<td>21.2</td>
<td>50.3</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.18</td>
<td>38.3</td>
<td>37.6</td>
<td>21.0</td>
<td>50.3</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>0.73</td>
<td></td>
<td>37.6</td>
<td>20.4</td>
<td>50.3</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1.42</td>
<td></td>
<td>37.6</td>
<td>20.3</td>
<td>50.3</td>
</tr>
</tbody>
</table>
ii) Reaction temperature: The reaction temperature was measured by the method described by Rastogi et al.7 The results are summarized in figure 13.

iii) Nonporous studies: Pellets of RSN, PHS, p-DAB, RSN + PHS, and of p-DAB + PHS were made with a hydraulic press applying a 100 lb. pressure. The radius of the pellet (0.5 gm of substance) so obtained was 6.5 mm. A piece of filter paper was placed at the bottom of a glass petridish; the p-DAB or the acidic p-DAB i.e. (p-DAB + PHS) pellet was placed on the filter paper. The RSN or the acidic RSN i.e. (RSN + PHS) pellet was then placed on top of the p-DAB or (p-DAB + PHS) pellets. The petridish was covered with a glass lid, the surface of the pellets turned light orange or red while the bulk of the pellets remained unchanged. The thickness of the coating increased with time. Some light orange crystals grew at the junction of the pellets.

iv) Conductance studies: For conductance measurements the pellet was placed in the sample holder and the conductance was measured with time. For this purpose, the instrument fabricated by Krishan Lal, et al.8 was used. Conductivity values were calculated using the equation (ii)

\[ \sigma^- = \frac{A}{TR} \]  

(ii)

where \( \sigma^- \) is the conductance, \( A \) is the area, \( T \) is the thickness
FIG. 13 REACTION TEMPERATURE RISE AS A FUNCTION OF TIME
and $R$ is the resistance of the pellet. The results obtained are given in table VI.

When solid RSN powder was placed at the bottom of a beaker and it was covered with a filter paper impregnated with p-DAB the paper turned light orange within two hours, on exposing the light orange paper to HCl vapour it turned red. In the reverse experiment i.e. p-DAB at the bottom and filter paper impregnated with RSN at the top the filter paper turned light orange in 5 days. Similar results were obtained from a set of experiments in which acidic p-DAB or acidic RSN powders placed at the bottom of the beaker which was covered with filter papers impregnated with RSN and p-DAB respectively and vice versa. p-DAB and RSN papers were prepared by immersing filter paper circle in 1% ethanolic solutions of the reagent concerned and then drying at 30°C. Similar experiments were carried out using sintered glass as the impregnated support in place of filter paper and same results were obtained. These results confirm that RSN is the diffusing species.

v) Phase diagram studies: Solid - liquid equilibrium data were obtained by the Thaw-melt method. Results are shown in figure 14.

vi) Spectral studies: The absorption spectra of p-DAB, RSN and the yellow product (obtained in the solid state reaction of RSN and p-DAB) in ethanol and of the saturated ethanolic solution of
**TABLE VI**

Conductance of the solid reactants (particle size 6-13 μ) and products at 25°С.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substance</th>
<th>Thickness of the pellet (T) (cm x 10⁻¹)</th>
<th>Resistance of the material (R) (ohm x 10¹⁰)</th>
<th>Conductance of the material (σ⁻) (ohm⁻¹ x 10⁻¹¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>RSN</td>
<td>2.86</td>
<td>0.70</td>
<td>66.5</td>
</tr>
<tr>
<td>2.</td>
<td>p-DAB</td>
<td>2.72</td>
<td>0.50</td>
<td>98.0</td>
</tr>
<tr>
<td>3.</td>
<td>PHS</td>
<td>1.25</td>
<td>12.00</td>
<td>8.9</td>
</tr>
<tr>
<td>4.</td>
<td>RSN+p-DAB (1:1 mole ratio)</td>
<td>2.46</td>
<td>0.25</td>
<td>216.0</td>
</tr>
<tr>
<td>5.</td>
<td>RSN+p-DAB (1:2 mole ratio)</td>
<td>4.22</td>
<td>0.31</td>
<td>105.0</td>
</tr>
<tr>
<td>6.</td>
<td>RSN+p-DAB (2:1 mole ratio)</td>
<td>3.60</td>
<td>0.04</td>
<td>94.7</td>
</tr>
<tr>
<td>7.</td>
<td>PHS+RSN (1:1 mole ratio)</td>
<td>1.60</td>
<td>13.00</td>
<td>6.4</td>
</tr>
<tr>
<td>8.</td>
<td>PHS+p-DAB (1:1 mole ratio)</td>
<td>1.82</td>
<td>13.00</td>
<td>5.6</td>
</tr>
<tr>
<td>9.</td>
<td>PHS+RSN+p-DAB (1:1:1 mole ratio)</td>
<td>2.66</td>
<td>13.00</td>
<td>3.8</td>
</tr>
</tbody>
</table>
FIG. 14 PHASE DIAGRAM OF p-DAB-RSN SYSTEM
the red product in the ultraviolet and the visible region (figure 15) were obtained. Reflectance spectra using Mg CO₃ as the reference (figure 15), and infrared spectra in nujol (figure 16) were taken as usual. The EPR spectra of the yellow and red products (figure 17) were obtained by preparing products at the time of the experiment. The yellow product was obtained by mixing RSN and p-DAB in the solid state in (1:1) ratio. The red product was obtained by adding excess of PHS to (1:1) mixture of RSN and p-DAB.

vii) Vapour-pressure studies: The vapour pressures of pure ethanol, 0.33% ethanolic solutions of RSN, of p-DAB and of the light orange product (obtained in the solid state) at 30°C and 745 mm Hg were found to be 1.5, 1.4, 0.8 and 1.1 lb./sq. inch respectively. The procedure used has been reported in the previous paper. These results show that RSN has a higher vapour pressure than that of p-DAB. Therefore, if the reaction is diffusion controlled the diffusing species is the RSN rather than the p-DAB or the product.

viii) Porous plug experiment: In this experiment p-DAB and RSN columns in the capillary were separated by a porous plug of glass wool (Figure i)

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(FIG. i)
FIG. 15 a ABSORPTION SPECTRA OF RSN, p-DAB, YELLOW PRODUCT AND RED PRODUCT IN THE VISIBLE REGION
FIG. 16  INFRA RED SPECTRA OF RSN, p-DAB, YELLOW PRODUCT AND RED PRODUCT
FIG. 17. EPR SPECTRA OF YELLOW AND RED PRODUCTS
The capillary was then placed in an oven at $65^\circ$C. It was noticed that immediately after keeping the capillary in the oven a yellow coloured boundary appeared between the glass wool and the p-DAB. The rate of movement of the yellow boundary was the same as in the absence of the plug. No coloured boundary was obtained at the (glass wool) - (RSN) junction. Glass capillaries were now packed in the following sequence:

ii) (p-DAB + PHS) - (glass wool) - (RSN)

iii) (RSN + PHS) - (glass wool) - (p - DAB)

In case (ii) a red boundary appeared at the (glass wool) - (p-DAB + PHS) junction. In case (iii) a yellow coloured boundary appeared at the (p-DAB) - (glass wool) junction. The movement of the red boundary in case (ii) was slower than the movement of the yellow boundary in case (iii).

The length of glass wool gaps was varied from 1 mm to 4 mm but no change in the rates of the movement of the yellow or the red boundary was observed.

**DISCUSSION**

According to Acheson et al., RSN reacts with p-DAB in the solution state in an acidic medium to give a red product. In the solid state it was found by Osipenko and Tishchenko that RSN reacts with p-DAB to give a yellow or light orange
product. It has been observed that in the solid state RSN reacts with p-DAB to give two compounds i.e. a yellow one in the neutral medium and a red one in the acidic medium. The yellow compound has not been detected in the solution state. This is one of the interesting examples where the reactions in the solid state are different from the one in solution state.

The mechanism of the p-DAB - RSN reaction is rather complex and it is not possible to establish the mechanism with the help of the available data. However, the following points emerge from the results obtained:

i) The porous plug experiment shows that RSN is the diffusing species and not p-DAB. Thus when the capillary is packed as in (Figure i) and kept in an oven at 65°C a yellow coloured boundary is developed at the (glass wool) - (p-DAB) junction. This experiment shows that diffusion takes place in the vapour phase. There is no effect on the movement of the yellow boundary when the length of the plug is varied from 0 - 4 mm. Further, there was no effect on the rate of diffusion when the particle size of RSN or p-DAB was varied from 50 to 200 mesh size. Both these observations are consistent with vapour phase diffusion.

When the capillary was packed as shown in (Figure ii) a yellow coloured boundary developed at the (glass wool) - (p - DAB) junction
but the movement of the boundary was slower than with arrangement (i). This was due to the fact that the RSN mole fraction was now lower and hence its vapour pressure was smaller.

When the capillary is packed as in (Figure iii) a red coloured boundary appears at the junction of the glass wool plug and the p-DAB + PHS mixture. However, the movement of the red boundary was much slower than in the first case. This may be due to the fact that the red product has to move through a mixture of p-DAB and PHS.

ii) Figure 8 shows that the rate of reaction is initially fast and then it slows with time. This is due to the fact that the reaction is diffusion controlled and hence the rate slows down with an increase in the thickness of the layer.

iii) Figures 9, 10 and 11 show that $\xi^2 dt$ i.e. a parabolic rate law is followed. Here $\xi$ is the thickness of the coloured boundary and $t$ is the time.

iv) Figure 12 shows that the Arrhenius equation is followed.

v) Figure 13 shows that the reaction temperature is very low and hence there is little possibility of the grain boundary
or bulk diffusion.

vi) Figure 14 shows that p-DAB and RSN react in the mole ratio 1:1 and the compound formed melts at 73°C. The same results were obtained by Osipenko et al.\(^3\).

vii) Figure 15 shows that the red product formed in the solution is the same as the one formed in the solid state.

viii) Figure 16 shows that the absorption due to the \(\overset{\gamma}{\mathrm{C}} = \overset{\xi}{\mathrm{O}}\) group is considerably diminished during the formation of the yellow and the red products.

ix) The e.s.r. spectra (Figure 17) show that the yellow and the red products both are free radicals.

x) Table V shows that the value of \(\Delta S\) for the red product is less than that for the yellow one showing thereby that the transition state for the red product is more ordered.

The greater value of energy of activation for the light orange (57.5 K Cal/mole) or red product (38.3 K Cal/mole) than the heat of sublimation of RSN (21.37 K Cal/mole) suggests that the vapour phase diffusion occurs. The heat of sublimation has been calculated from the heat of fusion\(^1^0\) and heat of vaporization\(^1^1\). Since the energy of activation is lower the possibility of bulk diffusion or volume diffusion is remote and surface migration appears to be predominant in the movement of the red coloured boundary.
xi) The conductance data (Table VI) show that there is no significant change in conductance during the reaction. This observation rules out an ionic mechanism and is consistent with the free radical mechanism postulated herein.

The mechanism proposed by Acheson\textsuperscript{4} did not explain the role of $[\text{H}^+]$ or the acid. The mechanism given by Osipenko\textsuperscript{3} for the light orange molecular compound does not account for the e.s.r. spectrum. Therefore the mechanism as shown in Scheme 7 may be tentatively postulated.
SCHEME 7 MECHANISM OF p-DIMETHYLMAMINO-
BENZALDEHYDE-RESORCINOL REACTION
IN THE SOLID STATE
REFERENCES