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Condensation reactions of phenolic resins VII: catalytic effect of sodium bicarbonate for the condensation of hydroxymethylphenols

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Abstract This article describes the catalytic effect of NaHCO_3 on condensation reactions of monomeric hydroxymethylphenols (HMPs) to elucidate the cure-acceleration mechanism. By comparison of the kinetics of self-condensations of HMPs, NaHCO_3 was proved to increase the reactivity of *para*-hydroxymethyl groups. The changes of ^{13}C nuclear magnetic resonance (NMR) chemical shifts on each HMP system with the additive indicated that the addition of NaHCO_3 enhanced some molecular interactions between HMPs and NaHCO_3 , facilitating a resonance effect that might play a similar role in dissociation of the phenolic hydroxyl groups of HMPs. In addition, computational modeling by molecular orbital calculations elucidated that hydrogen carbonate anion (HCO_3^-) forms an interaction between either the *para*-hydroxymethyl group and the phenolic hydroxyl group or between the two *para*-hydroxymethyl groups of HMPs by hydrogen bonds. From the experimental results, the authors proposed the mechanism of the catalytic action of NaHCO_3 ; it appears to be due to the delocalization of an electron initiated by the interaction of the *para*-hydroxymethyl groups and the phenolic hydroxyl of HMPs with HCO_3^- through hydrogen bonds, which results in facilitating the formation of active species.

Key words Condensation · Cure-acceleration · Hydroxymethylphenol · Phenolic resin · Sodium bicarbonate

Introduction

Alkaline phenol–formaldehyde (PF) resin is one of the most important adhesives for manufacturing wood composites. Its application will be extended if the cure conditions,

such as a high reaction temperature and long reaction time, can be mitigated. Extensive studies have been so far carried out for acceleration of curing PF resins such as employment of prepolymerization and the addition of cure accelerators.^{1–4} These investigations achieved considerable improvement of the cure conditions. However, PF resins still need a curing temperature that is about 10°C higher than that for amino resins. For further improvement, the mechanism of the curing reaction of PF resins and the effects of cure accelerators must be elucidated. In previous work, we studied the cure-acceleration effects of propylene carbonate (PC) on the condensation reactions of hydroxymethylphenols (HMPs) as model compounds for PF resins and found that PC increased the reactivity of the *ortho*-hydroxymethyl group, presumably through transesterification.⁴ At the same time, we recognized that sodium bicarbonate (NaHCO_3), which can be formed by either the hydrolysis of PC or the decomposition of the transesterified HMPs, showed catalytic action for condensations on the *para*-hydroxymethyl group. In the present study, we therefore focus on the catalytic action of NaHCO_3 .

Sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), and potassium bicarbonate (KHCO_3), as well as NaHCO_3 , are employed as cure accelerators. To date, many reports on the cure-acceleration effects of the carbonates have been published. Higuchi et al.⁵ found that the catalytic activity of Na_2CO_3 and K_2CO_3 could be ascribed to the hydrogen carbonate ion, and also assumed that hydrogen carbonate ion interacted concurrently with two hydroxymethyl groups to form activated complexes, which may facilitate the formation of dimethylene-ether intermediates or cause the direct formation of methylene linkages. Later, it was found that the theoretical amount of NaHCO_3 was almost completely obtained from PC that was rapidly hydrolyzed in alkaline media, and thereby considered that the cure acceleration by the addition of PC could be ascribed to the catalytic action of the hydrogen carbonate ion.⁶ Pizzi et al.⁷ compared the cure effects of some additives by thermomechanical analysis (TMA) and concluded that Na_2CO_3 appeared to exert an acceleration effect on the polycondensation reaction. Park et al.⁸ investigated the

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thermal behavior of carbonate-modified PF resin by differential scanning calorimetry (DSC) and reported that Na_2CO_3 and K_2CO_3 showed n th-order kinetics with a partial autocatalytic effect. Recently, Park and Riedl⁹ proposed that the addition of Na_2CO_3 or K_2CO_3 into PF resins apparently resulted in the appearance of *ortho-ortho* methylene linkages using liquid-state and solid-state ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. Zhao et al.¹⁰ used ^{13}C -NMR spectroscopy to show that the mechanisms involved in the acceleration of PF resins introduced by both guanidine carbonate and triacetin appeared to be based on facilitating reactions of cross-linking involving carbonic acid ions present in the resin solution.

Although the effect of carbonates has been already reported as described above, the mechanism has not yet been elucidated. Thus, in this study, 2-hydroxymethylphenol (2-HMP), 4-hydroxymethylphenol (4-HMP), and 2,4,6-trihydroxymethylphenol (THMP) were used as model compounds, and the effect of NaHCO_3 on the condensation reactions of the HMPs was investigated to elucidate the cure-acceleration mechanism by focusing on the difference in structure of the HMPs. The catalytic effect of NaHCO_3 was discussed in light of the experimental results and following modeling of the molecular interactions between HMPs and NaHCO_3 by molecular orbital calculations.

Materials and methods

Chemicals

Sodium bicarbonate (99.8%) and sodium hydroxide (96%) were purchased from Wako. 2-Hydroxymethylphenol (2-HMP; 99%) and 4-hydroxymethylphenol (4-HMP; 99%) were purchased from Tokyo Kasei Kogyo and from Aldrich, respectively. The procedures for preparing 2,4,6-trihydroxymethylphenol (THMP) were the same as those described in our previous report.¹¹

Determination of quantity and rate of reaction of HMPs

The changes in the concentrations of THMP during reaction were calculated from the corresponding peak areas of the high performance liquid chromatography (HPLC) chromatograms. The concentrations of the reaction products were determined from the corresponding peak areas of the HPLC chromatograms using calibration curves based on the results with 3,3',5,5'-tetrahydroxymethyl-2,4'-dihydroxydiphenylmethane and 3,3',5,5'-tetrahydroxymethyl-4,4'-dihydroxydiphenylmethane. The errors involved in the concentrations of the HMPs determined by this method were confirmed to be lower than 3%, and the reproducibility of each reaction was checked by a duplicate experiment. The reaction rate at an arbitrary time was determined as $([\text{HMP}]_t - [\text{HMP}]_0)/t$, and it was plotted as a function of time, $t/2$. The value at time zero obtained by extrapolation reflecting the initial decrease rate of THMP or the initial formation rate of dimers was taken as

the initial rate of reaction, where $[\text{HMP}]_t$ and $[\text{HMP}]_0$ denote the concentrations of HMP at time t and zero, respectively.

Identification of reaction products and analyses using HPLC and ^{13}C nuclear magnetic resonance (NMR) analyses

Reaction products were identified by HPLC and NMR analyses. For HPLC analysis, a Shimadzu 10AD liquid chromatograph equipped an UV detector set at 280 nm was used with an Inertsil ODS-3 column of 4.6×250 mm ID (GL Science) at 25°C. Water–acetonitrile gradient system was used as a mobile phase. For the 2-HMP system, the volume ratio of acetonitrile started at 5%, rose to 10% at 10 min, 20% at 15 min, 30% at 20 min, 70% at 25 min, and finally to 100% after 40 min. For the 4-HMP and THMP systems, the volume ratio of acetonitrile started at 15%, rose to 70% at 10 min, and finally to 100% after 30 min. The flow rate of the mobile phase was 1.0 ml/min.

For ^{13}C -NMR analysis, a Jeol JNM-AL 400FT NMR spectrometer was used. ^{13}C -NMR spectra were obtained using deuterium oxide (D_2O) as the solvent and sodium-3-(trimethylsilyl)propionate-2,2,3,3- d_4 (TSP- d_4) as the internal standard. The pulse delay time was 1.8 s, the number of scans was 1200, and spectra were recorded at 25°C.

Molecular orbital calculations

All molecular orbital calculations were performed with WinMOPAC ver. 3.5 (Fujitsu). The geometries of HMP molecules and their association were optimized using PM3 Hamiltonian. Electron density distributions were calculated using MNDO Hamiltonian. Solvent effects of water were estimated by the COSMO method using dielectric constant of 78.4.

Results and discussion

Effect of NaHCO_3 on the self-condensation reactions of HMPs

Figure 1 shows HPLC chromatograms in the early stage of the self-condensation of THMP with and without NaHCO_3 . There was no difference in the reaction products although some difference was observed in the amount of each reaction product. In the case of 2-HMP and 4-HMP, there was no difference in the reaction products. From the results, it was confirmed that NaHCO_3 did not contribute to the structures of condensation products proposed by Pizzi et al.⁷

In our previous article,⁴ NaHCO_3 was confirmed to increase the reactivity of *para*-hydroxymethyl groups in the NaOH -catalyzed condensations of HMPs. In this article, the effects of NaHCO_3 on the decrease of the concentration

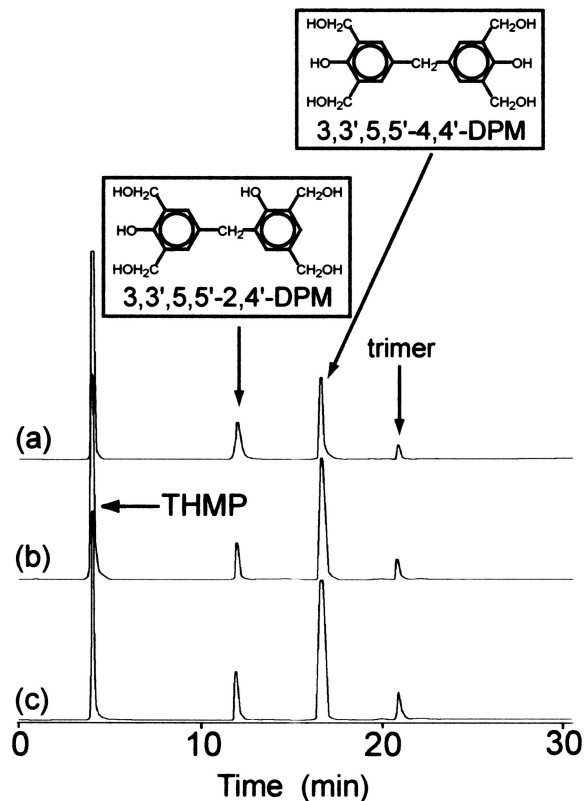


Fig. 1a–c. High performance liquid chromatograph chromatograms of the reaction systems of trihydroxymethylphenol (THMP) with NaOH (a), THMP with NaHCO₃ (b), and THMP with both NaOH and NaHCO₃ (c). Reaction conditions: [THMP]: 0.1 M; 70°C; 60 min; (a) NaOH/THMP molar ratio 0.1; (b) NaHCO₃/THMP molar ratio 1; (c) NaOH/THMP molar ratio 0.1, NaHCO₃/THMP molar ratio 1

of HMPs in the self-condensation systems as a function of the reaction time are shown in Fig. 2. In the THMP and 4-HMP systems, the concentrations of HMPs significantly decreased with the addition of NaHCO₃. On the other hand, in the 2-HMP systems, the addition of NaHCO₃ did not affect the rate of decrease in the concentration of 2-HMP. Thus, NaHCO₃ seems to increase the reactivity of the *para*-hydroxymethyl groups of HMPs.

To investigate the difference of the acceleration effect of NaHCO₃ between *ortho*- and *para*-hydroxymethyl groups, the reaction rate of the formation of two dimers from THMP, 3,3',5,5'-tetrahydroxymethyl-2,4'-dihydroxydiphenylmethane (3,3',5,5'-2,4'-DPM) and 3,3',5,5'-tetrahydroxymethyl-4,4'-dihydroxydiphenylmethane (3,3',5,5'-4,4'-DPM) shown in Fig. 1 were compared. As shown in Fig. 3, the acceleration effect of NaHCO₃ for producing 3,3',5,5'-4,4'-DPM was remarkable. The formation of 3,3',5,5'-4,4'-DPM involves a *para-para* methylene bond. The effect increased with an increase in the concentration of NaHCO₃. On the other hand, NaHCO₃ did not contribute to the formation of 3,3',5,5'-2,4'-DPM involving a *ortho-para* methylene bond. Therefore, it was found that NaHCO₃ selectively increased the reactivity of *para*-hydroxymethyl groups.

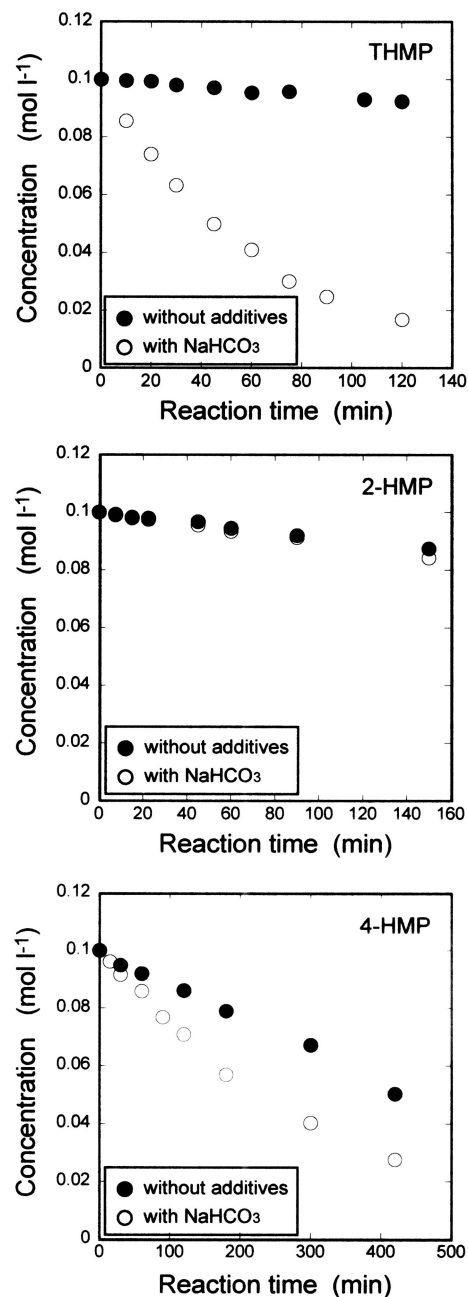


Fig. 2. Effects of NaHCO₃ on the decrease of the concentration of hydroxymethylphenols (HMPs) in the self-condensation systems as a function of the reaction time. Reaction conditions: [HMP]: 0.1 M; 70°C; (HMP with NaHCO₃ systems): NaHCO₃/HMP molar ratio 1

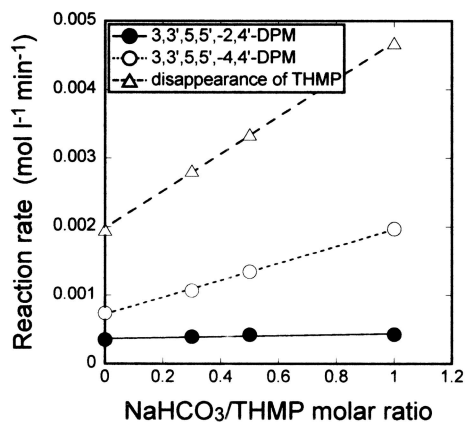
Changes of electron densities of HMP molecules with additives

To estimate the effects of additives on HMP molecules, the ¹³C-NMR spectra of THMP with and without additives are compared in Fig. 4. Significant changes in chemical shifts were observed for *ortho*-, *meta*-, and *para*-carbons and C1 carbon with the addition of either NaOH or NaHCO₃, or both NaOH and NaHCO₃. In the individual cases of 2-HMP and 4-HMP, similar behaviors of the ¹³C-NMR chemical shifts were observed. The changes of the chemical shifts in

Table 1. Changes of ^{13}C nuclear magnetic resonance chemical shifts (ppm) of hydroxymethylphenols (HMPs) by the addition of NaOH and NaHCO_3

	Position	Basis	+NaOH	+ NaHCO_3	+NaOH + NaHCO_3
THMP	C1	152.38	10.50	0.37	7.45
	<i>ortho</i>	127.84	1.48	0.06	1.09
	<i>meta</i>	128.90	-0.77	-0.03	-0.52
	<i>para</i>	132.88	-7.26	-0.26	-5.12
	<i>o</i> - CH_2OH	60.78	1.11	0.40	0.80
	<i>p</i> - CH_2OH	64.15	0.80	0.03	0.57
	NaHCO_3	161.11 ^a	-	-0.30	2.40
2-HMP	C1	154.45	5.52	0.29	3.57
	<i>ortho</i> (substituted)	127.06	1.36	0.12	0.89
	<i>meta</i>	130.11	-0.44	0.02	-0.27
	<i>para</i>	121.15	-3.24	-0.13	-2.16
	<i>meta</i>	130.26	-0.27	-0.01	-0.26
	<i>ortho</i>	116.13	1.91	0.14	1.28
	<i>o</i> - CH_2OH	60.20	0.77	0.08	0.64
	NaHCO_3	161.11 ^a	-	-0.11	2.05
4-HMP	C1	155.58	5.85	0.27	4.28
	<i>ortho</i>	116.00	1.81	0.10	1.35
	<i>meta</i>	130.10	0.23	0.02	0.17
	<i>para</i>	132.72	-3.34	-0.11	-2.39
	<i>p</i> - CH_2OH	64.23	0.33	0.03	0.27
	NaHCO_3	161.11 ^a	-	-0.27	1.98

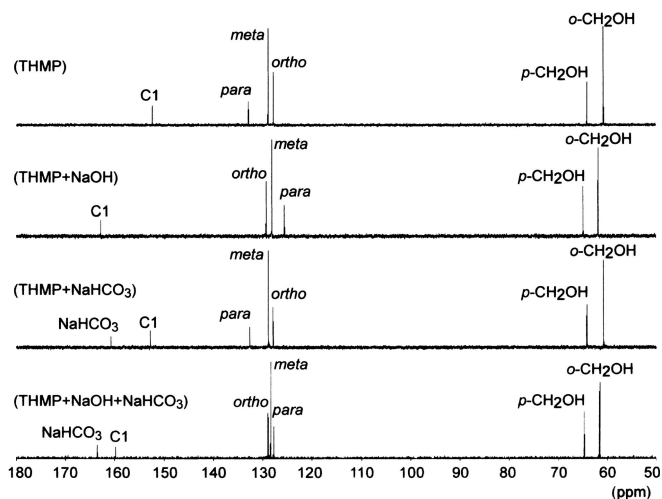
THMP, trihydroxymethylphenol

^a Solution of NaHCO_3 only**Fig. 3.** Acceleration effects of NaHCO_3 on the formation rate of dimers. Reaction conditions: $[\text{THMP}]$: 0.2 M; NaOH/THMP molar ratio 0.1; 70°C

each HMP system with the addition of additives are summarized in Table 1. In all systems of HMP with additives, the signals of C1 carbons shifted downfield due to withdrawal of electron density, whereas the signals of the carbons at the *para* position shifted upfield due to higher electron density. The signals of the hydroxymethyl groups shifted downfield presumably due to the decrease in the electron density. Because the $\text{p}K_{\text{a}}$ values of HMPs are between $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ of carbonic acid, as summarized in Table 2, NaHCO_3 is not strong enough as a base to dissociate the phenolic hydroxyls of HMPs. However, the addition of NaHCO_3 is assumed to facilitate a resonance effect that may play a similar role in dissociation of the phenolic hydroxyl of HMPs. The changes of electron densities in the HMPs with NaHCO_3 systems indicate the presence of some molecular interactions be-

Table 2. $\text{p}K_{\text{a}}$ values of HMPs and carbonic acid

Compound	$\text{p}K_{\text{a}}$ (25°C)
THMP	9.47 ^a
2-HMP	9.83 ^a
4-HMP	9.73 ^a
H_2CO_3 ($\text{p}K_{\text{a}1}$)	6.35
HCO_3^- ($\text{p}K_{\text{a}2}$)	10.33

^a Sprengling and Lewis¹²**Fig. 4.** Effect of additives on ^{13}C nuclear magnetic resonance spectra of THMP. Measurement conditions: 25°C; $[\text{THMP}]$: 0.1 M; (HMP with NaOH systems): NaOH/THMP molar ratio 1; (HMP with NaHCO_3 systems): NaHCO_3 /THMP molar ratio 1

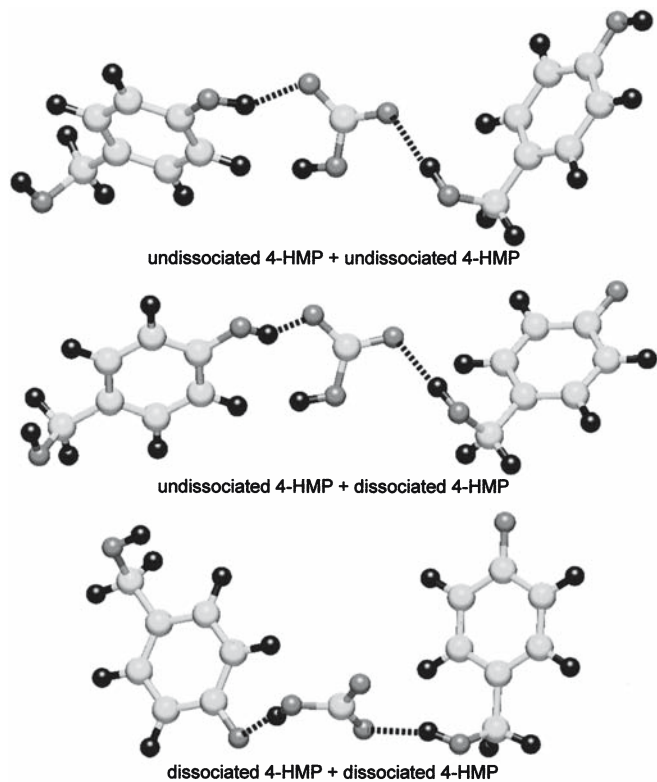


Fig. 5. Molecular interactions between 4-HMP and hydrogen carbonate ion as estimated by molecular orbital (MO) calculations

tween HMPs and NaHCO_3 . In aqueous solutions, NaHCO_3 exists as sodium cation and hydrogen carbonate (HCO_3^-) anion. The HCO_3^- anion is assumed to form hydrogen bonds in a bridging fashion between the hydroxymethyl groups and the phenolic hydroxyls of HMPs to cause electron delocalization.

Computational modeling of molecular interactions between HMPs and HCO_3^-

To confirm the above assumption, the most energetically stable configurations of two HMP molecules interacting with one HCO_3^- molecule were determined by molecular orbital (MO) calculation. The geometrical optimization was performed for all initial parameters, such as bond distances and bond angles. In addition, the calculations were performed in the following three combinations of HMPs: (1) two undissociated HMPs; (2) undissociated HMP and dissociated HMP; and (3) two dissociated HMPs. In the case of 4-HMP, three structures were obtained as shown in Fig. 5. In all the structures, HCO_3^- is supposed to engage in hydrogen bonding interactions between the *para*-hydroxymethyl group and the phenolic hydroxyl group. In the case of THMP, three structures were obtained as shown in Fig. 6. In combination with two dissociated THMP molecules, HCO_3^- is supposed to engage in hydrogen bonding between the two *para*-hydroxymethyl groups. In the other combinations of THMP, structures in which HCO_3^- engages in hydrogen

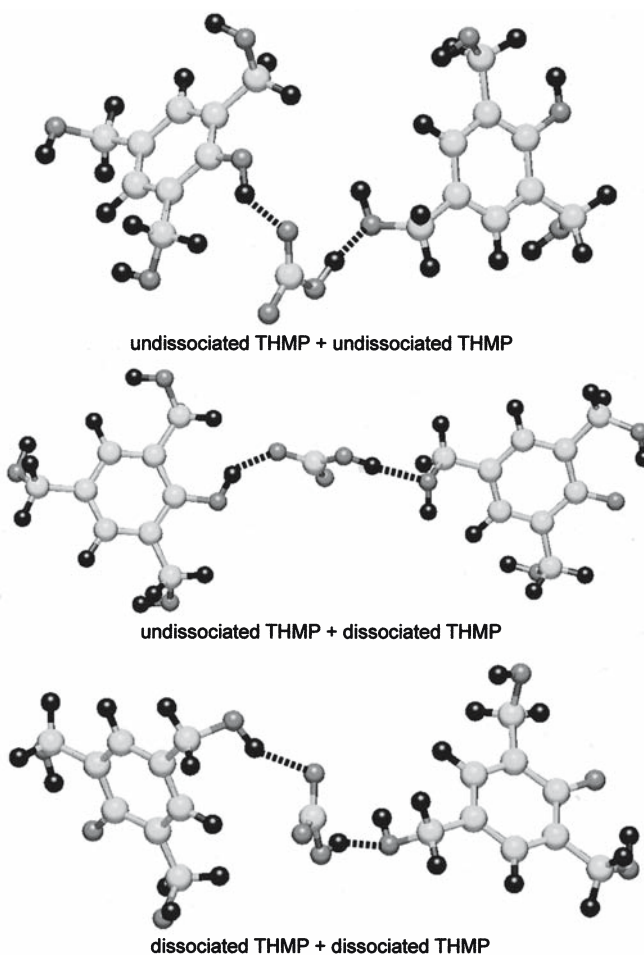


Fig. 6. Molecular interactions between THMP and hydrogen carbonate ion as estimated by MO calculations

bonding between the *para*-hydroxymethyl group and the phenolic hydroxyl group were obtained. In the case of 2-HMP, no structure was found in which HCO_3^- formed an interaction between two 2-HMP molecules.

From the above results, it is considered that the delocalization of electrons through hydrogen bonds facilitates the formation of active species such as the *para*-carbocation or the *para*-quinone methide as shown in Fig. 7. This consideration is consistent with the kinetic results in Figs. 2 and 3, suggesting that formation of the above interaction is most likely to represent the actual mechanisms.

Conclusions

By the comparison of the kinetics of the condensation of HMPs, the trends in the ^{13}C -NMR chemical shifts, and computational molecular modeling, the mechanism of the catalytic action of NaHCO_3 was proposed. In the mechanism, a resonance effect due to the interaction either between the *para*-hydroxymethyl and the phenolic hydroxyl groups or between the two *para*-hydroxymethyl groups with HCO_3^- ,

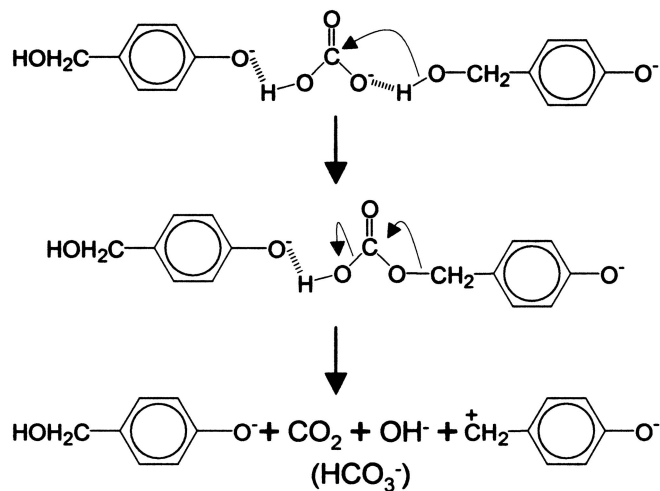


Fig. 7. Presumed catalytic action of NaHCO_3 on the condensation of HMPs

was supposed to facilitate formation of the active species such as the *para*-carbocation or the *para*-quinone methide.

Thus, it is predicted that the facile and effective delocalization of an electron on *p*- CH_2OH to form the active species may accelerate the condensation reaction of HMPs. Therefore, additives having such effects are expected to provide further acceleration effects for the condensation of PF resins.

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