

<https://doi.org/10.3176/oil.1999.4.10>

CONDENSATION OF METHYLOLPHENOLS

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Results of 100 MHz ^1H NMR study of melt condensation of ortho- and para-methylolphenol mixture in different catalytic conditions and in the presence of phenol are presented. Reaction rate and chemical composition of intermediates and polycondensates are the main points highlighted. Two different mechanisms for alkali-catalyzed condensation and for condensations in other catalytic conditions have been ascertained. The co-condensation rate is dependent mainly on methylolphenol reactivity and catalyst, and is similar in reactions with phenol and with the most abundant component of oil shale alkylresorcinols-5-methylresorcinol.

Introduction

Phenol-formaldehyde reaction proceeds through the first-step formation of methylolphenols [1]. The product obtained in the resin synthesis practice contains all possible five methylol derivatives and a certain amount of precondensate. Monofunctionalized derivatives are the major species in this mixture. However, the synthesis for the preparation of pure methylol compounds proceeds by more convenient methods.

Co-condensation rate of synthesised methylolphenols with resorcinol and with typical components of oil shale alkylresorcinols (5-methylresorcinol, 2,5-dimethylresorcinol) was evaluated by the first-order rate constants with respect to methylol content [2, 3]. Phenolic precondensates can be characterized by different NMR techniques ([4] with references). The identification of co-condensates with different resorcinols [5] and with additional phenol [6] by methylene ^1H chemical shifts was successful in most cases.

The greater reactivity of resorcinols gives no possibility to the parallel self-condensation of methylolphenols. Hence, the co-condensation mechanism, independently of catalysis conditions, includes direct substitution with *ortho*- and *para*-methylolphenol, mostly as 4 and 4,6-substitution in resorcinolic ring [2]. In case of self-condensation of

methylolphenols and homo-condensation with phenol, the direct substitution in free *ortho*- and *para*-positions of methylol compound or phenol predominates only in alkali-catalyzed reactions [6].

In other catalytic conditions the formation of dimethylene ether and hemiformal intermediates according to the second-order kinetics precedes the following methylene coupling of phenolic rings. The mechanism accepted generally proposes the formaldehyde departure from dimethylene ether [e.g. 7] with subsequent methylation. It is not possible to support this concept. The final isomeric distribution of methylenes enables to conclude that the cleavage of ethers by unsubstituted *ortho*- and *para*-aromatic positions (phenolysis) is the predominant coupling mechanism.

In this paper the results of condensation in systems containing obligatorily both monomethylolphenols are presented. In some experiments the phenol as an additional component was used. This enables to compare the results of co-condensation with different phenolic substrates including the main components of oil shale diatomic phenols.

Experimental

Used reagents: *Ortho*- and *para*-methylolphenol (*o*-MP; *p*-MP) were synthesized and purified as described previously [2] and characterized by their melting points (84 °C and 124 °C, correspondingly) and by ¹H NMR spectrum. Reagent-grade vacuum-redistilled phenol (P) was recrystallized twice from *n*-hexane (m.p. 40.9 °C).

Studied systems: Three series of reactions in the melt at 120 °C were carried out:

- The uncatalytic condensation of mixture *o*-MP/*p*-MP with molar ratio 2/1; 1/1; 1/2.
- The condensation of *o*-MP/*p*-MP equimolar mixture in the presence of 0.1 mole of NaOH, 0.02 mole of zinc acetate, and 0.1 mole of benzoic acid.
- The condensation of *o*-MP/*p*-MP equimolar mixture with phenol (1/1/2) in the presence of 0.1 mole of NaOH, 0.02 mole of zinc acetate, and 0.1 mole of benzoic acid.

Analysis: 100 MHz ¹H NMR spectra were recorded to follow the reaction rate and to determine the product composition. ¹H chemical shifts for 20-25 % solutions of samples in pyridine-*d*₅ were measured from internal hexamethyldisiloxane and expressed in ppm from tetramethylsilane (TMS). Quantitative changes in molar concentrations of components during the reaction were calculated from the averages of integral intensities of corresponding methylene proton signals. The molar concentrations of methylols can be determined separately in the mixture by ¹H methylene signals for *o*-MP (5.16 ppm) and for *p*-MP (4.81 ppm).

Condensation of Methylphenols

Catalyst	Molar ratio <i>o</i> -MP/ <i>p</i> -MP/P/catalyst	Maximum amount, mole-%		Methylenes in final resin, mole-%			Reaction rate, <i>o/p</i>		
		Ethers all <i>o,o'</i> / <i>o,p'</i> / <i>p,p'</i>	Hemiformal	<i>o,o'</i>	<i>o,p'</i>	<i>p,p'</i>	$\tau_{1/2}$, min	Rate constant $\times 10^3$	
								min ⁻¹	kg min ⁻¹ mole ⁻¹
No	2/1/-	66/31/26/9	9(<i>o</i>)	5	19	5	37/19.5	18.7/35.5	5.0/19.1
No	1/1/-	58/19/26/13	14(5+9)	6	29	16	38/17	18.2/40.8	6.5/14.6
No	1/2/-	58/10/26/22	18(<i>p</i>)	-	15	15	29/16	23.9/43.3	12.8/11.6
NaOH	1/1/-0.1	-	-	5	46	21	24.2/4.9	28.6/141.5	-
ZnAc	1/1/-0.02	38/12/17/9	7	11	20	25	11/8.7	63.0/79.6	22.6/28.5
C ₆ H ₅ COOH	1/1/-0.1	42/10/23/9	8	5	22	17	12.1/3.2	57.3/312.5	21.6/81.8
No	1/1/2/-	36/12/19/5	14	18/9	47	26	42/37.5	16.5/18.5	10.4/11.6
NaOH	1/1/2/0.1	-	-	12(P)	57	31	34/7.5	20.4/92.5	-
ZnAc	1/1/2/0.02	20/6/10/4	12	22/15	29	34	10.5/6	66.0/115.5	41.9/72.8
C ₆ H ₅ COOH	1/1/2/0.1	27/9/13/5	8	19/6	49	26	33.7/10.5	20.6/66.0	13.3/42.9

Results and Discussion

Some results characterizing the reaction course in different conditions are presented in Table. The alkaline catalyst promotes the direct substitution in free *ortho*- and *para*-positions of phenolic ring. In other conditions the dimethylene ether formation is the factor determining the rate and constitution. The peculiarity of *o*-MP/*p*-MP condensation in comparison with the condensation of individual methylol compound lies in the formation of unsymmetrically substituted dimethylene ether. Two ^1H methylene signals of equal intensity at 4.86 and 4.58 ppm belong to *o,p'*-ether. The same signals for *o,o'*- and *p,p'*-dimethylene ethers with different ^1H chemical shifts (4.95 and 4.47 ppm, respectively) can be assigned. Ether formation is, to some extent, accompanied with hemiformal formation (5.31 and 4.92 ppm in *ortho*- and *para*-position, respectively). The purpose was not in obtaining the maximum methylene content. Hence, the methylene distribution shows that in the products a random and different conversion step has taken place.

Uncatalyzed *o*-MP/*p*-MP Condensation

The condensation proceeds through the formation of dimethylene ethers (Table). The favored formation of ether from *o*-MP is not so accentuated as in case of individual condensation of *o*-MP in comparison with *p*-MP [6]. The maximum amount of *o,p'*-dimethylene ether is quite constant. The ratio of *o*-MP/*p*-MP influences mainly the maximum content of *o,o'*- and *p,p'*-dimethylene ether. The hemiformal is formed preferably from *p*-MP. In case of unequimolar mixture the methylol in shortage is expended entirely for dimethylene ether formation, and the mixture contains the hemiformal formed only from methylol in excess. The condensation course (example in Fig. 1) is directed to the accumulation of ethers, as in uncatalytic conditions the further reactions with participation of ethers occur slowly. No formaldehyde release from ethers causing the change in the initial *ortho/para* ratio is observed.

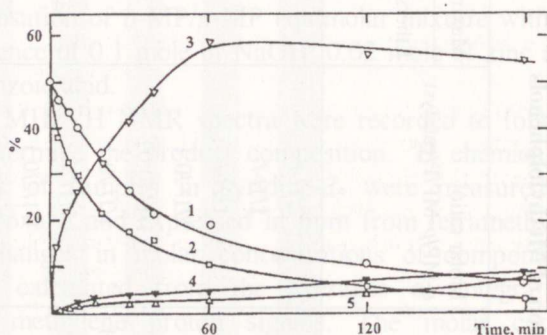
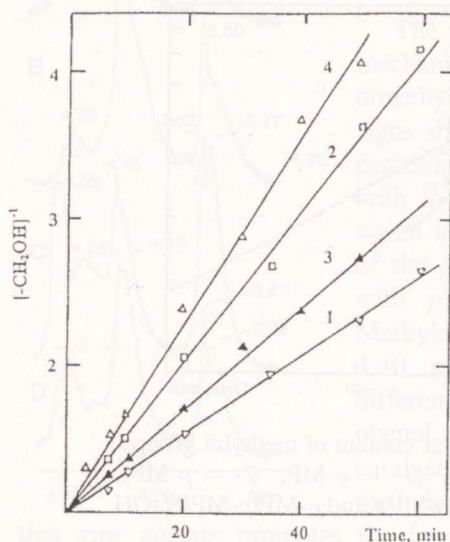


Fig. 1. Time dependence of molar composition of reaction mixture *o*-MP/*p*-MP 1/1: 1 - *o*-MP; 2 - *p*-MP; 3 - dimethylene ether; 4 - hemiformal; 5 - methylene

Differently from *p*-MP condensation [6], in *o*-MP/*p*-MP condensation there appears the possibility for the most preferred variant of phenolysis of *p,p'*-dimethylene ether by the free *p*-position of *o*-MP. It causes the change in the isomeric composition of methylenes. The condensation rate of *p*-MP



in comparison with *o*-MP (1/1) by second order kinetics is more than two times higher (examples in Fig. 2). The half-lives of methylol are not very sensitive to the change in the initial molar ratio of methylols. So, the complicated kinetics of the condensation, consisting of several parallel and consequent reactions, should rather be approximated to the first order.

Fig. 2. Time dependence of molar content of methylol groups: *o*-MP/*p*-MP 2/1 (1 - *o*-MP; 2 - *p*-MP), and *o*-MP/*p*-MP 1/2 (3 - *o*-MP; 4 - *p*-MP)

o-MP/*p*-MP Condensation in the Presence of Catalysts

The presence of an alkali catalyst causes a great change in condensation of *p*-MP in the mixture with *o*-MP as compared to that of individual *p*-MP. The reaction of *p*-MP according to the first-order kinetics (Fig. 3) proceeds through *p*-position of *o*-MP and *o*-positions of both methylol compounds leaving no chance to *p,p'*-dimethylene ether formation with subsequent formaldehyde release [6]. *o*-MP reacts preferably with the same *p*-position according to the first-order kinetics. The formation of *o,o'*-methylene becomes more essential only after the occupation of the free *p*-position. Alkali catalyst promotes the condensation of *p*-methylol in comparison with *o*-methylol, and that is expressed in an increased ratio of corresponding rate constants as compared to uncatalytic condensation (Table).

In other catalytic conditions reactions proceed through dimethylene ether intermediate. The reduced maximum amount of dimethylene ethers is caused by the increased rate of subsequent phenolysis reactions. Acid and especially zinc acetate promote the phenolysis of *p,p'*-ether by *para*-position of *o*-MP. The first order in case of *o*-MP condensation in the presence of zinc acetate (Fig. 3) can be explained with a special *ortho*-directing role of this catalyst. Intramolecular Zn-co-ordination bond system reveals as the rate-determining factor. It is not essential whether there occur the self-condensation or homocondensation with P [6], or co-reaction with *p*-MP. Zinc acetate promotes also the phenolysis of *o,o'*-ether by *ortho*-position which reveals in a greater amount of *o,o'*-methylenes and in preferred acceleration of the

reaction of *o*-MP in comparison with *p*-MP. Despite different condensation mechanisms in the presence of NaOH and benzoic acid, both catalysts promote the condensation of *p*-MP as compared to *o*-MP.

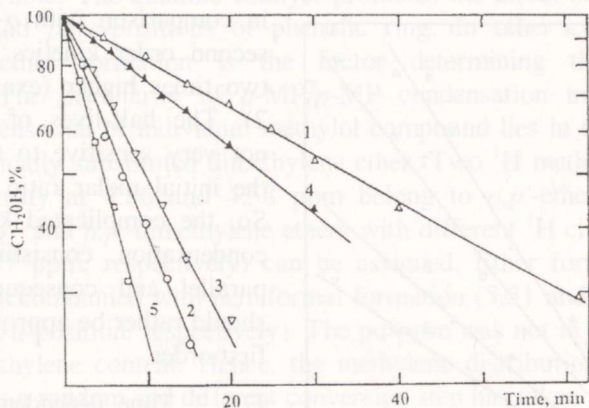


Fig. 3. Time dependence of molar content of methylol groups: *o*-MP/*p*-MP/P/NaOH 1/1/2/0.1 (1 - *o*-MP; 2 - *p*-MP); *o*-MP/*p*-MP/ZnAc 1/1/0.02 (3 - *o*-MP), and *o*-MP/*p*-MP/NaOH 1/1/0.1 (4 - *o*-MP; 5 - *p*-MP)

o-MP/*p*-MP Condensation with Phenol

In the resin practice, resolic phenol-formaldehyde prepolymers and phenol-resorcinol(alkylresorcinol)-formaldehyde co-condensates are synthesized predominantly in the presence of alkaline catalysts. The condensation is controlled by the first order kinetics with respect to methylol concentration in all cases (Examples in Fig 3). It gives a good possibility for comparison of condensation of *o*-MP/*p*-MP mixture with different substrates. The condensation rate with phenol (Table) is not much smaller as compared with resorcinol ($28.3/133.3 \cdot 10^{-3} \text{ min}^{-1}$) and with 5-methyl-resorcinol ($28.0/106.7 \cdot 10^{-3} \text{ min}^{-1}$) [2]. By that the reaction with resorcinols occurs as a pure co-condensation independently of conditions. The reaction with phenol in the presence of an alkaline catalyst becomes simpler because of direct substitution.

The predominant occurrence of methylene ^1H signals at 3.80 and 4.35 ppm (Fig. 4) shows that alkali promotes the reaction with *ortho*- and *para*-positions of phenol in comparison with these positions of methylolphenols. Alkaline catalyst has little influence on the reaction rate of *o*-MP (Table). Otherwise, the effect of this catalyst on the reactivity of *p*-MP is very great promoting first of all the formation of *p,p'*-methylenes. As the *o,o'*-methylene is the most unfavoured methylene isomer in the presence of an alkaline catalyst, slow condensation of *o*-MP leads preferably to the *o,p'*-methylene.

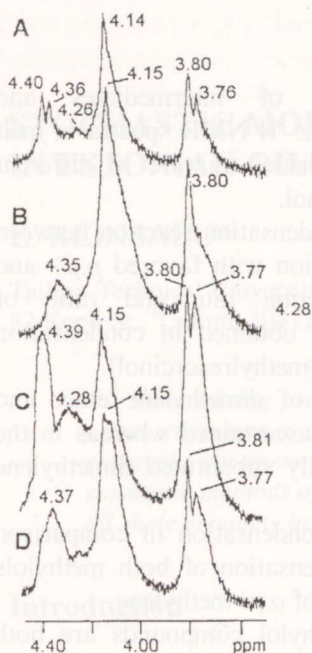


Fig. 4. Methylene region of ^1H NMR spectra of final co-condensates in pyridine- d_5 : *o*-MP/*p*-MP/P 1/1/2 (A - without catalyst; B - NaOH 0.1 ;C - ZnAc 0.02; D - benzoic acid 0.1)

The presence of phenol does not change the mechanism of condensation through dimethylene ethers in other conditions. Two signs showing the participation of free aromatic positions of phenol and methylol compound both in the condensation can be stressed. The signal in the upper field (3.77 ppm) is the result of the *p,p'*-methylene formation in the reaction with *para*-position of *o*-MP (Fig 4). *o,o'*-Methylene compounds give ^1H signals at 4.36-4.40 ppm and 4.26-4.28 ppm because of different substituent effects in compounds with phenol and methylolphenols. Zinc acetate is a catalyst clearly increasing the amount of *o,o'*-methylenes in products. It should be mentioned that zinc acetate promotes the formation of *p,p'*-methylenes as well, and therefore *o,p'*-methylenes are most unfavoured in the case of this catalyst.

The low rate of *p*-MP reaction in uncatalyzed condensation (Table) enforces a part of *p*-MP (about 30 %) to react with higher rate by a direct reaction (Fig. 5), at which the formation of *o,p'*-methylenes prevails. At the same time the phenolysis occurs predominantly as the cleavage of *p,p'*-di-methylene ether by the free aromatic *para*-position. Zinc acetate promotes the high-rate condensation of both methylols, whereas the *o*-methylol follows the first order kinetics. The acid catalyst enhances preferably the condensation rate of *p*-MP (Table). In case of *o*-MP the presence of phenol retards the reaction rate similarly to that observed in condensation of individual *o*-MP in phenol [6].

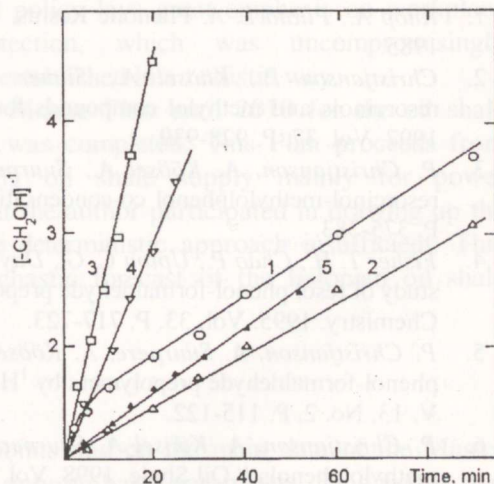


Fig. 5. Time dependence of molar content of methylol groups: *o*-MP/*p*-MP/P 1/1/2 (1 - *p*-MP; 2 - *o*-MP); *o*-MP/*p*-MP/P/ZnAc 1/1/2/0.02 (3 - *p*-MP); *o*-MP/*p*-MP/P/benzoic acid 1/1/2/0.1 (4 - *p*-MP; 5 - *o*-MP)

Conclusions

1. Reaction rate and chemical structure of intermediates and polycondensates were determined by 100 MHz ^1H NMR spectra in melt condensation of *ortho*- and *para*-methylphenol mixture in different catalytic conditions and in the presence of phenol.
2. The alkaline catalyst promotes the direct condensation reaction between methylol and aromatic *ortho*- and *para*-position with favored *p,p'*- and *o,p'*-methylene formation. A similar reaction rate and ratio of *p*-MP/*o*-MP disappearance rate (3.8-4.7) is obtained in condensation with different substrates (phenol, resorcinol, 5-methylresorcinol).
3. In other catalytic conditions the formation of dimethylene ether and hemiformal with subsequent phenolysis was ascertained whereas in the studied case the formation of unsymmetrically substituted dimethylene ether was peculiar to the process.
4. Alkaline and acid catalysts further *p*-MP condensation in comparison with *o*-MP. Zinc acetate promotes the condensation of both methylols whereas the most unfavoured is the formation of *o,p'*-methylene.
5. Free aromatic positions of phenol and methylol compounds are both active in condensation, whereas the alkali catalyst promotes the participation of phenol in condensation.

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