

Phenolic and Tannin-Based Adhesive Resins by Reactions of Coordinated Metal Ligands. I. Phenolic Chelates

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Synopsis

Bivalent and trivalent metallic ions, respectively, accelerate and inhibit the reaction of phenols with formaldehyde. The catalytic effect of these metallic ions is equivalent, though more marked, to that of hydrogen ions, and it is due to their stronger charge. Metallic ions/phenols/formaldehyde complexes are formed. The stability of these complexes and mainly their rate of metal exchange in solution are the determining factors in the accelerating or retarding action. Identified stable chromium (III)-resorcinol-formaldehyde and chromium (III)-phenol-formaldehyde complexes have slow rates of metal exchange and inhibit the resorcinol-formaldehyde and phenol-formaldehyde reactions. The opposite is valid for lead (II), zinc (II), and other bivalent metallic ions. A scale showing the order of the accelerating effect of a series of metallic ions is given. The presence of polymeric complexes has also been observed.

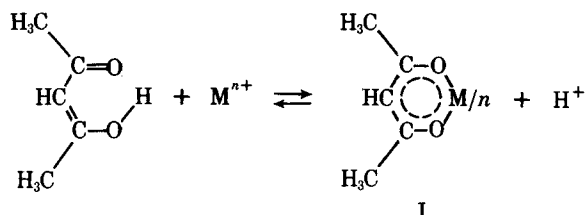
INTRODUCTION

Phenol formaldehyde resins may be prepared by carrying out phenol/formaldehyde condensations under such conditions that a high proportion of 2- and 2,6-substituted phenolic nuclei are produced.^{1,2} The term "high-ortho-substitution" refers to phenolic resins prepared under such conditions. It has been reported that if the reaction is carried out within the pH range 4-7 in the presence of salts of bivalent metals, an *ortho*-directing effect occurs, resulting in the production of "high-ortho" phenolic resins.^{1,2} The bivalent metallic salts apparently also accelerate both the reaction of formaldehyde with the phenolic nuclei and the condensation of methylolphenols with other phenolic nuclei in the preparation of resins. This catalytic effect is attributed to the bivalent metallic ions, while no effect on the reaction has been attributed to the various anions used. The reaction mechanism of this effect has not been elucidated. Conversely, trivalent metallic ions do not show this catalytic effect at all, but tend to slow down the reaction.^{1,2} This work deals with the effect of different bivalent and trivalent ions on phenols/formaldehyde and tannins/formaldehyde adhesive resins with a view to determining the following:

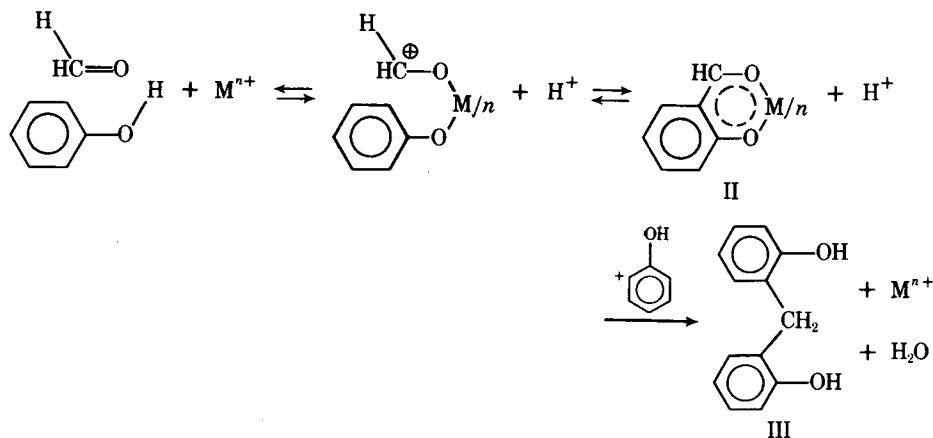
1. the type of catalysis involved and its mechanism,
2. the reason for the difference in effect given by bivalent and trivalent ions, and
3. the nature of the catalytic species.

APPROACH

The type of mechanism which seems the most likely is one which involves the formation of a chelate ring, similar to that suggested by Price and Sachanan³ for phenol-formaldehyde alkaline condensations. The chelating mechanism may involve the primary formation of a metal/formaldehyde complex or a metal phenate, as suggested by Fraser et al.^{1,2} Reviews^{4,5} of metal acetylacetonates indicate instead that chelates of type I are readily formed by many metals:

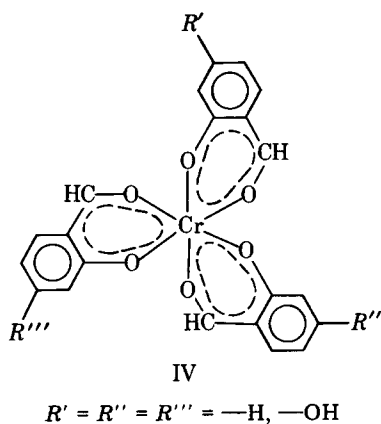


It was then assumed that a similar reaction could take place in the case of phenols and formaldehyde (or other aldehydes) in the presence of a metallic ion and that complexes of type II could be formed:

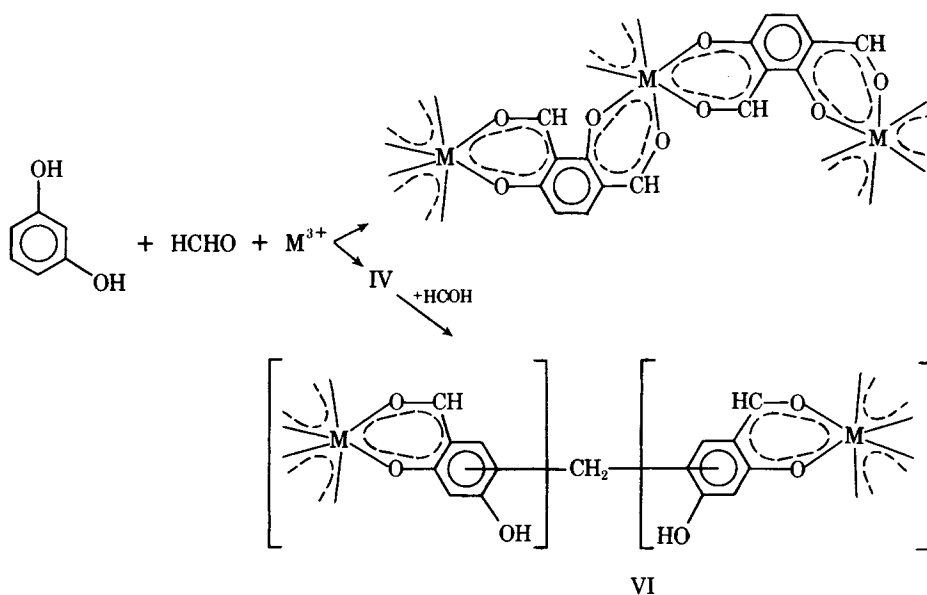


The rate of metal exchange in solution^{6,7} and the instability of the complex II formed should determine the accelerating or inhibiting effect of the metal in the reaction of phenol and formaldehyde. The more stable complex II is, the slower the reaction should proceed to the formation of resin III. A completely stable complex II should stop the reaction proceeding to resin III. If complex II is not stable, the reaction will proceed to form phenol/formaldehyde resins of type III, the rate of reaction being directly proportional to the instability or the rate of metal exchange of complex II. Reviews⁶ of acetylacetonates show that a few trivalent metals such as chromium (III) cobalt (III) and rhodium (III) give kinetically stable nonionic acetylacetonates complexes, while many bivalent metal ions give labile complexes subjected to rapid metal exchange in solution.

Trivalent chromium was chosen to investigate this hypothesis. This metal forms relatively stable acetylacetonates and was used to avoid reactions likely to be attended by chelate ring opening. Stable complexes of type IV were prepared and characterized:



As in the case of the equivalent acetylacetonates,⁶ the nature of the bonding between metal and ligands in these chelates is at least partly covalent and their stability may be ascribed to their partly aromatic character. While the formation of these chelates can explain the inerte of some trivalent metallic ions in accelerating the reaction of phenolic compounds with formaldehyde, they could also be used to prepare new types of phenolic polymers. Hydroxyphenols such as resorcinol or catechol could be used for this purpose. The reactions involved are probably the following:



Indication of the existence of "dimers" of tentative structure V and VI was obtained. However, as stable acetylacetonates chelate rings have been reported to be partly aromatic, and as such able to undergo the common reactions of aromatic rings,⁶ reaction of formaldehyde on the partly aromatic etherocyclic ring could also be possible. "Dimers" of structure VI were identified for resorcinol. To determine the extent of the accelerating or retarding effects of different bivalent and trivalent metallic ions, the gel times at 100°C of mixtures of resorcinol or catechol and formaldehyde were measured in the presence of various metallic salts.

EXPERIMENTAL

Preparation of Stable Chelates

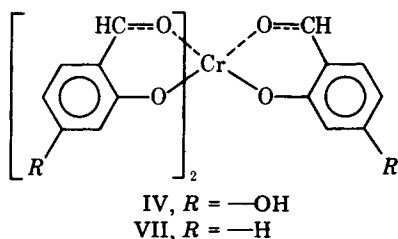
Resorcinol–Chromium. To 4.4 g resorcinol dissolved in 44.0 g water were added 1.95 g chromic sulfate, 1.3 g sodium acetate anhydrous, and 1.62 g 37% formalin solution. A white precipitate of sodium sulfate formed, which redissolved again after a few minutes. The color of the solution was turquoise green.

Phenol–Chromium. To 2.8 g phenol in 28.0 g water were added 1.90 g chromic sulfate, 1.3 g sodium acetate anhydrous, and 2.43 g 37% formalin solution. The solution obtained was blue.

Characterization of Stable Chelates

Both phenol and resorcinol solutions were separated through a Knauer high-pressure liquid chromatograph using a reverse phase RP18 preparative column and water/methanol, 85:15, as mobile phase. Flow speed was 3.5 ml/min with uv_{254} and differential refractometer detectors and a chart speed of 4 cm/min. Salts and resorcinol (or phenol) eluted first, followed after 5 min from injection by a huge peak composed of one compound for phenol and more than one compound in the case of resorcinol. TLC separation (benzene/acetone, 70:30, PF₂₅₄) showed that in the case of resorcinol, one of the compounds was a small amount of a resorcinol-CH₂-resorcinol dimer already identified.^{7,8} No higher polymers of similar nature were present for resorcinol. No linear condensates were present in the case of phenol. The compounds obtained by HPLC, all white crystalline solids, were examined by mass, infrared, and atomic absorption spectrometry for both phenol and resorcinol. The presence of combined chromium was proved by atomic absorption spectrometry for both phenol and resorcinol. Mass spectra were made on a Hewlett-Packard quadrupole electric mass spectrometer by scanning for 10 min at 3-sec intervals up to mass 1000. In the case of resorcinol, the complexes started to emerge after 5 min of scanning. Evidence of complexes of types IV, V, and VI was obtained by the following masses and fragmentation patterns.

Resorcinol. M^+ 463, m/e 463(1), 446(3.5), 355(2), 326(1), 191(7), 189(4), 139(8), 137(10), 123(35), 110(100). Infrared: 3150 cm^{-1} (3550–3000 cm^{-1}) (–OH), 1610 cm^{-1} ($\text{>C}=\text{O}$), 1150 cm^{-1} , 960 cm^{-1} , 845 cm^{-1} , 770 cm^{-1} , 720 cm^{-1} , 680 cm^{-1} . Cr^{III} percentage, 11.2%. This compound was tentatively assigned structure IV:



Resorcinol. Other complexes showing the following masses (M^+) were present: $M^+987(2)$, $M^+968(2)$, $M^+966(7)$, $M^+964(7)$, $M^+962(15)$. These compounds can be assumed to be a mixture of complexes of types V and VI, though they could not be identified with certainty. M^+964 could be assumed to be a complex of type IV in which three further resorcinol nuclei are bound by methylene bridges to the three resorcinols coordinated to the chromium. M^+966 could be a complex of type V in which two chromium atoms are involved and in which to one of the resorcinol ligands is bound a $-\text{CH}_2\text{-resorcinol}$. M^+987 and 968 could be fragments of complexes of higher mass; they probably are complexes of type IV linked by a methylene or methylene-ether bridge.

Phenol. $M^+415(1)$, $401(2)$, $385(2)$, $372(2)$, $371(3)$, $362(2)$, $357(3)$, $355(2)$, $354(2)$, $343(3)$, $342(2)$, $323(2)$, $294(3)$, $281(6)$, $280(4)$, $264(4)$, $263(6)$, $251(14)$, $250(4)$, $249(18)$, $235(7)$, $234(4)$, $233(8)$, $173(16)$, $121(12)$, $100(100)$, $95(62)$, $94(10)$, $77(14)$, $65(14)$. Cr^{III} percentage, 12.5%. This compound was tentatively assigned to structure VII.

Gel Times of Resorcinol/Formaldehyde and Catechol/Formaldehyde Mixtures of Molar Ratio 1:1

To 10 g 46% aqueous resorcinol solution in a test tube were added 1.3 g 96% paraformaldehyde powder and the different salts indicated in Tables I and II. The mixture was then immersed in a boiling water bath (96°C) and gently, continuously, and rapidly stirred with a thin stainless-steel coil using an upward-downward movement until gelation occurred. The gel time was measured from the start of immersion of the test tube in boiling water to gelation. Ten measurements for each specimen were made. The gel times obtained are shown in Tables I and II.

DISCUSSION

The results shown in Tables I and II indicate that many metals do function as accelerators for the reaction of phenols with formaldehyde. Many heavy-metal catalysts, of other types of reactions, are known to depend on the ability of the metal ion to exist in more than one oxidation state.⁵ In such cases the metal may act as an electron carrier and may act catalytically in a manner which is fundamentally different from the catalytic activity of hydrogen ions.⁵ When, however, as in the phenols-formaldehyde reactions investigated, the metal does not change its valence state, it interacts with molecules or ions containing electron

TABLE I
Accelerating and Retarding Effect of Different Metallic Catalysts

Catalyst	Resorcinol:formaldehyde, 1:1	
	Metallic ion/ resorcinol, mol/mol	Average gel time, sec
No metal salts	—	297
Al ^{III} acetate	0.01	636
Cd ^{III} acetate	0.01	112
Co ^{II} acetate	0.01	160
Cu ^{II} acetate	0.01	158
Cr ^{III} acetate	0.01	651
Cr ^{III} sulfate + Na acetate	0.01	665
Fe ^{III} acetate	0.01	201
Fe ^{III} chloride + Na acetate	0.01	215
Pb ^{II} acetate	0.01	103
Mn ^{II} acetate	0.01	132
Mn ^{II} chloride + Na acetate	0.01	148
Mg ^{II} acetate	0.01	151
Mg ^{II} chloride + Na acetate	0.01	168
Ni ^{II} acetate	0.01	119
Ni ^{II} chloride + Na acetate	0.01	128
Zn ^{II} acetate	0.01	108
Zn ^{II} chloride + Na acetate	0.01	117
Zn ^{II} chloride	0.01	277

donor groups and accelerates reactions in a manner similar to hydrogen ions.⁵ When this occurs the acid catalysis due to the metal ion differs only in degree from that of the hydrogen ion.⁵ The effect of the metal is much stronger than that of hydrogen ions, since, because of higher charge and greater covalance, its interaction with donor groups is often much greater.⁵ This is important, since in the preparation of phenol-formaldehyde adhesives for wood, very acid pHs cannot be used if the deterioration of the wood is to be avoided. Metal ion catalysts have then, at higher pH, the same catalytic effect on the preparation and setting of the resin as is shown by higher hydrogen ion concentrations, hence lower pHs. This allows setting of phenolic resin adhesives in milder acid conditions with no lengthening of setting time and without any wood deterioration.

The gel times with formaldehyde obtained for resorcinol and catechol indicate that the metal catalysis effect is probably valid for most phenols having a free *ortho*-position to the hydroxy group. The results shown in Tables I and II indicate that most bivalent metallic ions accelerate phenol-formaldehyde reactions. The extent of this effect is directly proportional to the quantity of metallic ion present. Bivalent metals, firstly, will not inhibit the reaction, as the complexes they form are unstable and their rates of exchange in solution are high, and secondly, they accelerate the reaction in a manner similar to hydrogen ions, though to a higher degree because of their stronger charge and greater covalence.

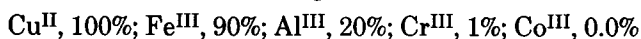
TABLE II
Effects of pH and Salts on Resorcinol-Formaldehyde and Catechol-Formaldehyde Reaction (96°C)

Catalyst	Metallic ion (mol) per mol of		Average gel time, sec		Catalyst	Metallic ion/resorcinol, mol/mol	pH	Average resorcinol gel time, sec
	Catechol	Resorcinol	Catechol	Resorcinol				
None	—	—	4200	297	None	0.01	3.55	276
Zn acetate	0.01	0.01	1290	108	None	0.01	4.7	297
Zn acetate	0.02	0.02	1020	97	None	0.01	5.7	237
Zn acetate	0.03	0.03	840	90	None	0.01	7.0	49
Zn ^{II} chloride + Na acetate	0.01	0.01		117	Zn ^{II} acetate	0.01	3.55	84
Zn ^{II} chloride + Na acetate	0.03	0.03		105	Zn ^{II} acetate	0.01	4.7	108
Zn ^{II} chloride + Na acetate	0.03	0.03		97	Zn ^{II} acetate	0.01	5.7	84
Cr ^{III} sulfate + Na acetate	0.005	0.01		>900	Zn ^{II} acetate	0.01	7.0	48
+ Na acetate	0.01	0.01		664	Zn ^{II} chloride	0.01	3.55	89
+ Na acetate	0.20	0.20		147	+ Na acetate	0.01	4.7	117
+ Na acetate	0.32	0.32		106	+ Na acetate	0.01	5.7	77
+ Na acetate	0.38	0.38		74	+ Na acetate	0.01	7.0	46
+ Na acetate	0.45	0.45		67	+ Na acetate	0.01		

The formation of the identified stable complexes of type IV slows down or inhibits the reaction from proceeding to phenol-formaldehyde resins of type III when trivalent metals are used. An exception is Fe^{III} , as shown by the effect of ferric acetate on the resorcinol/formaldehyde gel time (Table I). This indicates that Fe^{III} is not capable of giving stable complexes of type IV or that the rate of metal exchange between complex and solution is high. This finding is consistent with the scale of metal exchange rates given by Kluiber^{6,7} for metal acetylacetonates in which a few metals are grouped in the following order of decreasing rate of exchange:



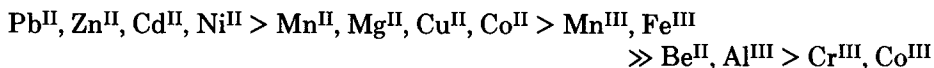
The rate of exchange expressed as percentage exchange in a given unit of time for the different metals is the following^{6,7}:



The order of the metals in the scale corresponds to the gel times obtained in the case of the resorcinol-formaldehyde condensation. It is possible then to express the extent of the accelerating or retarding effect of the metal ions in the order of their metal rates of exchange in solution better than in the order of their stability. The Fraser scale¹ can consequently be considerably modified as follows:

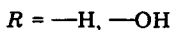
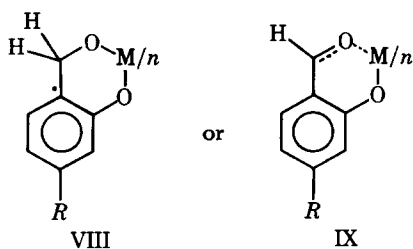


Furthermore, the position of other metals in the scale given can be deduced from the Kluiber scale,^{6,7} so that an expanded scale of the extent of the metal ions accelerating effect would be as follows:



It is possible to see that not all bivalent metals are accelerators and particularly that not all trivalent metals are inhibitors of phenol-formaldehyde reactions.

The formation of polymeric condensates of types V and VI is interesting, since they represent new types of phenol-formaldehyde resins. The formation of condensates of type V is probably substantiated by the gel times of resorcinol/formaldehyde mixtures to which increasing amounts of Cr^{III} ion have been added. The shortening of the gel time observed by increasing the percentage of Cr^{III} ion (Table II) could be ascribed to both the formation of polymeric condensates of type V and to the increased total amount of metal exchanged due to the increased amount of Cr^{III} ions present. The existence of structures of types V and VI can be deduced by the presence of complexes of high molecular weight observed in the case of resorcinol. However, it is not possible to judge their true nature and structures by the data available. Such polymers were not observed in the case of phenol.



An interesting structural question involves which of the above two complexes of type IV is formed:

The presence of a >C=O group band in the infrared spectra shifted to a slightly lower field for partial aromatic nature (less than a double bond, more than a single bond) indicates that complex IX is the one formed. This substantiates the assumption that the metal-containing etherocyclic ring is partly aromatic in nature, as assumed by analogy to equivalent acetylacetonates metal complexes. However, some of the masses of the higher molecular weight resorcinol/chromium/formaldehyde complexes of unidentified nature could indicate that structures of type VIII are also possible. The mechanism presented also explains the *ortho*-orientating effect of these metal ions. The results in Table II show that the accelerating effect is stronger around pH 4.7 and is partially masked by the higher reactivity of the phenol/formaldehyde system at lower and higher pHs.

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