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## CHARACTERIZATION OF RESORCINOL- AND PHENOL-FORMALDEHYDE PREPOLYMERS BY $^1\text{H}$ NMR SPECTROSCOPY

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*Homo- and co-condensate prepolymers, obtained along with the most typical components of oil-shale alkylresorcinols (5-methylresorcinol, 2,5-dimethylresorcinol), have been characterized using  $^1\text{H}$  NMR spectroscopy.*

*Methylene  $^1\text{H}$  chemical shift assignments are discussed considering solvent effects and structural characteristics of hydroxyl- and methyl-effects arising from resorcinolic and phenolic co-reagents.*

### Introduction

The most important example of the practical use of phenol-resorcinol-formaldehyde co-condensate prepolymer resins is the production of glue-laminated timber constructions. A similar resin has been successfully synthesized, substituting oil shale alkylresorcinols for the resorcinol. The oil shale alkylresorcinols contain about 50 % 5-methylresorcinol and 30 % other alkylresorcinols (among these are 5-ethylresorcinol, 2,5- and 4,5-dimethylresorcinol) [1]. The reaction of phenolic methylol oligomers with the resorcinolic component is responsible for the production of a maximum amount of co-condensates.

Most NMR studies on phenol-formaldehyde model compounds and resins, and to a much lesser extent on resorcinol-formaldehyde resins, were carried out using  $^{13}\text{C}$  assignments [2]. The carbon shifts can be calculated considering structural characteristics. Thus, *ortho*-hydroxyls have the main effect on bridge carbon shifts from *p,p'*-methylene (39.7 ppm) to 2,2'-methylene (18.5 ppm) with quite similar values for *o,o'*- and 4,4'-bridge carbons (29.2 and 29.9 ppm, respectively). Some  $^{13}\text{C}$  assignments are not specific for phenol-resorcinol co-condensates, particularly in the presence of homo-condensates. Despite that, GPC/ $^{13}\text{C}$  NMR analysis enables one to conclude that the co-condensates of methylolphenols with resorcinol and 5-methylresorcinol are quite similar. The co-condensate 4,*o'*- and 4,*p'*-methylenes are the dominant constituents [3].

Without connoting any negative aspect to  $^{13}\text{C}$  NMR, we have used the  $^1\text{H}$  NMR as the more convenient method for quantitative determination of the content of structural fragments in the course of the formation of co- and homo-condensates. The main attention was directed to the kinetic evaluation of reactions [4-6]. In an attempt to exclude complications imparted by the formaldehyde reagent while promoting the co-condensation, some pure methylolphenols were synthesized for this homo- and co-condensation study. Among these are *ortho*- and *para*-methylolphenols, which are the first-formed and most abundant compounds in the phenol-formaldehyde reaction. *Ortho*- and *para*-substituted methylolxylenols and dimethylolcresols were also used in order to eliminate the possibility of condensation through aromatic free positions.

Resorcinol, as the highly reactive phenol of commercial interest, is usually used in polycondensation studies of phenols with formaldehyde [7]. Besides resorcinol, 5-methylresorcinol was specifically chosen since it is the most reactive resorcinol and the most abundant component in oil shale alkylresorcinols. The other typical and available component of oil shale products is 2,5-dimethylresorcinol. The peculiarities of this resorcinol lie in its high melting point (161.5 °C), low solubility and reduced reactivity. The latter is due to the opposite influence of methyl groups.

One understands that the prediction of  $^1\text{H}$  chemical shifts, as compared to  $^{13}\text{C}$  shifts, in phenolic prepolymer and resin spectra is not so successful. At the same time extensive experimental material discussed in this paper addresses the influence of various effects on  $^1\text{H}$  chemical shifts assignments.

## Experimental

Commercial grade resorcinol (R) and 5-methylresorcinol (5MR) were used in the condensation reactions. R and 5MR were recrystallized from benzene (m.p. 110.8 and 110.2 °C, respectively). 2,5-Dimethylresorcinol (2,5DMR) was separated from oil shale alkylresorcinols at the Institute of Chemistry (Estonian Academy of Science) (m.p. 161.5 °C, content of main substance 98.4 %). Methylol compounds were synthesized and purified as described previously [4-6] and characterized by melting point and  $^1\text{H}$  NMR spectrum.

Self-condensates of methylolphenols (MP) and their co-condensates with R and 5MR (preferably with equimolar ratio) were obtained in the melt-condensation at 120 °C without a catalyst and in the presence of various catalysts ( $\text{NaOH}$ ,  $\text{Zn}(\text{OCOCH}_3)_2$ ,  $\text{C}_6\text{H}_5\text{COOH}$ ). The amount of catalyst was varied from 0.005 to 0.1 mole per 1 mole of MP. In the case of 2,5DMR the temperature of melt-condensation was raised to 150 °C. The samples were taken at various times depending on the rate of methylol disappearance from the reaction mixture. For comparison, the homo-condensates of R, 5MR and 2,5DMR were synthesized in the reaction with 37 % formalin (molar ratio 1:0.5). This was accomplished by heating at 80-90 °C for 2 hours.

$^1\text{H}$  methylene chemical shifts were found in 100 MHz spectra for methylol, dimethylene ether and methylene model compounds and resins. Methylene shifts were measured from internal hexamethyldisiloxane and referenced to TMS. Pyridine- $\text{d}_5$  (Py) was preferred as the NMR solvent. Quantitative changes in molar concentrations during the reaction were calculated from integral intensities of the corresponding methylene signals.

## Results and Discussion

$^1\text{H}$  chemical shifts, assigned to various condensation product spectra are presented in Tables 1-3.

### *Methylolphenol Self-Condensates*

Depending on catalytic conditions and the conversion step, the self-condensates contain different amounts of dimethylene ethers and methylene compounds. Self-condensation of methylolxylenols and dimethylolcresols proceeds through dimethylene ether successfully under all conditions. *p,p'*-Ethers release formaldehyde and the product consists mainly of *p,p'*-methylenes. Otherwise, *o,o'*-ethers are very stable and only a small amount of *o,o'*-methylene is formed. Alkali is the best catalyst for formaldehyde release from *o,o'*-ether. The self-condensate of *o,p*- dimethylol-2-cresol consists mainly of ethers. The catalysts promote the liberation of formaldehyde preferentially from *p,p'*-ether. As an exception, alkali catalyst helps to release formaldehyde also from other ethers.

The self-condensates of *o*-methylolphenol (*o*-MP) and *p*-methylolphenol (*p*-MP) preferentially contain *o,p'*-methylenes, but the route of their formation is different. The direct reaction of methylol with aromatic free position occurs in the presence of alkali. Under other conditions, the self-condensation proceeds preferentially through dimethylene ethers. The formaldehyde release from ethers is not as important as the phenolysis of ethers by aromatic free positions.

$^1\text{H}$  methylene chemical shifts of methylolphenol self-condensates are given in Table 1.

### *Phenol-Resorcinol-Formaldehyde Co-Condensates*

Co-condensation of methylolphenols with resorcinols was the only reaction observed under the conditions used. There were no signs of parallel self-condensation of MP or of formaldehyde release with subsequent reaction with resorcinols. The aromatic ring is preferentially substituted at the two equal positions. Only the alkaline catalyst, in the case of the *ortho*-methylol derivative has an influence on the composition of co-condensates with R and 5MR (2,5DMR). This enhances the amount of C4C6 disubstituted rings. In other cases, the composition of co-condensates does not depend on the type and amount of catalyst. The extent of C2 substitution in R and 5MR, independent of MP or catalyst used, forms about 10-15%. C2 methylenes give more than one signal

Table 1. Methylene <sup>1</sup>H Chemical Shifts of Methylphenol Self-Condensates

Compound	Methylol		Dimethylene ether			Methylene		
	<i>o,o'</i>	<i>p,p'</i>	<i>o,p'</i>	<i>p,p'</i>	<i>o,o'</i>	<i>o,p'</i>	<i>p,p'</i>	
<i>o</i> -Methylol-phenol	5.16	-	4.95	4.86; 4.58	4.30 (4.26)	} 4.17 (4.11)	-	
<i>p</i> -Methylol-phenol	4.81	-	-	-	-	-	3.81 (±0.01)	
<i>o</i> -Methylol-4,6-xyleneol	5.05	4.80	4.80	-	4.20	} 4.15	-	
<i>p</i> -Methylol-2,6-xyleneol	4.81	-	-	-	-	-	3.83	
<i>o,o</i> -Dimethylol-4-cresol	5.07	4.76-4.82	4.81	-	4.21	-	-	
<i>o,p</i> -Dimethylol-2-cresol	4.80 ( <i>p</i> ) 5.08 ( <i>o</i> )	4.76; 4.48	4.81	4.76; 4.48	-	4.12-4.14	3.82 (3.79)	

Table 2. <sup>1</sup>H Chemical Shifts of Co-Condensate Methylene Group

Methylol Compound	Resorcinol			5-Methylresorcinol			2,5-Dimethylresorcinol		
	C4	C4C6	C2	C4	C4C6	C2	C4	C4C6	
<i>o</i> -Methylol-phenol	4.37	4.33	4.47-4.55	4.48	4.60	-	4.40	4.54	
<i>p</i> -Methylol-phenol	4.13	4.13	4.47-4.55	4.21	4.30	4.47-4.55	4.23	4.33	
<i>o</i> -Methylol-4,6-xyleneol	4.20	4.13	4.41	4.30	4.40	4.50	4.32	4.44	
<i>p</i> -Methylol-2,6-xyleneol	4.15	4.15	4.48-4.55	4.23	4.32	4.48-4.55	4.27	4.37	
<i>o,o</i> -Dimethylol-4-cresol	4.29	4.23	4.49	4.39	4.47	-	4.41	4.55	
<i>o,p</i> -Dimethylol-2-cresol	4.14 ( <i>p</i> ) 4.20 ( <i>o</i> )	4.14 ( <i>p</i> )	4.40-4.50	4.20 ( <i>p</i> ) 4.30 ( <i>o</i> )	4.33-4.44	-	4.22 ( <i>p</i> ) 4.32 ( <i>o</i> )	-	

belonging to mono-, di- and trisubstitued compounds. Regardless of the polymeric character of co-condensates with dimethylolphenols the methylene shifts preferentially follow the difference between C4 and C4C6 substitution in resorcinols. In the case of *o,p*-dimethylol derivatives, the formation of co-condensates with *p*-methylol is favoured.

$^1\text{H}$  chemical shifts of co-condensate methylene groups are given in Table 2.

Table 3. Methylene  $^1\text{H}$  Chemical Shifts of Resorcinol-Formaldehyde Homo-Condensates

Compound	4,4'	2,4'	4,4' (resin)
Resorcinol	4.35	4.47	-4.25
5-Methylresorcinol	4.46	-	-
2,5-Dimethylresorcinol	4.21	-	-4.25

### Solvent Effects

Proton NMR spectra of phenolic resins and model compounds have been reported in a variety of solvents (ref. in [8]). Py, as NMR solvent, is not used very often.  $^1\text{H}$  chemical shifts in Py are strongly affected by the mutual orientation between phenolic hydroxyls and Py nitrogen. We prefer Py for this useful phenomenon, leading to a better resolution of  $^1\text{H}$  signals of differently located methylenes. The greatest difference between methylene shifts of *o*-MP and *p*-MP is observed in Py (0.35 ppm in Table 1). The same difference in acetone- $d_6$  [8] is 0.22 ppm (4.74 and 4.52 ppm, respectively) and in DMSO- $d_6$  [9] it is only 0.13 ppm (4.47 and 4.34 ppm, respectively). The better resolution also remains in force for signals of bridge methylenes. The shift difference from *o,o'*- and *p,p'*-methylenes (0.49 ppm in Py) diminishes in acetone solution [8] to 0.2 ppm (3.95 and 3.75 ppm, respectively). Distinct resolution of  $^1\text{H}$  signals from *ortho*- and *para*-methylols also allows us to follow their co-condensation. The shift difference from *o,o'*- and *p,p'*-dimethylene ethers is practically the same (0.48 ppm). The mutual influence along the dimethylene ether bond gives the well-resolved signals for *o,p'*-ether (4.86 and 4.58 ppm).

### *ortho*-Hydroxyl Effects

The downfield  $^1\text{H}$  shift is mainly determined by the electronegativity of oxygen linked to methylene. It means that the regions of  $^1\text{H}$  shifts of bridge methylenes are different in diphenylmethanes and of oxygen-linked methylenes in methylols and dimethylene ethers (3.81-4.30 ppm and 4.47-5.16 ppm in Table 1). The methylene shifts of ethers in comparison with methylols appear in the upper field due to the high electron density distribution of oxygen between two methylene groups. At the limits of these regions, the *ortho*-hydroxyl effects are responsible for the downfield shift of methylene signals. This effect is more pronounced in Py solution and it is the main reason for better resolution of signals. In Py solutions

the effect of the first *ortho*-hydroxyl is more significant (Table 1) as compared to acetone solutions [8].

Co-condensates of *o*-MP with R (C4 substitution), phenolic and resorcinolic homo-condensates show the similar methylene  $^1\text{H}$  shifts (4, *o*'-4,37 ppm, *o*,*o*'-4,30 ppm, 4,4'-4,35 ppm in Tables 1-3). This means that the additional contribution of the *para*-hydroxyl in systems with R is small in comparison with two *ortho*-hydroxyl effects. The greatest effect is from the influence of two *ortho*-hydroxyls in the case of C2 substitution in R. This leads to the substantial downfield shift of the methylene signal (4,47-4,55 ppm in Table 2 and 4,47 ppm in Table 3). The difference between methylene shifts, as observed in C4 substitution with *o*- and *p*-MP (4,37 and 4,13 ppm), is not notable in the case of C2 substitution. This proves the stronger influence of the second *ortho*-hydroxyl effect coming from R instead of the phenol and the negligible influence of the additional third *ortho*-hydroxyl effect on the methylene  $^1\text{H}$  shift.

The above-mentioned positions, regarding the hydroxyl-effects, are valid also for compounds obtained from substituted phenols and resorcinols but the additional substituent effects should be considered.

### Methyl Effects

The methyl effects are more complicated, especially in the case of the simultaneous presence of substituents in R (5MR, 2,5DMR) and phenol (methylolxylenols or dimethylolcresols). One can see (Table 1) that the methylene  $^1\text{H}$  shift of *p*-methylols and *p,p'*-diphenylmethanes does not depend substantially on the methyl (methylol) substituent. The peculiarity of these compounds is that both *ortho*-positions with respect to methylene are free and the influence of non-existent substituents is small. The other situation occurs with *ortho*-derivatives. The methyl (or methylol) group next to the hydroxyl (in the *meta*-position with respect to methylene) diminishes the *ortho*-hydroxyl effect, giving the upfield shift of the signal about 0,1 ppm (Table 1).

The methylene shifts of the co-condensates, obtained in the C4 substitution of R, are found following the same principles (Table 2). The methyl effect can only be seen in the case of *o*-methylol substituents. The methylene shifts of C4C6 disubstituted compounds are similar. The small upfield shift of methylene signal can be observed in the case of co-influences with the *ortho*-hydroxyl.

The same reason is responsible for the upfield shift of methylene signals in the course of polycondensation of phenolic and resorcinolic prepolymers. Naturally, *p,p'*-methylene shifts (Table 1) are not very dependent on the conversion step. Methylenes in the *meta*-position with respect to each other (under the influence of *ortho*-hydroxyls) give the signals in the upper field. This is the case for *o,p'*- and *o,o'*-methylenes (Table 1) and 4,4'-methylenes as well (Table 3). The appearance of 2,4'-methylene signal in the lower field is consistent with the influence of hydroxyl effects in R.

C4 substitution in 5MR (in comparison with R) leads to the downfield shift of the methylene signal as a result of the *ortho*-directing effect of the methyl group (Table 2). Both, the *ortho*-hydroxyl effects and the *ortho*-

methyl effects in comparison with phenolic co-reagent from resorcinolic one are stronger in co-condensates. This means that in the case of C4C6 disubstitution, the downfield shift of methylene signals occurs with all methylol compounds. In some cases (e.g. with *o*-MP), the signals of C4C6 and C2 substitution coincide (Table 2). The spectrum of 5MR homo-condensate occurs in accordance with the previous position. Only one methylene  $^1\text{H}$  shift can be assigned (Table 3). Most likely the methylene, saturated in all structural fragments similarly with four *ortho*-effects, shows the chemical shift in a very narrow region independent of other structural characteristics.

The opposite directing effect of methyl substituents in 2,5DMR is manifest in the lower reactivity with formaldehyde. The methylene shifts of 2,5DMR and 5MR co-condensates with methylolphenols are similar (Table 2) due to the predominant influence of *ortho*-effects. At the same time, the appearance of the methylene shift of 2,5DMR homo-condensate relative to the 5MR homo-condensate in the upper field can be predicted (Table 3). Regarding the methylene shifts of 2,5DMR homo- and co-condensates, one can once again state that the effects of substituents (here 2- $\text{CH}_3$ ) arising from resorcinolic reagent are far stronger in comparison with those from a phenolic co-reagent.

## Conclusions

Various phenol- and resorcinol-formaldehyde homo-condensates and co-condensates of resorcinols with methylolphenols were synthesized and characterized using  $^1\text{H}$  NMR assignments. Phenolic hydroxyl-pyridine mutual orientation gives the best resolution of  $^1\text{H}$  signals of differently located methylene protons in methylol, dimethylene ether and methylene compounds. *ortho*-Hydroxyl-effects are responsible for the downfield shift of methylene  $^1\text{H}$  signals. This shift is amplified in the case of 5MR compounds due to the additional *ortho*-methyl effect. On the contrary, the *ortho*-hydroxyl effect diminishes due to the methyl(methylene) group in the *meta*-position (*ortho* to hydroxyl). The substituent effects, arising from the occurrence of resorcinols rather than phenols, are stronger on methylene  $^1\text{H}$  chemical shifts.  $^1\text{H}$  NMR assignments of methylolphenol self-condensates, resorcinol-formaldehyde homo-condensates and methylolphenol-resorcinol co-condensates are in good accordance and can be successfully used alongside of  $^{13}\text{C}$  NMR for identification of resin structure.

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