Pakistan J. Sci. Ind. Res., Vol. 16, No. 6, December 1973

THE ROLE OF ORGANIC ACIDS IN CONTROLLING THE REACTION OF PHENOL WITH FORMALDEHYDE TO FORM PHENOLIC RESINS

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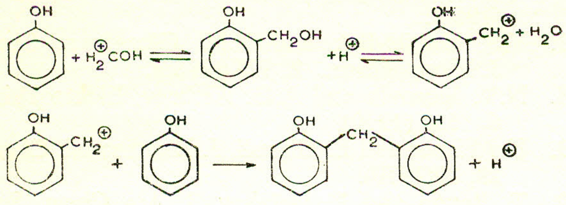
(Received October 18, 1972; revised September 12, 1973)

Abstract. A study has been made of the acid-catalysed phenol–formaldehyde reactions using ten carboxylic acids of different basicities. It has been observed that the molecular weights of resultant resin seem to be dependent upon the acid concentration a, p*K* value of the acid and other reaction variables

A great deal of studies[1–5] have been made on the acid-catalysed reactions of phenol and substituted-phenols with formaldehyde since Bakeland[7] showed that acid-catalysed reaction of phenol with formaldehyde leads to the formation of 1, 1-dihydroxydiphenylmethane. In most of the studies emphasis has been laid on the properties of the products by varying the aromatic compounds and in a few [7–10] cases the acids but these too for the sake of the properties of the polymeric products (resin) obtained. Little data is available on the affect of the nature of the acids on the properties of the resins thus obtained, such as molecular weight, cross-linking and stability.

In the case of phenols under acidic conditions the methylol groups are most likely converted to benzylic carbonium ion which quickly reacts with other phenolic nuclei by an electrophilic substitution reaction (I) to form dihydroxydiphenylmethane.



I

Because these compounds exist as short-lived intermediates[1] their life and further reactions are most likely to be controlled by two parameters of these acids used in the catalysis reactions, i.e. the concentration and the nature of the acid. Nature of the acid, will thus be the only prime factor in controlling the nature of the product under identical comparative studies, using various acids.

In the present work phenol–formaldehyde acid-catalysed reactions have been studied using ten different organic carboxylic acids of various basicities. It has been observed that molecular weights of the resins are controlled by the p*K* values of the acids and also at low concentration (less than 0.4M) the molecular weights are dependent on the acid concentration.

Materials

Formaldehyde. Formalin (E. Merck, 37%) was used throughout these investigations without further purification.

Acids. All acids used were of A.R. grade and hence further purification was avoided.

Phenol. Commercial phenol was twice distilled and central fractions boiling at 180–81°C were stored in vacuum-sealed vessels and opened just before the experimental runs in the atmosphere of nitrogen.

Methods

Reaction Technique. Ten gram phenol and 20 ml formalin (app. 1:2 molar ratio) were charged to a long-necked round-bottom flask containing a pre-weighed quantity of the catalysing acid so as to give a normality of 0.15N of the mixture on the basis of catalysing acid alone. A water condenser was fitted to the flask and the same was immersed in a thermostatically controlled bath maintained at 180±2°C. The mixture was refluxed till a vigorous reaction was started. The reaction was allowed to proceed for $\frac{1}{2}$ hr, from the first appearance of the milkiness. The flask was taken out of the bath and quickly transferred to ice water-bath to freeze further reaction. The resinous product was allowed to settle down and the clear supernatant liquid drained off. The resin was successively washed with distilled water and benzene to remove unreacted acid, phenol and formalin. The purified resin was dried to a constant weight in vacuum oven at 60°C.

Molecular Weight Determination. The number-average molecular weight (M_n) of the resin samples were determined by using a Mackro Laboratory electro-osmometer model 301A, using acetone as solvent. The change in resistance due to the heat exchange between solvent and solution ($\triangle$H) of the resin and the standard compound benzil were measured at 37.0±0.001°C at five different concentrations and molecular weights were computed by extrapolation to zero concentration.

The results were also compared ebullioscopically and difference in molecular weights was found to be less than 2%.

Results and Discussion

Properties of the acid-catalysed phenol–formaldehyde resin depend greatly on the reaction mixture ratio of phenol and formalin. The composition of the mixture is usually determined by the end-use of the resulting resin and has been discussed in detail in

TABLE 1

Picric acid		Oxalic acid		Fumaric acid	
Concn	M_n	Concn	M_n	Concn	M_n
0·0132	510	0·0132	230	0·0132	120
0·106	612	0·106	380	0·106	220
0·1585	750	0·1585	585	0·1585	410
0·3963	930	0·3963	750	0·3963	590
0·5548	1080	0·5548	850	0·5548	630

TABLE 2

Acid catalyst	pK value in water[12]	Induction period (min)	M_n	Water insoluble product (%)
Picric	0·38	10	617	25·47
Trichloroacetic	0·80	150	417	21·14
Oxalic	pK_1—1.19;pK_2—4.21	60	565	38·7
Maleic	pK_1—2.00;pK_2—6.26	25	407	15·35
Salicylic	pK_1—2.97;pK_2—13.44	75	292	18·8
Fumaric	pK_1—3.03;pK_2—4.47	75	222	16·73
Tartaric	pK_1—3.02;pK_2—4.54	60	330	19·32
Adipic	4·43	55	330	27·26
Benzoic	4·20	—	—	—
Citric	—	225	410	16·82

the litrature.[9] A thermosetting resin is obtained if formalin is in excess and a thermoplastic resin if phenol is in excess. These studies were conducted at a constant phenol–formalin composition of 1:2 molar ratio[11] giving an ideal thermosetting resin, using ten different acids at different concentrations.

The effect of acid concentration on the molecular weight of the resin, after ½ hr induction period, in the case of these acids, is given in Table 1 (two distinct layers are formed). Dependence of molecular weight on the acid concentration is apparent up to 0.25 mole/litre and above this concentration the increase in acid concentration has a slight effect on molecular weights up to 0.4 mole/litre concentration but beyond this limit there is little change in molecular weight and further increase in the acid concentration makes the reaction uncontrollable and a gel product insoluble in any solvent is obtained.

The electrophilic substitution reaction of phenol under these conditions is thus dependent on the acid concentration but as the availability of protons in different acids of the same concentration is different, it is of great interest to see the effect of the various acids on the catalysed reactions. Ten acids differing in ionisibility have been used at a constant concentration. The induction periods, yield and molecular weights of the resulting resins seem to depend on proton availability of the acids (Table 2). Acids which are highly ionised show less induction period, higher yield of the resin and the high molecular weights than the less ionised acids.

The molecular weights of the resins obtained in the case of different acids seem to depend upon the pK values of the acids (Table 2). Acids with low values of pK give higher molecular weight resins while with high pK values give resins of lower molecular weights. Trichloroacetic acid seems to be an exception to this rule as this acid having the lowest pK value (0.80) gives resin of the same order of molecular weight as that of maleic acid.

The position of benzoic acid is also anomalous as this acid has the same order pK value as that of adipic acid but no resin was obtained by using this acid as catalyst probably due to very low solubility of the acid.

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