Study of the reaction between resorcinol and formaldehyde*

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The reactions between resorcinol and formaldehyde were led in aluminium pans of a d.s.c. Perkin Elmer calorimeter. The products were separated by means of high performance liquid chromatography and identified by ^{1}H and ^{13}C n.m.r. Depending on the catalyst concentration and molar ratio the mixtures reacted at two different temperature ranges, 317–332K and 332–366K. The heat of the reaction in the first temperature range was between 16.8 and 45.0 kJ mol^{-1} for molar ratios 1:1 and 1:3 respectively. By ^{1}H and ^{13}C n.m.r. spectroscopy five addition products were determined. The reaction heat in the second temperature range was 73.5 kJ mol^{-1} and was attributed to condensation reactions. The activation energies were 95.0 and 120.0 kJ mol^{-1} for addition and condensation reactions respectively. For addition, order two and for condensation, order one of reaction was established. On the basis of these foundings tentative reaction schemes were prepared.

INTRODUCTION

The distribution of the electron density in the benzene ring increases the reactivity of the *ortho* and *para* position of resorcinol[1]. Resorcinol reacts with formaldehyde in alkaline medium at low temperature already. The reaction products are mixtures of addition and condensation compounds which react further to form high molecular compounds, mostly infusible and insoluble.

In this paper the results of the study of the reactions between resorcinol and formaldehyde are reported. The reactions were led in a differential scanning calorimeter. High performance (adsorption) liquid chromatography was used to separate the reaction products and ^{1}H and ^{13}C n.m.r. spectroscopy were used for their identification.

EXPERIMENTAL

Resorcinol and formaldehyde were products of Schuchardt, München and Carlo Erba, Milano. All reagents used in the work were analytical grade.

For the preparation of resins resorcinol and formaldehyde (37% aqueous solution) were mixed in the molar ratio 1:1, 1:2 and 1:3. 0.002–0.02 mol of sodium hydroxide as catalyst was added. The mixtures were cooled below 0°C and weighed in aluminium pans in which the reactions were led in a DSC–2B, Perkin Elmer calorimeter. The temperature of the DSC–2B was programmed from 290 to 390K at the heating rate 2.5K min^{-1}. The resins used for h.p.l.c. separation were prepared at 40°C, the duration of the reaction being 30 min. The columns of the h.p.l.c. were filled with Merckosorb Si 60, 10 μ using the slurry packing technique. Before use the columns were washed with the separation solution[2], which was dichlormethane:dioxane:methanol in the proportion of 250:10:10. The flow rate was 0.75 ml min^{-1}. For detection, a u.v. spectrophotometer monitoring at 254 nm was used. The samples which were collected manually at the detector outlet were the accumulations of 20 separations. The ^{13}C n.m.r. spectra were recorded using the Bruker SXF 100 at ambient temperature. The samples (50% w/v) were dissolved in H_2O and D_2O. The spectra were 5 kilo accumulations with pulse width of 5 μ s. Coupling of the carbon nuclei with the neighbouring protons was removed. Tetramethylsilane was used as the standard.

RESULTS AND DISCUSSIONS

The formation of resorcinol resins is accomplished in three steps: the addition of formaldehyde to resorcinol to form hydroxymethyl resorcinols, the condensation of hydroxymethyl resorcinols to form methylene and methylene ether bridged di- or high-molecular compounds and the disproportionation of methylene ether bridge to methylene-bridged resorcinol and formaldehyde. Zavitsas and others[3] suggested that the addition of formaldehyde passes over the phenolate ion, concentration of which is proportional to the rate of reaction. The reaction is very fast and starts at room temperature immediately.

Figure 1 shows the thermograms of the reaction between resorcinol and formaldehyde. All thermograms have two peaks, belonging to two different types of reactions. The temperature of peaks lowers with increasing amount of catalyst and decreasing molar ratio between resorcinol and formaldehyde. By i.r. ^{1}H and ^{13}C n.m.r. spectroscopy it was found that the first peak belongs to the addition reaction and the second to the condensation reaction. The peaks of the thermograms were separated mathematically on a computer.

The heat of polymerization for the addition reaction is increasing from 16.8 to 45.0 kJ mol^{-1} by increasing the

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molar ratio between resorcinol and formaldehyde. The heat of the condensation reaction depends only slightly on the molar ratio (*Table 1*).

Although three theoretical ratios between resorcinol and formaldehyde were used, some formaldehyde was always left unreacted.

The activation energy and reaction order can be calculated using the following equation[4]:

$$\frac{\ln(d_2/d_1)}{\ln\dfrac{(A-a_2)}{(A-a_1)}} = \frac{E_a}{R}\cdot\frac{(1/T_2-1/T_1)}{\ln\dfrac{(A-a_2)}{(A-a_1)}} + x \qquad (1)$$

where T_1 and T_2 are any temperatures within the temperature range of reaction, a_1 and a_2 (mJ) the corresponding areas and d_1 and d_2 (mJ s^{-1}) the corresponding distance curve baseline. A is the total area under the curve (mJ) and x is the reaction order. By plotting the left hand side of equation (1) vs. $(1/T_2-1/T_1)/(\ln\ (A-a_2/A-a_1)$, the activation energy from the slope of the resulting straight line is obtained. The intersection with the abscissa gives the reaction order. The representative plots of addition and condensation reactions with 0.01 mol of NaOH as catalyst are presented in *Figure 2*. In *Table 1* the values of activation energies calculated from this plots are also presented. The reaction order for addition is 2 and for condensation is 1.

The rate constants for the reaction between resorcinol and formaldehyde can be calculated using equation (2):

$$K = \frac{\left(\dfrac{V.A}{n_0}\right)^{x-1}\dfrac{dH}{dt}}{(A-a)^x} \qquad (2)$$

where V is volume and n_0 the number of moles of reactants present initially. $\dfrac{dH}{dt}$ is the rate of heat evolution. In *Table 1* the values of the rate constants for addition and condensation are also given.

The mixture of products obtained from the reaction between resorcinol and formaldehyde at 40°C and 30 min duration of the reaction were separated by h.p.l.c. Individual conpounds were analysed by i.r. and n.m.r. spectroscopy. On *Figure 3* a representative chromatogram is shown.

I.r. spectra of the second component has two peaks at 765 and 740 cm^{-1}, respectively, belonging to out-of-plane C–H bonding of 1,2,3, trisubstituted benzene rings. They can be ascribed to 2-hydroxymethyl resorcinol. On the base of the frequency at 830 cm^{-1} the third compound can be ascribed to 4- and 6-hydroxymethyl resorcinol.

At lower molar ratio 4-hydroxy and 6-hydroxymethyl resorcinol are dominantly formed. Those products react with formaldehyde to 2,6- and 4,6-dihydroxydimethyl resorcinol to which belong the fourth and fifth peak in the chromatogram in *Figure 3*. The sixth peak belongs to 2,4,6-trihydroxytrimethyl resorcinol.

In *Table 2* the concentrations of components appearing in the reaction between resorcinol and formaldehyde are given. The ratio between *ortho* (position 2) and *ortho para*

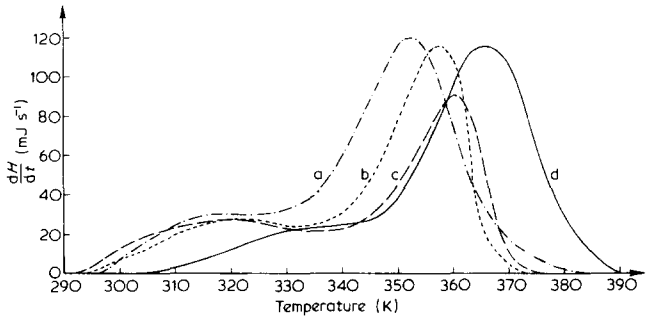

Figure 1 Thermograms of the resins. The molar ratio between resorcinol: formaldehyde and NaOH was 1 : 1 : 0.01 (a), 1 : 2 : 0.02 (b), 1 : 3 : 0.01 (c) and 1 : 3 : 0.002 (d)

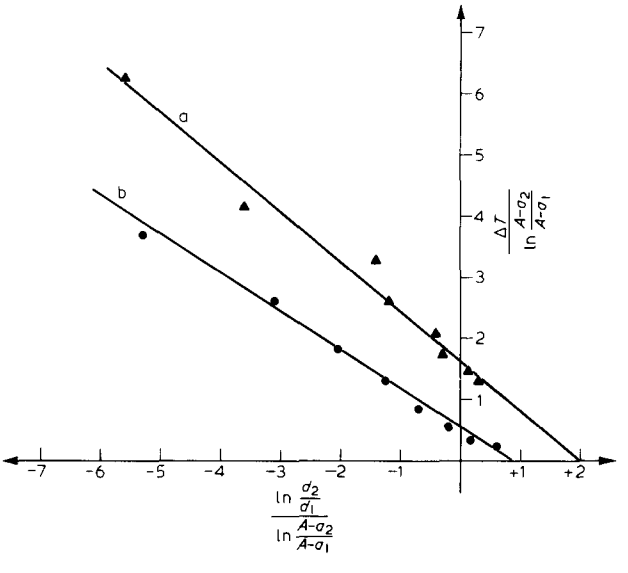

Figure 2 The representative plots from which the activation energies and reaction order for addition and condensation reactions were obtained. Addition (a), condensation (b)

Table 1 Kinetic parameters of reactions between resorcinol and formaldehyde

	Molar ratio between resorcinol: formaldehyde: NaOH			
	1 : 1 : 0.01	1 : 2 : 0.01	1 : 3 : 0.01	1 : 2 : 0.02
Addition				
Temp. maximum (K)	317.5	320	320	332
Heat evolved (kJ mol^{-1})	16.8	29.4	45.0	20.1
Activation energies (kJ mol^{-1})	92.3	94.8	98.2	–
Rate constants (1 mol^{-1} S^{-1})	0.00026	0.00019	0.00017	–
Condensation				
Temp. maximum (K)	352	357.5	360	366
Heat evolved (kJ mol^{-1})	72.6	73.4	74.7	86.0
Activation energies (kJ mol^{-1})	103.0	127.9	132.5	134
Rate constants (S)	0.0039	0.0030	0.0018	–

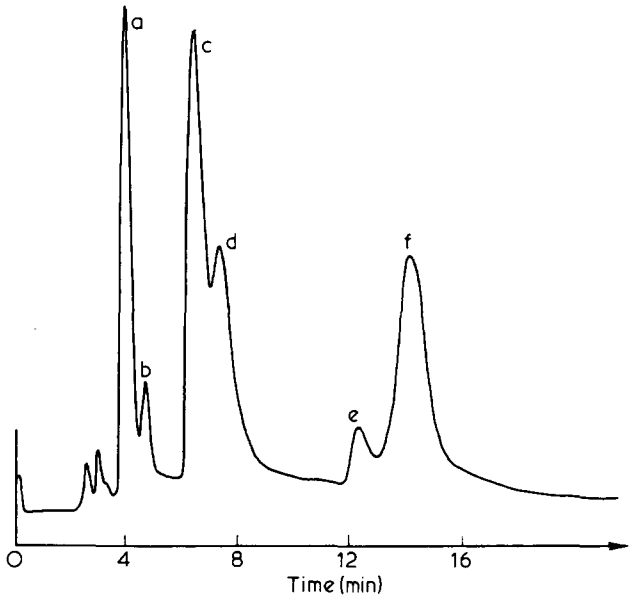

Figure 3 Chromatogram of the mixture resulting from the reaction between resorcinol and formaldehyde (1 : 2) at 40°C resorcinol (a), 2-hydroxymethyl resorcinol (b), 4-hydroxymethyl resorcinol (c), 2,4-dihydroxydimethyl resorcinol (d), 4,6-dihydroxydimethyl resorcinol (e), 2,4,6-trihydroxytrimethyl resorcinol (f)

Table 2 Concentrations of components appearing in the reactions between resorcinol and formaldehyde at 40°C, 30 min

	Molar ratio resorcinol: formaldehyde: NaOH		
	1 : 1 : 0.01	1 : 2 : 0.01	1 : 3 : 0.01
Resorcinol	31.4	20.4	9.1
2-hydroxymethyl resorcinol	5.0	4.5	7.8
4-hydroxymethyl resorcinol	39.3	33.4	30.1
2,4-dihydroxydimethyl resorcinol	2.1	5.7	6.3
4,6-dihydroxydimethyl resorcinol	1.5	2.4	3.2
2,4,6-trihydroxytrimethyl resorcinol	15.4	26.7	30.5
high-molecular products	5.3	6.9	13.0

(position 4 and 6) substituted forms of the molecules is 1:7. Three samples of resins prepared from resorcinol and formaldehyde at molar ratio 1:1, 1:2 and 1:3 were analysed by ^{13}C n.m.r. in D_2O.

As it was described[6,7] the signals at 115.0 ppm (*Figure 4*) and 118.0 ppm belong to the aromatic carbon on *ortho–ortho* (2) and *ortho–para* (4,6) position of resorcinol, which are occupied by $-CH_2-OH$ groups. At lower molar ratio, the reaction via *ortho–para* position (4,6) is favoured. The ratio between electron density in the *ortho* position (2) and *ortho–para* position (4 or 6) is 5,8. Comparing those ratios for others phenols[8], it can be seen that in this case position 2 is sterically hindered by both neighbouring hydroxyl groups and reacts little with formaldehyde. This finding is

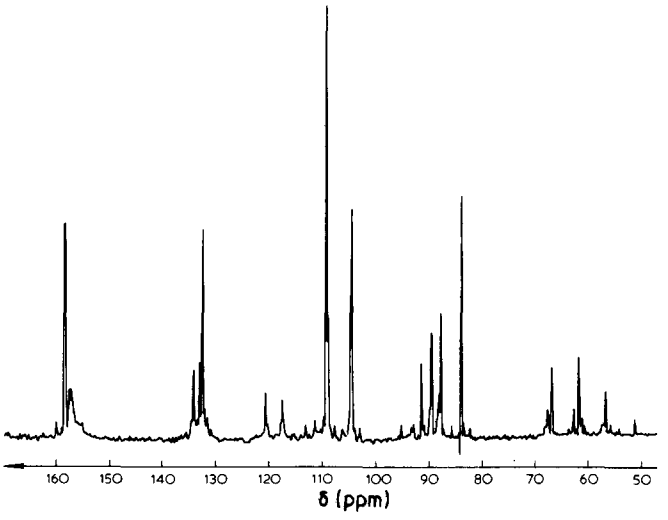

Figure 4 ^{13}C n.m.r. spectrum of resin prepared from 1 : 2 resorcinol: formaldehyde at 40°C

in agreement with those of Breat *et al.*[7] who did not find the *ortho–ortho* substituted forms in the spectrum of the resorcinol novolak. The signals at 59 to 64 ppm belong to the hydroxymethyl groups in the *ortho–ortho* position and *ortho–para* position of mono- and dihydroxymethyl resorcinol.

In the spectrum of the resorcinol resins it can be seen that the signals between 20 and 40 ppm which belong to the methylene bridge between phenyl groups, are very small if compared to signals at 59 and 64 ppm. That means that the condensation between resorcinol and formaldehyde does not readily take place under earlier described conditions.

CONCLUSION

From the presented preliminary studies it is evident that the combined use of h.p.l.c., d.s.c, i.r. and n.m.r. spectroscopy allows the course and kinetic parameters of the reaction between resorcinol and formaldehyde to be followed. D.s.c. has proved useful for studying the kinetics of the quite complex reaction between resorcinol and formaldehyde. ^{13}C n.m.r. and h.p.l.c. can provide details of the relative amounts and position of hydroxymethyl groups attached to benzene ring.

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