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Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics

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We have investigated the influence of the type of basic catalyst on the mechanisms and kinetics of phenol–formaldehyde reactions in perfectly controlled conditions of synthesis (temperature, stoichiometry and pH). The results obtained using liquid-state physicochemical analysis techniques, such as high performance liquid chromatography, ^{13}C nuclear magnetic resonance spectroscopy and chemical assays, indicate that the nature of the basic catalyst affects the mechanisms and kinetics of condensation and thus the composition of the reaction medium. The results show that the valence and ionic radius of hydrated cations affect the changes of species in the reaction medium. The catalysts were classified into two families as a function of their behaviour: KOH, NaOH and LiOH, and $Ba(OH)_2$ and $Mg(OH)_2$. We have found the formation of certain monomers and dimers, particularly *ortho*-substituted species. Copyright © 1996 Elsevier Science Ltd.

(Keywords: phenol–formaldehyde; catalyst; mechanism)

INTRODUCTION

Reaction of phenol–formaldehyde systems in a basic medium yields thermosetting materials with good fire resistance properties[1–5]. It is necessary to include a catalyst to initiate and orient the addition reactions of formaldehyde on phenolic compounds[6]. The catalyst included in the reaction medium is composed of a hydroxide anion and a metal cation. The OH-anion contributes to the formation of phenates by abstracting the alcoholic proton (*Figure 1*). The concentration of this anion in the reaction medium and its nature determine the imposed basic pH value (pH = 8). Published data[7–9] show that the mono- or divalent cation is involved in the

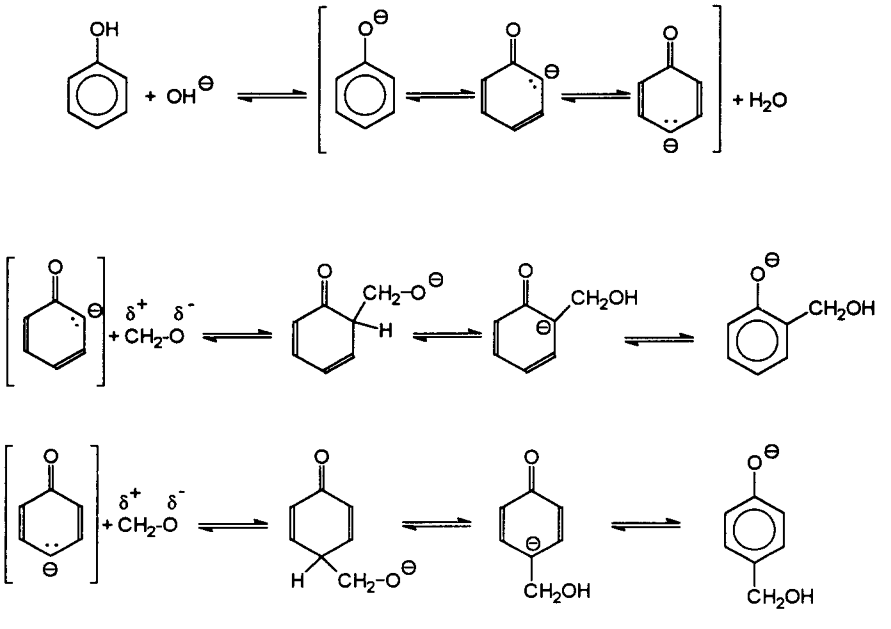

Figure 1 Reaction mechanism for the addition of formaldehyde on phenol in basic medium

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Table 1 Rate constants, and ionic radius and valence of hydrated cations used

Cation	k (l mol^{-1} h^{-1})	Size (Å)^a	Valency
K^+	0.106	3	1
Na^+	0.119	4	1
Li^+	0.153	6	1
Ba^{2+}	0.164	5	2
Ca^{2+}	0.226	6	2
Mg^{2+}	0.413	8	2

^{a} From ref. 10

reaction mechanism of addition of formaldehyde on phenol by participating in establishing the intermediate chelated form.

In order to prove or disprove these results, we have undertaken a study of the effect of size and valence of the cation on the mechanisms and kinetics of formaldehyde addition on phenol. This was done by comparing changes in formaldehyde, phenol and the different species formed (substituted phenols and compounds of order higher than one) using alkaline hydroxide catalysts whose cations are listed in *Table 1*.

EXPERIMENTAL

Materials

Phenol **1** (>99%), formaldehyde (37% w/w solution) and alkaline hydroxides [NaOH (97%), LiOH (98%), KOH (99.9%), $Ba(OH)_2$ (98%), $Ca(OH)_2$ (98%) and $Mg(OH)_2$ (95%)] were commercial products (Aldrich, Fluka and Prolabo), used without further purification.

Resols were synthesized by mixing phenol (P) and formaldehyde (F) at 60°C in a ratio of $R = [F]/[P] = 1.5$. The pH was then adjusted to 8 with different titred solutions of alkaline hydroxide.

Techniques

High performance liquid chromatography (h.p.l.c.). Analyses were conducted as follows:

- with a Varian 5000 chromatograph equipped with an ultraviolet (u.v.) detector set at 273 nm. The mobile phase (acetonitrile–water) was used with an elution gradient of 10 to 80% acetonitrile in 70 min; and
- with a Varian 9010 chromatograph equipped with a u.v. photodiode matrix detector (detection at 273 nm). The mobile phase (acetonitrile–water) was used with an elution gradient of 10 min at 10% acetonitrile, then 10 to 70% acetonitrile in 50 min.

Columns were 25 cm long, packed with Spherisorb ODS-2.

Nuclear magnetic resonance (n.m.r.) spectroscopy. High resolution liquid-state ^{13}C n.m.r. spectra were recorded with a Bruker AM 400 spectrometer. Conditions for recording spectra were: pulse angle of 90° (4.2 μs ^{13}C) and digital resolution of 0.375 Hz/pt, corresponding to a spectral range of 20 000 Hz for a memory space of 128 K.

Samples were dissolved in monodeuterated ethanol [$\delta^{13}C$ (CH_3CH_2OD) = 17.9 and 57.3 ppm relative to tetramethylsilane (TMS)] or in deuterated dimethylsulfoxide (δ ^{13}C ($DMSO\text{-}d_6$) = 39.5 ppm/TMS).

ANALYSIS OF RESULTS

Kinetics of the disappearance of formaldehyde and phenol

Changes in formaldehyde concentration were followed as a function of time by chemical assay[11] with each of the catalysts mentioned above. The kinetics of formaldehyde disappearance with time is depicted in *Figure 2*.

The curves led to residual formaldehyde values that differed as a function of the catalyst and it is seen that the difference in formaldehyde reactivity depends on the catalyst used. *Table 1* lists the rate constants obtained by simulating the curves in *Figure 1* using a second-order equation of the type $dx/dt = k(1 - x)^2$ during the first 8 h of reaction, as well as the ionic radii of hydrated cations and their valence. Thus, based on the results in *Table 1*, it is seen that for the same valence, the rate constant for formaldehyde disappearance is related to

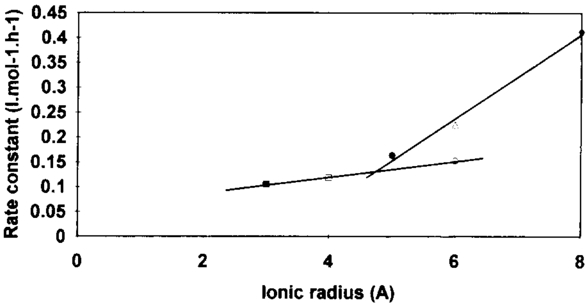

Figure 3 Influence of the size of hydrated cations on the rate of disappearance of formaldehyde: ■, KOH; □, NaOH; ○, LiOH; ●, $Ba(OH)_2$; ◇, $Ca(OH)_2$; ◆, $Mg(OH)_2$

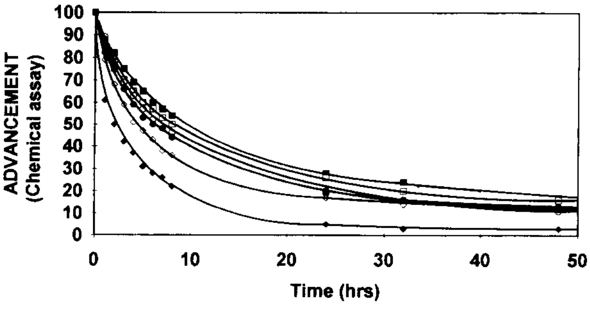

Figure 2 Disappearance of formaldehyde by chemical assay. Effect of the catalyst: ■, KOH; □, NaOH; ○, LiOH; ●, $Ba(OH)_2$; ◇, $Ca(OH)_2$; ◆, $Mg(OH)_2$

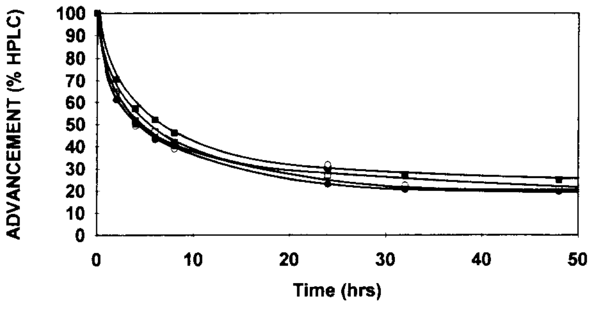

Figure 4 Disappearance of phenol by h.p.l.c. in the presence of: ■, KOH; □, NaOH; ○, LiOH; ●, $Ba(OH)_2$

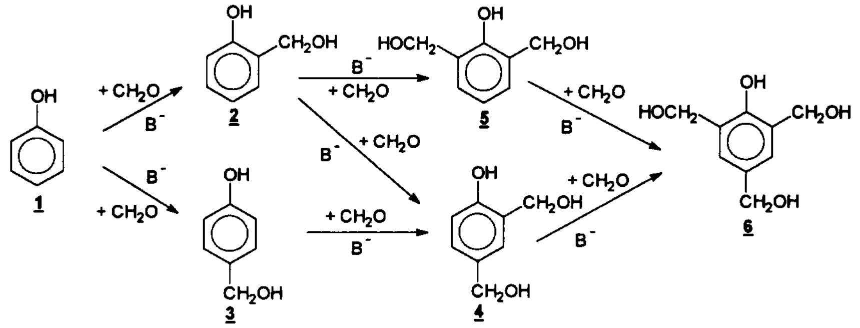

Figure 5 Addition of formaldehyde on phenol. Formation of phenolic monomers

the ionic radius of the hydrated cation. Kinetics are proportional to the size of the hydrated cation with the sequence:

$$k_{\mathrm{Li}^+} > k_{\mathrm{Na}^-} > k_{\mathrm{K}^+} \quad \text{and} \quad k_{\mathrm{Mg}^{2+}} > k_{\mathrm{Ca}^{2+}} > k_{\mathrm{Ba}^{2+}}$$

In addition, even though the ionic radii of Ba^{2+} and Ca^{2+} are smaller than or equal to that of Li^+, divalent cations lead to higher rates of formaldehyde disappearance than the monovalent cation. Similarly, the Mg^{2+} cation, which has a larger ionic radius than Li^+, results in a higher reaction rate.

Figure 3 shows the change in rate constant of formaldehyde disappearance as a function of the ionic radius of the hydrated cation. It is seen that there is a linear relationship for both monovalent and divalent cations. The slope of the line increases with cation valence, thereby confirming the influence of this parameter on reaction kinetics. These initial results clearly confirm that the nature of the cation modifies the kinetics of formaldehyde disappearance and that the two parameters studied (ionic radius and valence of the hydrated cation) play an important role.

Figure 4 shows the disappearance of phenol (**1**) with time when KOH, NaOH, LiOH and $\mathrm{Ba(OH)_2}$ were used as catalysts. As in the case of formaldehyde, it can be stated that the reaction mechanism for phenol disappearance principally involves formaldehyde. Thus the rate of disappearance of phenol increases with increasing ionic radius of the cation.

Kinetic and mechanistic monitoring of the appearance and disappearance of the first condensates

The addition of formaldehyde on phenol leads to the formation of substituted phenolic monomers **2** to **6** (*Figure 5*). These model compounds were synthesized and analysed by h.p.l.c. and ^{13}C n.m.r. We had determined their chromatographic (retention volumes) and spectroscopic (^{13}C n.m.r. chemical shifts) characteristics in previous work[6].

Monitoring by h.p.l.c. Kinetics determined with phenol–formaldehyde systems are shown in *Figure 6* with LiOH as catalyst. The reaction path is similar in each case studied: the decrease in phenol (**1**) was followed by the formation of phenolic species **2** and **3**, which then diminished beyond 10 h of reaction. After that time, disubstituted phenolic species **4** and **5** formed, and finally compound **6**. Compounds **5** and **6** then disappeared in favour of dimeric species, while compound **4** accumulated in the medium.

To study the influence of the catalyst on changes of the created or transient species, we compared the appearance and disappearance of each phenolic monomer with the four catalysts used (KOH, NaOH, LiOH and $\mathrm{Ba(OH)_2}$). The changes of each compound with time and with each catalyst are shown in *Figures 7a–c*.

In the case of monosubstituted phenolic compounds **2** and **3** (*Figures 7a* and *b*), their proportion in the reaction medium was higher with NaOH, slightly lower with KOH and even lower with $\mathrm{Ba(OH)_2}$. In the presence of LiOH, the considerable formation of these two compounds was followed by a substantial decrease beyond 10 h of reaction, leading to the lowest values of residual after 48 h of reaction.

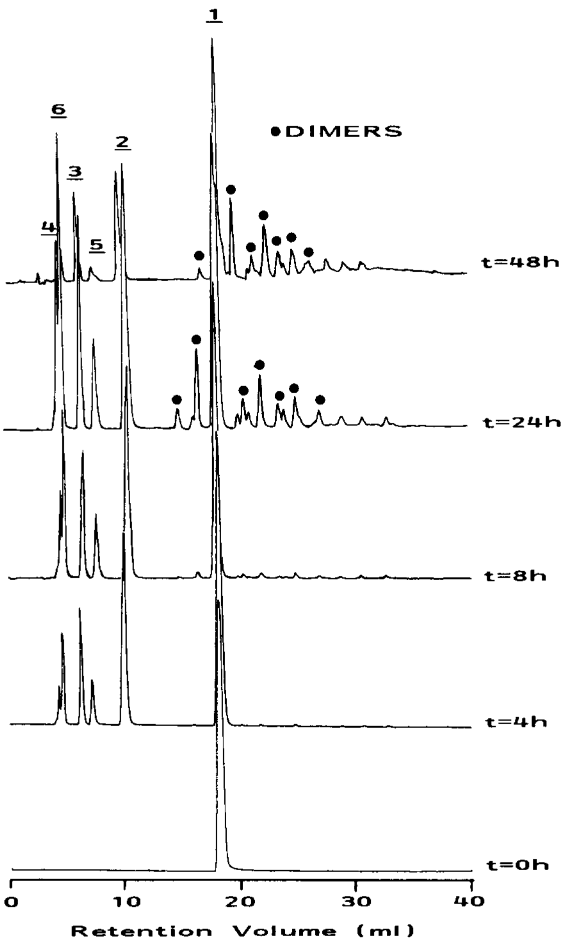

Figure 6 Kinetics followed by h.p.l.c.: $T = 60°\mathrm{C}$; $R = \mathrm{F/P} = 1.5$; LiOH (see *Figure 5* for the numeration of compounds)

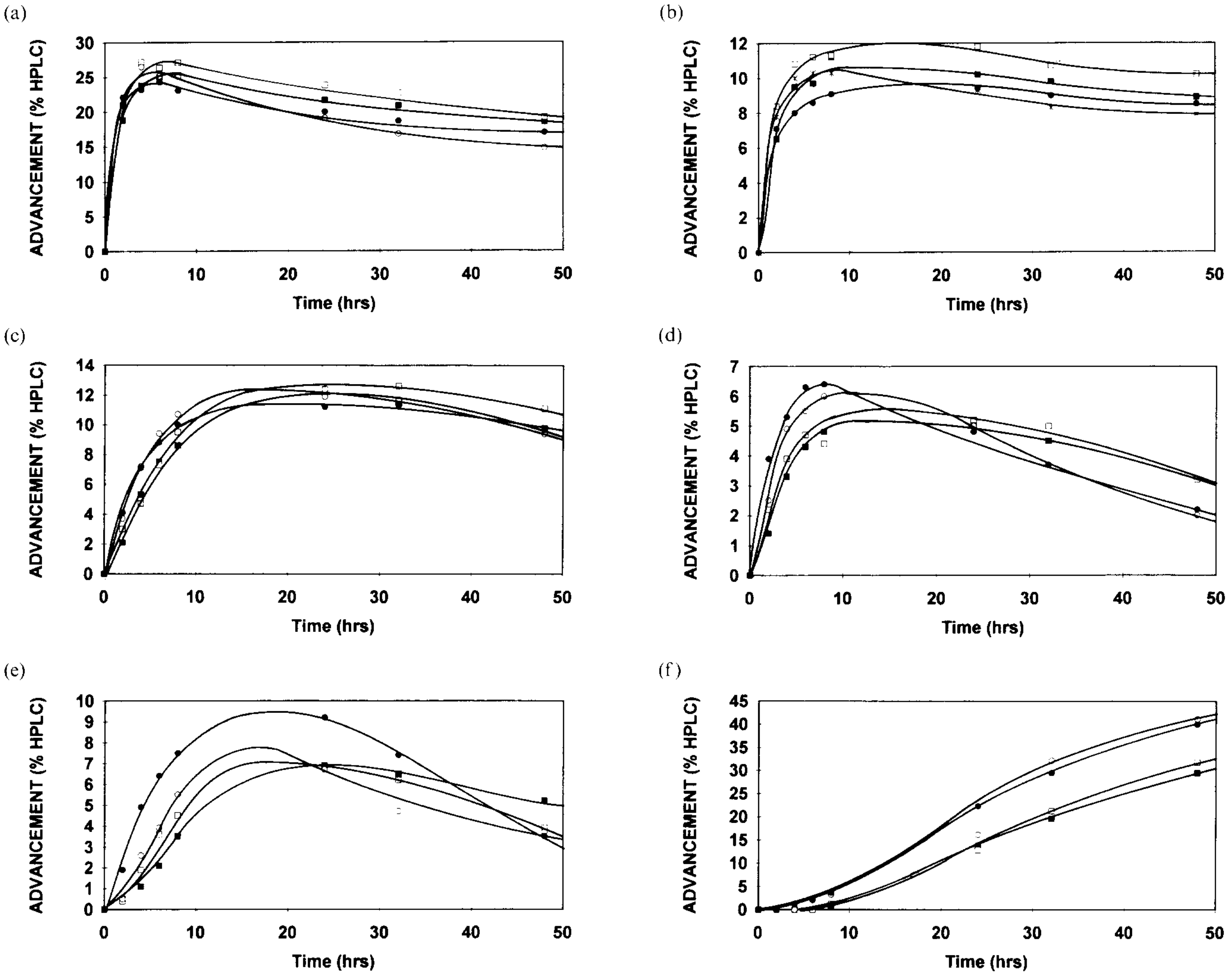

Figure 7 Quantification of (a) 2-HMP (**2**), (b) 4-HMP (**3**), (c) 2,4-DHMP (**4**), (d) 2,6-DHMP (**5**), (e) 2,4,6-THMP (**6**) and (f) oligomers in the reaction medium with time as a function of the catalyst. ■, KOH; □, NaOH; ○, LiOH; ●, $Ba(OH)_2$

Concerning compound **4** (*Figure 7c*), the difference as a function catalyst was not very pronounced, but we still observed the same trend in the case of LiOH: rapid formation during the first 20 h of reaction, followed by a decrease until 48 h, leading to a lower residual value than with the other catalysts.

In the case of compound **5** (*Figure 7d*), the catalysts can be divided into two groups: NaOH and KOH, and LiOH and $Ba(OH)_2$. In the presence of a catalyst from the first group, compound **5** disappeared slowly after 24 h of formation, while in the presence of LiOH or $Ba(OH)_2$, 2,6-DHMP (**5**) formed in high proportions with a high rate, then decreased very rapidly in the reaction medium, reaching a residual value after 48 h that was lower than those observed with NaOH and KOH.

Changes in compound **6** (*Figure 7e*) using $Ba(OH)_2$ were also characterized by formation in high proportions during the first 20 h, followed by a rapid decrease beyond that time. Using the other three catalysts, the formation of 2,4,6-THMP (**6**) was similar, but disappearance was favoured by small cations (Li^+).

The disappearance of the monomers studied is due to substitution on the aromatic ring (except in the case of compound **6**) and to condensation reactions that lead to the formation of oligomers. The changes in these species as a function of the catalyst used are shown in *Figure 7f*. As expected, KOH and NaOH resulted in a small proportion of oligomers, whereas LiOH and $Ba(OH)_2$ resulted in higher proportions of condensed species in the medium.

There are relatively few differences in terms of dimers in the chromatograms of *Figure 6*. Highly substituted compounds are present in higher proportions than other dimers.

Analysis by ^{13}C n.m.r. The 160–150 ppm spectral zone is shown in *Figure 8* after 48 h of reaction with KOH, NaOH, LiOH, $Ba(OH)_2$ and $Mg(OH)_2$. There are few significant qualitative differences in the spectra as a function of the catalyst used. As shown by h.p.l.c., the proportion of 2,6-DHMP (**5**) was lower with LiOH and $Ba(OH)_2$. The use of catalysts other than NaOH did not lead to any perceptible preferential orientation of chemical structures, which were the same and are present in similar proportions regardless of the catalyst used.

The peaks obtained in the 45–30 ppm region, integrated and expressed on the basis of the total integration of the 160–150 ppm zone (used as reference since all the aromatic rings possess a carbon that resonates in this zone), are shown in *Figures 9A* and *B*. Again the catalysts

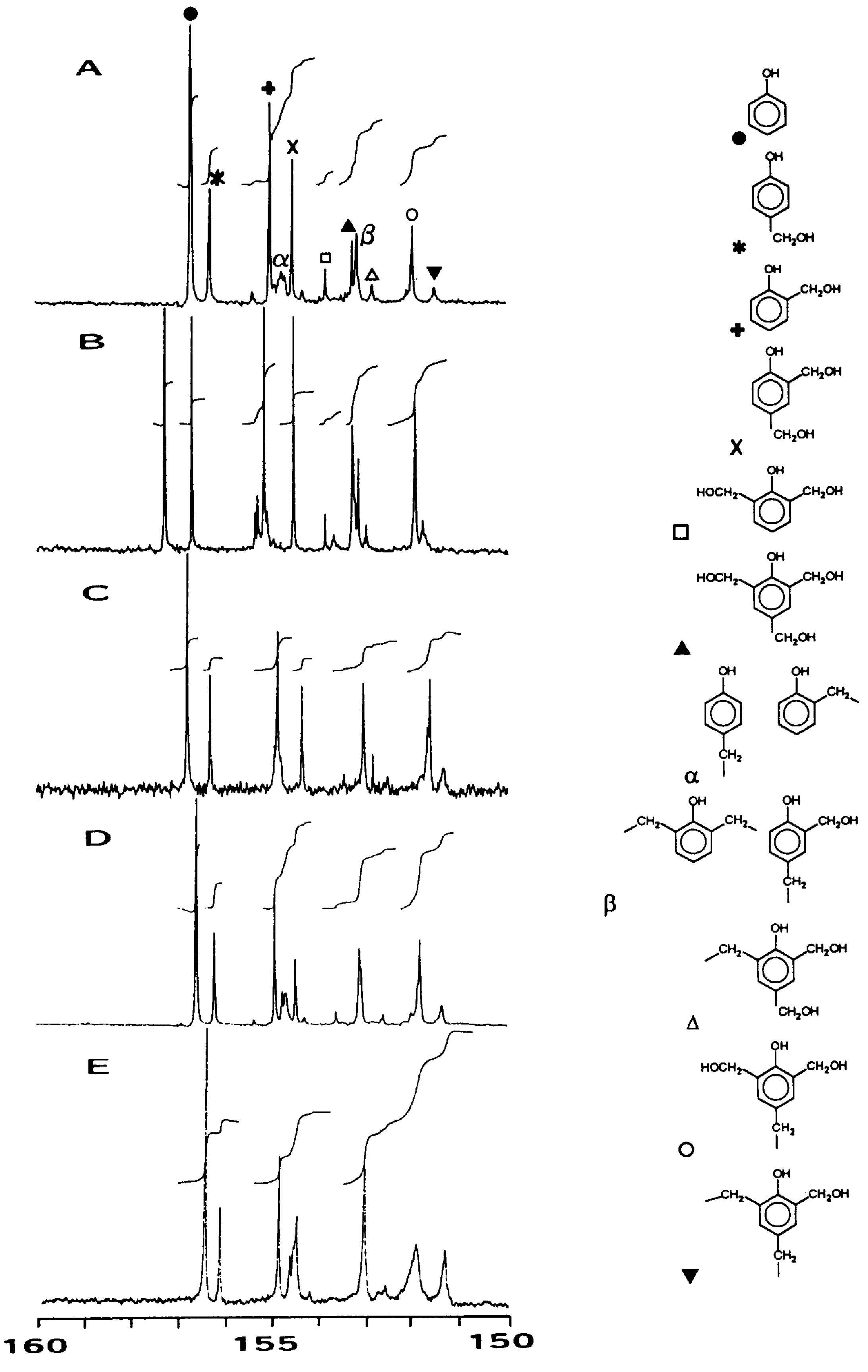

Figure 8 Kinetics followed by ^{13}C n.m.r. 160–150 ppm region; $t = 48$ h; $R = F/P = 1.5$; $T = 60°C$. A, KOH; B, NaOH; C, LiOH; D, Ba(OH)$_2$; E, Mg(OH)$_2$

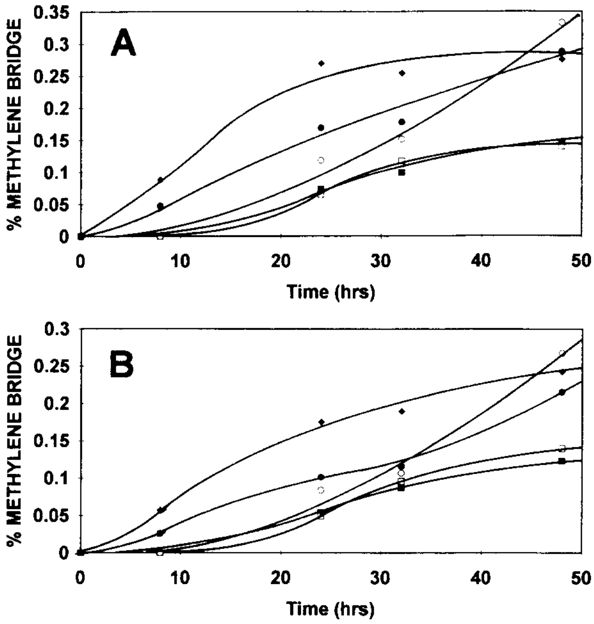

Figure 9 Quantification by ^{13}C n.m.r.: 45–30 ppm region; $t = 48$ h; $R = F/P = 1.5$; $T = 60°C$. A, peak at 40 ppm; B, peak at 35 ppm. ■, KOH; □, NaOH; ○, LiOH; ●, $Ba(OH)_2$; ◆, $Mg(OH)_2$

can be divided into two groups: NaOH and KOH, and LiOH, $Ba(OH)_2$ and $Mg(OH)_2$. In the presence of KOH and NaOH, formation of methylene bridges (cross-linking) was slow and reached an apparent plateau after around 48 h of reaction; the ordinate of this plateau is 0.1. The results obtained with LiOH, $Ba(OH)_2$ and $Mg(OH)_2$ are very different. Methylene bridges formed much more rapidly and as early as 24 h of reaction, the values reached being higher than those obtained with KOH and NaOH. Then there was a decrease for an ordinate close to 0.1, followed by a considerable increase beyond 32 h of reaction.

The progression of the reaction was thus greater in the case of LiOH, $Ba(OH)_2$ and $Mg(OH)_2$. Nevertheless, the rate decrease observed with these catalysts beginning at 24 h of reaction corresponds to that observed with KOH and NaOH starting at 48 h. This latent phenomenon was not observed on the curves generated by h.p.l.c. results (*Figure 7f*). On the other hand, we clearly find the separation of catalysts into two groups depending on their influence on the reaction medium.

Regardless of the catalyst used, the proportion of *para–para* methylene bridges was consistently higher than the proportion of *ortho–para* methylene bridges, and *ortho–ortho* methylene bridges (≈ 30 ppm) were never observed.

Based on published data[7–9], the catalyst in the reaction medium participates in the establishment of an intermediate chelate (*Figure 10*). The results obtained in this study lead to the following comments.

1) From a mechanistic standpoint, given the orientation of the reaction towards the formation of substituted species in h.p.l.c. and ^{13}C n.m.r., it may be presumed that the reaction mechanism proposed by De Jong and De Jong[7], Peer[8] and Price[9] is effectively operating in the reaction medium in our experimental conditions. Nevertheless, in the course of this work we noted an influence of the valence of the cation as well as of the ionic radius of the hydrated species resulting from the dissociation of the base. Given the chemical structure of the chelate showing the presence of charges, the increase in positive charge borne by the cation favours the stability of the complex and thus the addition of formaldehyde on the phenol ring. Concerning the effect of the ionic radius of the hydrated cation, two hypotheses can be formulated: (i) there exists an optimum radius of the hydrated cation for chelate formation; and (ii) the equilibria between the associated and dissociated forms of alkaline hydroxides (catalysts) are sensitive to the solvation of the cations. The solvation of the cation increases as the ionic radius of the cation decreases. Thus solvation shifts equilibria towards the dissociated form of the catalyst, increasing its availability to intervene in the reaction mechanism.
2) From a kinetic standpoint, chelate formation favours the approach of the phenol ring to the reactive species of formaldehyde and accelerates the disappearance of phenol. The reaction path via *ortho*-substituted monomers is preferential and a higher proportion of these compounds in the reaction medium is observed.

CONCLUSIONS

The basic catalysts of the reaction between formaldehyde and phenol studied in this research affect the kinetics and the mechanisms of addition, as well as condensation mechanisms. The results show that the valence and ionic radius of hydrated cations affect the changes of species

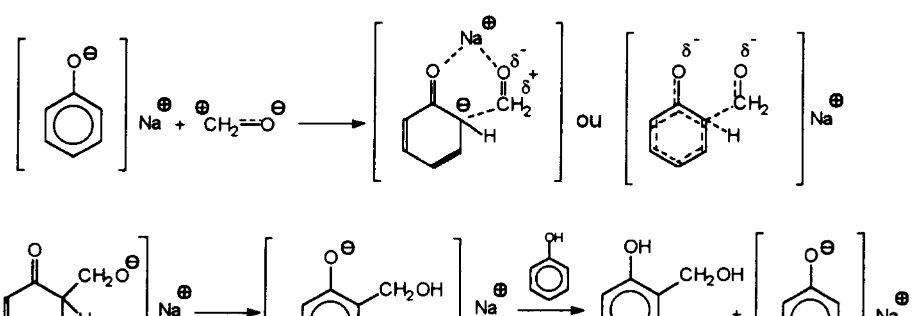

Figure 10 Reaction mechanism of the addition of formaldehyde on phenol in the presence of alkaline catalyst according to refs 7–9

in the reaction medium. We noted an orientation of reaction paths towards the formation of certain monomers and dimers, particularly *ortho*-substituted species. The use of new catalysts, however, does not change the types of oligomer methylene bridge: *para–para* are formed in a higher proportion than *ortho–para*, and *ortho–ortho* was not observed.

The catalysts were classified into two families as a function of their behaviour: KOH, NaOH and LiOH, and $Ba(OH)_2$ and $Mg(OH)_2$. The reaction medium changes of all the initial monomers **2** to **6** are similar for NaOH and KOH, with only a slight difference observed for the proportion of species in the medium. However, LiOH, $Ba(OH)_2$ and $Mg(OH)_2$, considerably modify the changes in substituted phenolic compounds with time. Thus, with LiOH, after the first 10 h of formation of compounds **2** to **6** there was a substantial decrease in the concentration of these compounds, leading to low residual values. This decrease is due either to additional substitution of the aromatic ring in the case of **2** to **5**, or to condensation reactions. In the case of the catalyst $Ba(OH)_2$, only compounds **5** and **6** were strongly influenced in the same conditions. As predicted in the literature[8,12,13], the use of the divalent cation Ba^{2+} modifies the reaction mechanism and directs reaction paths towards the formation of *ortho*-substituted species [2,6-DHMP (**5**) and 2,4,6-THMP (**6**)].

Nevertheless, we also noted an influence on condensation reactions of the nature of the cation used. The presence of catalysts of the group LiOH and $Ba(OH)_2$ favour the disappearance of 2,4,6-THMP (**6**). It is possible that the considerable decrease of compounds **2** to **5** after their formation in the reaction medium in the presence of LiOH is also due to greater condensation reactions in this case. This is an interesting result, since it leads to a reaction medium depleted in monomers, yielding better crosslinking of networks.

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