EVALUATION OF CONDENSATION RATE
OF METHYLOLPHENOLS

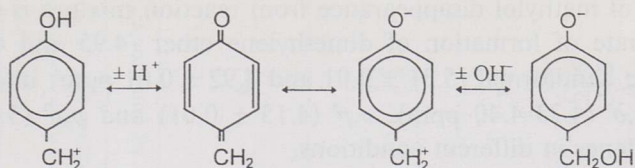P. CHRISTJANSON
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100 MHz NMR study of self-condensation of ortho- and para-methylolphenol and their co-condensation with phenol is presented. Reaction rate, co-reaction with phenol, dimethylene ether and phenolic hemiformal intermediates, methylene groups distribution and reaction mechanism in different catalytic conditions are the main topics discussed. The co-condensation rate is mainly dependent on methylolphenol reactivity and is similar with phenol and components of oil shale alkylresorcinols.

Introduction

Irrespective of conditions, the phenol-formaldehyde reaction proceeds through the formation of methylolphenols [1]. The methylol stage is stabilized in the presence of alkali catalyst and pure methylol derivatives or resol type oligomers can be obtained. Co-condensation of the latter with resorcinol is the reaction widely used in the manufacture of glue resins for the production of laminated timber constructions. A similar resin has been successfully produced substituting oil shale alkylresorcinols for the resorcinol [2]. The mixture of alkylresorcinols used in practice contains about 50 % of 5-methylresorcinol but a higher concentration is also possible.

The condensation mechanism of methylolphenols is not very clear, but the idea of quinone methides as reaction intermediates [3] has been increasingly popular [e.g. 4]. The intramolecular dehydration of methylol or its dimeric anhydro form gives the quinone methides as resonance hybrids between quinoid and benzenoid structures with higher probability of *para*- in comparison with *ortho*-species. A high reactivity to electrophiles and nucleophiles promotes the condensation in the presence of acid catalyst by benzylic carbonium ion formation or in the presence of alkali catalyst through the methylol phenoxide ion.

$$\text{OH} \quad \underset{\pm H^+}{\rightleftharpoons} \quad \text{O} \quad \longleftrightarrow \quad \text{O}^- \quad \underset{\pm OH^-}{\rightleftharpoons} \quad \text{O}^-$$

$$CH_2^+ \qquad CH_2 \qquad CH_2^+ \qquad CH_2OH$$

^{13}C NMR in combination with high performance liquid chromatography study of the reaction of phenol and methylolphenols with formaldehyde in the presence of basic catalysts is the most modern approach in phenol-formaldehyde chemistry [5, 6]. Pre-polymers synthesized in different conditions were characterized also by different NMR technics [7]. The structural characterization of resorcinol-formaldehyde resins was mainly performed using ^{13}C NMR [8, 9].

Ortho- and *para*-methylolphenol are the first-formed and most abundant compounds in the phenol-formaldehyde reaction. The study of their self-condensation and co-condensation with phenol in melt applying different catalytic conditions was the main purpose of this work. The comparison of condensation rate of methylolphenols with different substrates including resorcinol, 5-methylresorcinol [10], and phenol was the other purpose. 5-Methylresorcinol was specifically chosen since it is the most reactive resorcinol and the most abundant component in oil shale alkylresorcinols.

Experimental

Materials: Mehtylolphenols (MP) were synthesized and purified as described previously [10] and characterized by melting point and ^{1}H NMR spectrum. Reagent grade vacuum-redistilled phenol (P) was recrystallized twice from *n*-hexane (m.p. 40.9 °C).

Studied systems: Self-condensation of *ortho-* and *para*-methylolphenol (*o*-MP and *p*-MP) and their co-condensation with P (molar ratio 1/1) were carried out in melt at 120 °C without catalyst and in the presence of 0.05 mole of NaOH, 0.01 mole of zinc acetate, and 0.05 mole of benzoic acid.

Analysis: 100 MHz ^{1}H NMR spectra were recorded to follow the reaction rate and to ascertain the product composition. ^{1}H chemical shifts for samples in pyridine-d$_5$ were measured from internal hexamethyldisiloxane and calculated from tetramethylsilane. Quantitative changes in molar concentrations of components during the reaction were calculated from the averages of integral intensities of corresponding methylene proton signals. The initial amount of bound formaldehyde (FA) is determined by molar concentration of *ortho-* and *para*-methylol (5.16 and 4.81 ppm).

The rate of methylol disappearance from reaction mixture is dependent on relative rate of formation of dimethylene ether (4.95 and 4.47 ppm) and phenolic hemiformal (5.31 ± 0.01 and 4.92 ± 0.01 ppm) intermediates and, final *o,o'* (4.23-4.40 ppm), *o,p'* (4.15 ± 0.01) and *p,p'* (3.81 ± 0.01 ppm) methylenes in different conditions.

Results and Discussion

Course of Reaction

Self-condensation of used methylolphenols or their co-condensation with P finally leads to methylene bridged resins. Relative reactivity of free aromatic positions of MP and P determines the composition of products. Two examples of ¹H NMR spectra of reaction mixtures are presented (Fig. 1a,b). The resolution of different signals enables to determine the composition of reaction mixture (distribution of condensating agent) for any moment of reaction (e.g. Fig. 2a,b).

The maximum amount of *o,o'-* or *p,p'*-dimethylene ether intermediates can be used for characterization of reactions in different conditions (Table). The *o,p'*-ethers were not detected (typical signals at 4.86 and 4.58 ppm) though their formation is expected due to probable release of formaldehyde from ethers and its subsequent inclusion to reaction. The great tendency of formaldehyde to polymerization reveals itself in the formation of phenolic hemiformal intermediates.
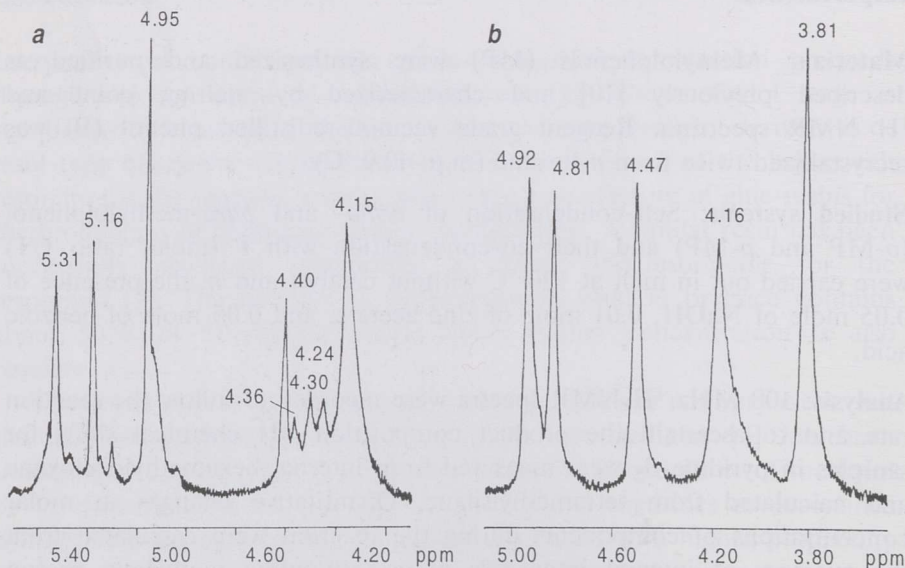

Fig. 1. ¹H NMR spectra of reaction mixture:
  a - *ortho*-methylolphenol/phenol 1/1 (120 °C, 4 h) in pyridine-d₅;
  b - *para*-methylolphenol/phenol 1/1 (120 °C, 6 h) in pyridine-d₅

Results of Condensation of Methylolphenols

Catalyst	Molar ratio catalyst/methylolphenol	Self-condensation (S) or co-condensation with phenol 1/1 (P)	Maximum amount, mole %		Methylenes in final product, mole %			Reaction rate		
			Ether	Hemiformal	o,o'	o,p'	p,p'	$\tau_{1/2}$, min	min^{-1}	$kg\ min^{-1}\ mole^{-1}$
ortho-Methylolphenol										
no	–	S	70	12	30	70	–	23	–	5.4
		P	44	14	23/21	56	–	35.2	–	6.2
NaOH	0.05	S	3	–	7	93	–	27.5	25.2	–
		P	2	–	10 (P)	90*	–	36	19.3	–
ZnAc	0.01	S	43	12	50	50	–	15.8	43.9	–
		P	25	15	25/38	37	–	16.3	42.5	–
C₆H₅COOH	0.05	S	48	4	25	75	–	17	–	7.3
		P	30	6	17/17	66	–	28.5	–	7.6
para-Methylolphenol										
no	–	S	36	26	–	82	18	21.4	–	5.8
		P	21	26	–	55	45	49	–	4.4
NaOH	0.05	S	11	–	19**	62	19	3.2	216.6	–
		P	2	–	–	54	46	4.8	144.4	–
ZnAc	0.01	S	32	16	–	83	17	5.5	–	22.6
		P	13	11	4	40	56	6.4	–	34.0
C₆H₅COOH	0.05	S	41	12	–	83	17	12.7	–	9.8
		P	20	11	–	53	47	13.2	–	16.5

* $o,o' + o,p'$ — methylenes.
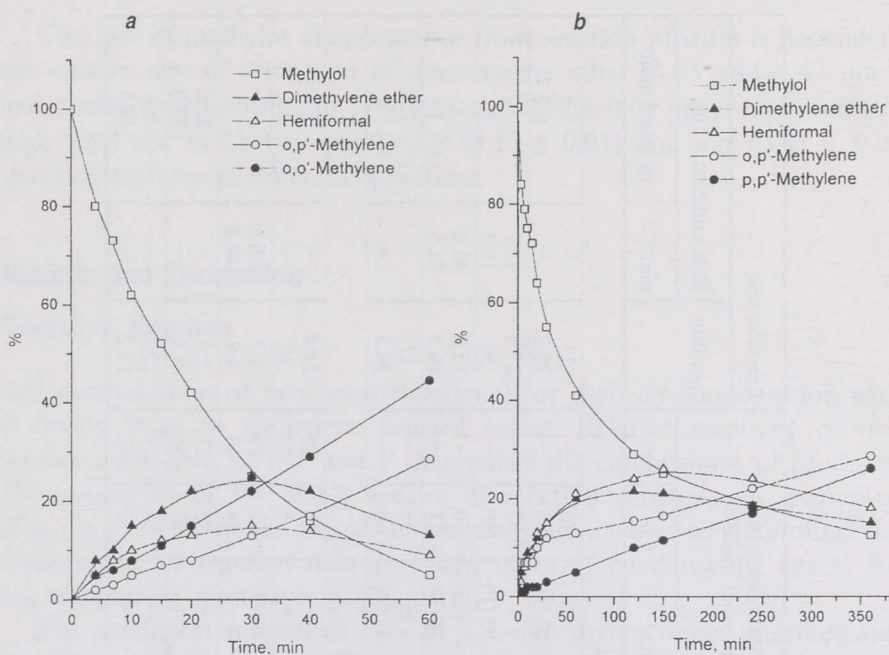** *ortho*-Methylol.

Fig. 2. Time dependence of composition of reaction mixture:
a - *ortho*-methylolphenol/phenol/ZnAc 1/1/0,01 (120 °C);
b - *para*-methylolphenol/phenol 1/1 (120 °C)

The appearance of well-resolved signals in the lower field (Fig. 1a - 5.31 ppm and Fig. 1b - 4.92 ppm) is typical for studied reactions. Only the presence of alkali catalyst does not favour the hemiformal formation (Table) in our case. Smaller amount of bound formaldehyde can be the reason as phenolic hemiformal structures are wellknown also in alkaline resol prepolymers and cured resins [11, 12].

Reaction Rate

Kinetic measurements show the linear dependence of the logarithm or reciprocal of o-MP and p-MP molar concentration on time. The half-life periods and the first or second order rate constants are presented in the Table. The apparent first order with respect to MP concentration (examples in Fig. 3a) in alkali-catalyzed reaction refers to the direct reaction between methylol group and free aromatic *para*- and *ortho*-positions.

Self-condensation gives preferably *o,p'*-methylenes (Table), while the reaction in the participation of *para*-methylol proceeds with substantially higher rate. Alkali promotes the parallel *p,p'*-dimethylene ether formation and the subsequent release of FA as well. To the moment of practically quantitative consumption of *p*-MP, the reaction mixture contains equal amounts of *p,p'*-methylenes and *ortho*-methylols (5.10 ppm).
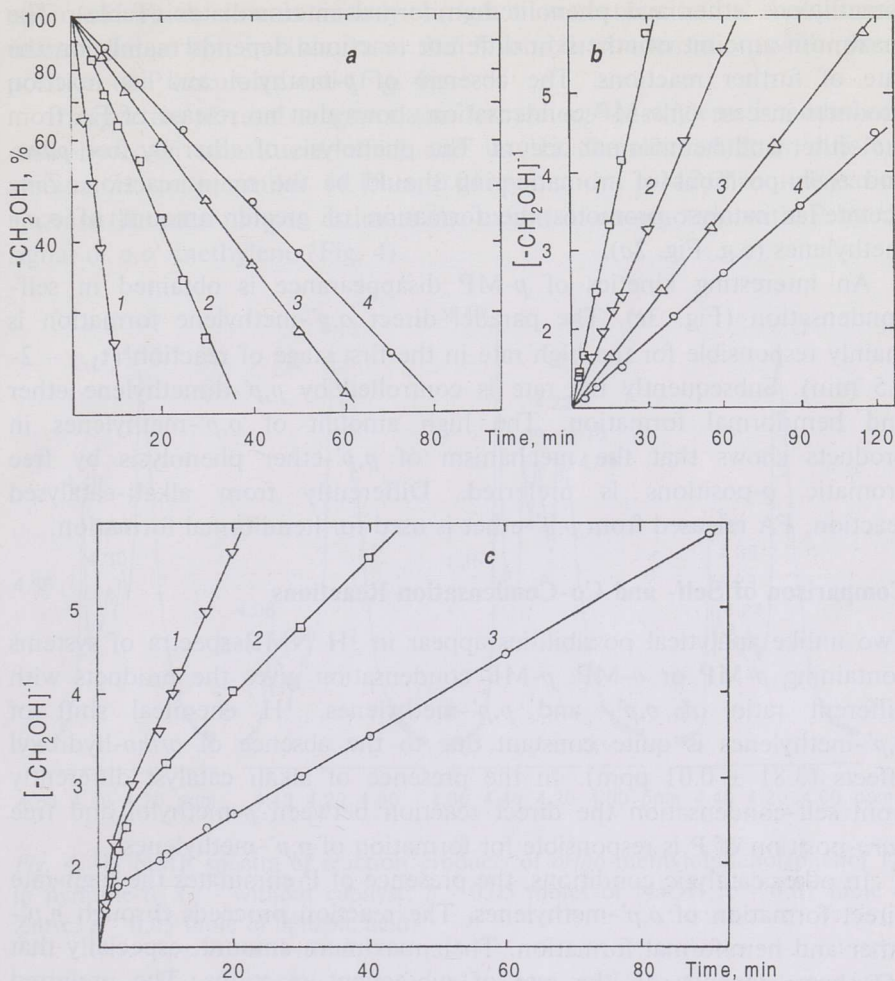
Fig. 3. Time dependence of molar content of methylol groups.
A: *1* - p-MP/P/NaOH (1/1/0.05); *2* - o-MP/P/Zn(OCOCH$_3$)$_2$ (1/1/0.01);
3 - o-MP/NaOH (1/0.05); *4* - o-MP/P/NaOH (1/1/0.05);
B: *1* - p-MP/P/Zn(OCOCH$_3$)$_2$ (1/1/0.01); *2* - p-MP/P/C$_6$H$_5$COOH (1/1/0.05);
3 - o-MP; *4* - o-MP/P (1/1);
C: *1* - p-MP/Zn(OCOCH$_3$)$_2$ (1/0.01); *2* - p-MP/C$_6$H$_5$COOH (1/0.05); *3* - p-MP

This fact explains the apparent first order of the disappearance of *para*-methylol in the presence of alkali. The first order in case of o-MP condensation in the presence of zinc acetate can be explained with special *ortho*-directing role of this catalyst. Intramolecular Zn-co-ordination bond system reveals as the rate-determining factor.

In most cases the disappearance of *p*- and *o*-methylols at self-condensation and co-condensation with P follows the second order kinetics (examples in Fig. 3*b*). It is in accordance with the formation of

dimethylene ether and phenolic hemiformal intermediates (Table). The maximum amount of ethers in different reactions depends mainly on the rate of further reactions. The absence of *p*-methylol and its reaction products in case of *o*-MP condensation shows that no release of FA from *o,o'*-ether and hemiformal occurs. The phenolysis of ether by free *para*- and *ortho*-positions of aromatic ring should be the main reaction. Zinc acetate as catalyst promotes the formation of greater amount of *o,o'*-methylenes (e.g. Fig. 2*a*).

An interesting kinetics of *p*-MP disappearance is obtained in self-condensation (Fig. 3*c*). The parallel direct *o,p'*-methylene formation is mainly responsible for the high rate in the first stage of reaction ($\tau_{1/2} \sim$ 2-2.5 min). Subsequently the rate is controlled by *p,p'*-dimethylene ether and hemiformal formation. The high amount of *o,p'*-methylenes in products shows that the mechanism of *p,p'*-ether phenolysis by free aromatic *o*-positions is preferred. Differently from alkali-catalysed reaction, FA released from *p,p'*-ether is used for hemiformal formation.

Comparison of Self- and Co-Condensation Reactions

Two unlike analytical possibilities appear in ^{1}H NMR spectra of systems containing *p*-MP or *o*-MP. *p*-MP condensation gives the products with different ratio of *o,p'*- and *p,p'*-methylenes. ^{1}H chemical shift of *p,p'*-methylenes is quite constant due to the absence of *ortho*-hydroxyl effects (3.81 ± 0.01 ppm). In the presence of alkali catalyst differently from self-condensation the direct reaction between *p*-methylol and free *para*-position of P is responsible for formation of *p,p'*-methylenes.

In other catalytic conditions, the presence of P eliminates the high-rate direct formation of *o,p'*-methylenes. The reaction proceeds through *p,p'*-ether and hemiformal formation. Their maximum amount, especially that of ethers, depends on the rate of subsequent reactions. The preferred formation of phenolic *para*-hemiformal structures in comparison with *ortho*-substituted derivatives is evident (Table). The participation of P is certainly proved by greater amount of *p,p'*-methylenes in products (Table).

The favoured mechanism involves the cleavage by free *para*-positions of P considering also the four time greater amount of free *ortho*-positions. The phenolysis course by *o*-positions is complicated due to different reactivity of these positions in P and *p*-MP or in formed oligomers. The downfield shift of *o,p'*-methylene signal in the region of 4.05-4.15 ppm is mainly caused from the conversion step. The similar *ortho*-hydroxyl effects give no possibility to assign the *o,p'*-methylenes to compounds either with P or *p*-MP. Paper chromatographic analysis ascertained that in alkali-catalyzed *p*-MP/P condensation the direct *o,p'*-methylene formation involves predominantly free *o*-positions of *p*-MP [13].

Zinc acetate and benzoic acid promote the phenolysis with *para*-position of P (Table). Low rate of uncatalytic condensation of *p*-MP is

observed which reveals mainly in great concentration of hemiformal intermediates but in this case the favoured condensation with *para*-position of P occurs as well (Fig. 4).

Irrespective of used reagents, the formed *o,p*'-methylene is under one *ortho*-hydroxyl substituent effect and its ^{1}H chemical shift in different systems is quite similar (4.15 ± 0.01 ppm). In *o*-MP/P condensation appears the possibility to estimate the extent of co-reaction with P by ^{1}H signal of *o,o*'-methylene (Fig. 4).
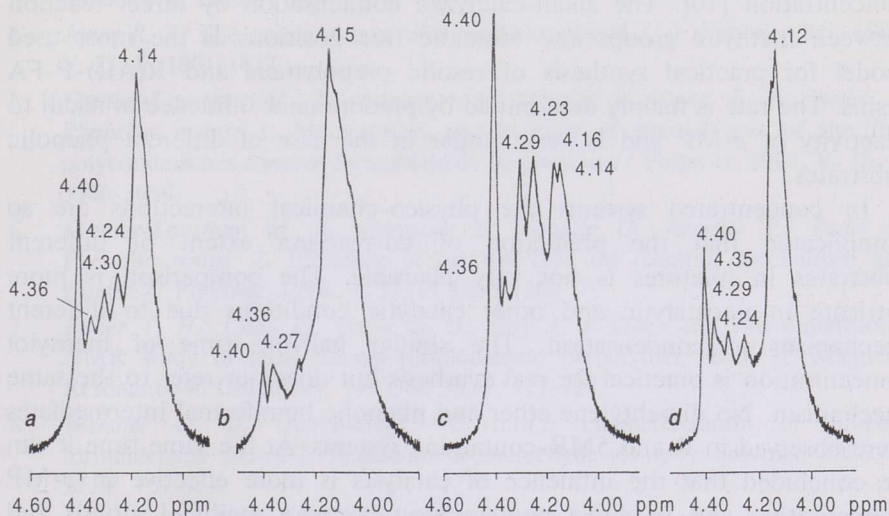

Fig. 4. ^{1}H NMR spectra of reaction products of *ortho*-methylolphenol/phenol 1/1 in pyridine-d$_5$ (*a* - without catalyst, *b* - 0,05 moles of NaOH, *c* - 0,01 mole of ZnAc, *d* - 0,05 mole of benzoic acid)

The resolution of signals depends on the other *ortho*-substituent. The reaction of *o*-methylol with *o*-positions of P gives the new signals at 4.40 ppm (2,2'-dihydroxy-diphenylmethane) and of P-con-taining condensates (4.36 ppm). The signals in the upper field (4.23-4.30 ppm) belong to the products of *o*-MP self-condensation. As various co-condensation models are possible, the methylene distribution (Table) refers only to the part of *o,o*'-methylenes (first number) appeared in the spectra due to the reaction in the presence of P.

In the presence of alkali catalyst, the formation of *o,o*'-methylenes is not favoured. The wide molecular mass distribution of condensates typical to this catalyst causes the overlapping of signals but the resolved signals at 4.40-4.36 ppm (Fig. 8) refer to a higher co-reaction with P as supposed earlier [13]. The presence of P brings no change in directing influence of catalysts but the relative amount of *o,o*'-methylenes increases propor-tionally in all cases. The methylene distribution and reaction rate (Table) show the similar reactivity of corresponding *o*- and *p*-positions in *o*-MP

and P. The role of phenolic hemiformals depends mainly on catalytic conditions and methylol position but not on the presence of added P.

Comparison of Co-Condensation of Methylolphenols with Different Phenols

Co-condensation of resorcinol (R) and 5-methylresorcinol (5MR) with above-mentioned methylolphenols, independently of catalytic conditions, was characterized by apparent first order kinetics with respect to methylol concentration [10]. The alkali-catalyzed condensation by direct reaction between methylol groups and aromatic free positions is the most used model for practical synthesis of resolic prepolymers and R(AR)-P-FA resins. The rate is mainly determined by predominant influence of alkali to reactivity of *p*-MP and is very similar in the case of different phenolic substrates.

In concentrated systems the physico-chemical interactions are so complicated that the prediction of co-reaction extent of different substrates in mixtures is not very plausible. The comparison is more intricate in uncatalytic and other catalytic conditions due to different mechanism of condensation. The similar half-life time of methylol concentration is practical for real synthesis but does not refer to the same mechanism. No dimehtylene ether and phenolic hemiformal intermediates were observed in R and 5MR-containing systems. At the same time it can be concluded that the influence of catalysts is more effective in *p*-MP condensation and in direct condensation between methylol groups and free aromatic positions.

Conclusions

1. 100 MHz ^{1}H NMR spectra for samples in pyridine-d$_5$ were used for study of *ortho*- and *para*-methylolphenol self-condensation and for co-condensation study with phenol.
2. Depending on reaction mechanism the first or second order rate constants with respect to methylol concentration were suitable for characterization of condensation in different conditions.
3. The co-reaction with phenol is ascertained in all cases studied by changes in the distribution of *o,o'/o,p'* and *o,p'/p,p'* methylenes.
4. The direct reaction between methylol group and free aromatic positions is responsible for the methylene formation in the presence of alkali catalyst whereas the influence of this catalyst to the reactivity of *para*-methylol is determinant.
5. The role of dimethylene ether and phenolic hemiformal intermediates was determined in different catalytic conditions of condensation.

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