Predicting the Reactivity of Adhesive Starting Materials

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Abstract

Phenolic compounds are important in the production of bonded-wood products. Phenolic compounds in addition to phenol and resorcinol are potential alternative feedstocks for producing adhesives. The reactivity of a wide variety of phenolic compounds with formaldehyde was investigated using semi-empirical and *ab initio* computational chemistry methods. Results of these calculations were compared with experimental data. The results indicate that *ab initio* computational chemistry methods coupled with newer methods for calculating atomic charges can be used to explain the relative reactivities of phenolic compounds with formaldehyde. These methods allow the separation of experimental rate constants into contributions that can be associated with each reactive center in proportion to the atomic charge at that reactive center. The methods not only correlate the reactivity of previously studied compounds but appear capable of predicting the reactivity of other compounds as well.

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Introduction

Adhesives constitute an important component in the manufacture of a wide array of products produced by the forest products industry. Approximately 57 percent of all phenolics are used for the production of wood adhesives and binders (1). In recent decades, various political and economic factors have caused the supply of wood adhesives to decrease dramatically from time to time, producing a concomitant marked increase in price. This situation has led to recognition of the importance of research on alternative sources of starting materials for the production of wood adhesives (2).

In general, the materials chosen for study as alternative sources of adhesives feedstock are structurally similar to materials already used for this purpose. For example, tannins and lignins have been studied as replacements for phenol in phenol-formaldehyde adhesives because they contain phenolic moieties within their chemical structures. However, chemical reactivity is dependent in very subtle ways on the chemical structure of a given compound. To select the best starting materials from an array of several alternatives, one must produce adhesive formulations that employ some or all of the alternative components in various proportions. Then, experiments must be conducted to assess the efficacy of each formulation as a wood adhesive. The efficiency of this trial-and-error approach would be greatly increased if one could predict *a priori* those materials that would constitute the most appropriate replacements for the various

components of an adhesive system, for example, the phenolic component of a phenolic adhesive. Thus, instead of testing all possible materials, the less promising materials could be eliminated at the outset.

The reactions of phenolic compounds with formaldehyde to form polymeric systems can be catalyzed by either acids or bases. Almost all phenolic adhesive systems used to bond wood are base catalyzed. Polymer formation occurs in two steps: 1) an addition reaction in which formaldehyde reacts with the phenolic compound to form hydroxymethyl derivatives; and 2) a condensation reaction in which the hydroxymethyl derivatives react to form oligimers and eventually crosslinked polymers. In the work reported here, computational chemistry methods were used to study the formation of hydroxymethyl derivatives on reacting formaldehyde with phenolic compounds under basic conditions,

Results and discussion

A number of kinetic studies have investigated the reactivity of phenolic compounds with formaldehyde (3-14). Sprung (3) undertook a particularly extensive study, reporting kinetic data for the reaction of a wide variety of phenolic compounds with formaldehyde under the same set of reaction conditions. The reactions were carried out under anhydrous conditions rather than the aqueous conditions typically employed for the preparation of phenolic adhesives; however, Sprung did note that the kinetic course of the reactions was similar to that typically observed in aqueous solution. Thus, the available data cannot be directly correlated in terms of reactions that are representative of those used in the preparation of adhesives for bonding wood. However, these data are useful for both qualitative assessments and for tests of the ability of computational methods to predict the relative reactivity of phenolics.

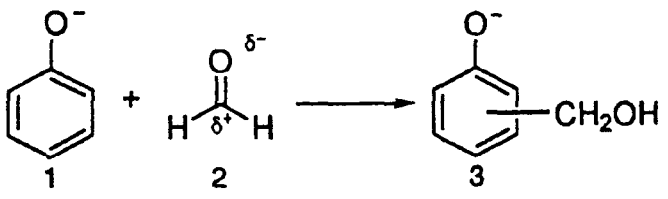

Figure 1.—*Scheme for reaction of phenol with formaldehyde.*

The reaction of phenolics (e.g., phenol) with formaldehyde, as shown schematically in Figure 1, corresponds to an electrophilic aromatic substitution (15). In basic media, the phenol reacts to form the phenolate anion in which the negative charge is stabilized by resonance delocalization with the *ortho*- and *para*-positions. Reaction with the partial positive charge on the carbon of formaldehyde can then occur at the *ortho*- and *para*-positions.

Calculations of total electron density at carbons of the phenol ring (16, 17) using CNDO/2 (18) and MNDO (19) have been used to explain the fact that formaldehyde reacts with phenol at the *ortho*- and *para*-positions but not at the *meta*-positions. However, calculations with MNDO suggested that reaction at the reactive centers is best explained by the electron density in the highest occupied molecular orbital (HOMO) of the reactant molecules (17). Recently, charges calculated by *ab initio* methods were used to explain the copper-catalyzed oxidative phenol coupling reaction (20).

Although calculated atomic charges have been used to explain differences in reactivity at specific sites on a given phenolic compound (i.e., phenol), such calculations have not been used to explain the differences in reactivity between phenolic compounds. Semi-empirical calculations (using RHF/PM3 as implemented in MOPAC 6.0 (2 1) or HyperChem (22)) of the total charge density or the charge density in the HOMO are not useful as the basis for correlating the reactivity of different phenolic compounds with formaldehyde, as exemplified by the array of phenolic compounds studied by Sprung (3). Therefore, in the study reported here, calculations using *ab initio* methods were undertaken in an attempt to gain insight into the differences in reactivity of these phenolic compounds.

Sprung (3) obtained kinetic data for the reactivity of formaldehyde with the phenolic compounds listed in Table 1. The fact that the relative reaction rates cover a wide range illustrates the subtle effect of chemical structure on reactivity The data were obtained under anhydrous conditions using a base catalyst. Because of the wide range of kinetic rate constants and the large number of compounds

studied under the same reaction conditions, Sprung's data constitute an ideal set of experimental data against which computational results can be compared. At the conditions employed for these reactions, only mono-addition reactions were thought to have occurred to any significant extent (3). Sprung obtained apparent first-order rate constants by following the disappearance of formaldehyde. Thus, the rates are overall rates that account for the reactions of formaldehyde at all of the possible reactive sites on the phenolic ring.

For purposes of determining reactivity by computational means, three criteria were considered necessary for the reaction to take place. Reaction of formaldehyde with a given phenolic compound would only occur at a phenolic ring position having 1) a substantial negative charge; 2) a significant component of the HOMO; and 3) no substituent other than hydrogen.

Initial calculations were conducted on the phenolate anions at the RHF/PM3//RHF/PM3 level of theory These calculations afforded information on the molecular orbitals and the charge at each atomic nucleus. For each of the compounds, the HOMOs were analogous to that shown for phenol in Figure 2, in which prominent portions of the orbital are located at positions *ortho* and *para* to the phenol oxygen, but not at positions *meta* to the phenol oxygen. The calculated total charges at those atomic sites of the phenolic ring on which the HOMO was localized and on which no substituent (other than hydrogen) was present were summed to give the quantity Σq. The charges at those sites with substituents were eliminated from Σq as a means of accounting for steric interactions that would interfere with the approach of the formaldehyde molecule. A plot of the relative reaction rate for each phenolic compound versus the absolute value of Σq calculated for that phenolic compound did not indicate any direct correlation.

Table 1.—*Relative reaction rates of formaldehyde with various phenols at 90°C under anhydrous conditions (3).*

Compound	Abbreviation	Relative reaction rate
3,5-xylenol	35 MP	7.75
m-cresol	3 MP	2.88
2,3,5-trimethylphenol	235 MP	1.49
Phenol	Phenol	1.00
3,4-xylenol	34 MP	0.83
2,5-xylenol	25 MP	0.71
p-cresol	4 MP	0.35
Saligenin	Saligenin	0.34
o-cresol	2 MP	0.26
2,6-xylenol	26 MP	0.16

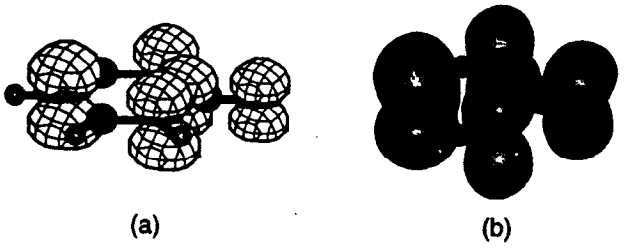

Figure 2.—*Graphical representation of HOMO of phenolate anion calculated at (a) RHF/PM3//RHF/PM3 and (b) RHF/6-31 +g//RHF/6-31 +g level of theory. Calculations conducted with HyperChem (22) (a) and Gaussian 94 (24) (b), respectively.*

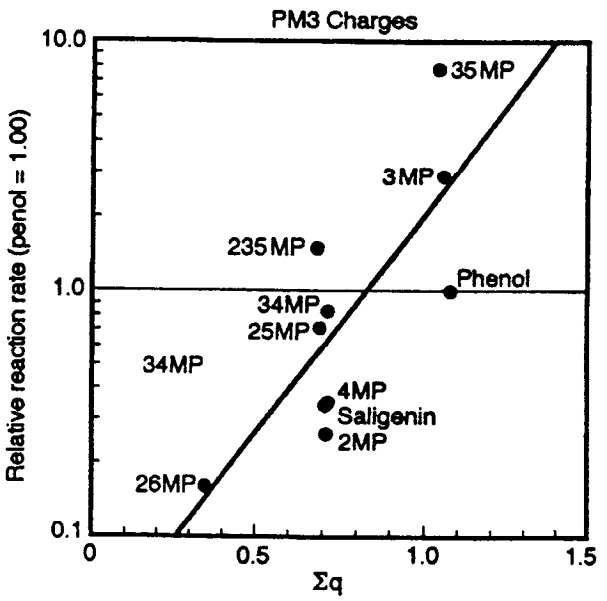

Figure 3.—*Semilog plot of relative reaction rate for reaction of phenols with formaldehyde versus absolute value of Σq. Σq was calculated at RHF/PM3//RHF/PM3 level of theory using HyperChem (22). Line represents first-order regression of data using SigmaPlot (30).*

Table 2.—Correlation of experimental kinetic data with Σ_q (3).[a]

Atomic charge method	Correlation coefficient (r^2)			
	RHF/PM3	RHF/6-31g	RHF/6-31+g	B3LYP/6-311+g (2d,p)
Mulliken	0.60	0.73	0.30	0.49
HOMO P_z electron density	0.62	- -	- -	- -
NBO	- -	0.66	- -	- -
CHelp	- -	0.77	0.81	0.80
CHelpG	- -	0.94	0.96	0.98
MK	- -	- -	0.97	0.95

[a] Σ_q was determined at various levels of computational theory using the indicated methods for calculating atomic charges. Correlation coefficients were determined from first-order regression of log of relative rate constants for reaction between formaldehyde and phenolic compounds studied by Sprung against Σq, using SigmaPlot (30).

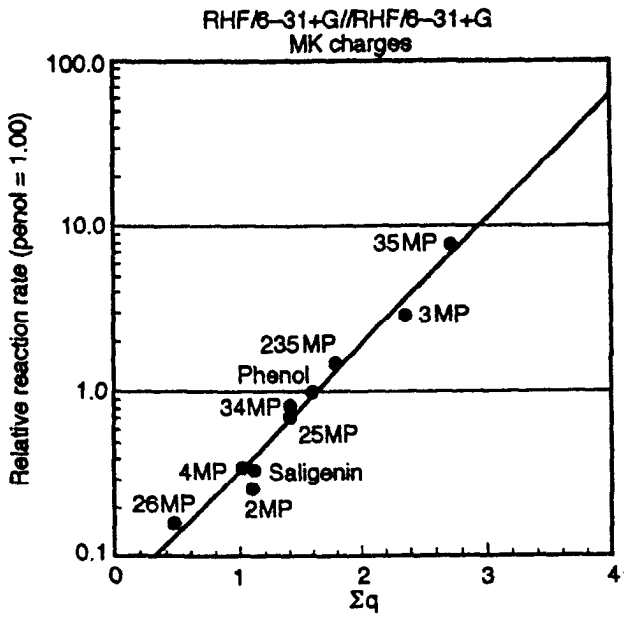

***Figure 4.**—Semilog plot of relative reaction rate for reaction of phenols with formaldehyde versus absolute value of* Σq. Σq *was calculated at* RHF/6-31 + *g//RHF/* 6-31+g *level of theory using Gaussian 94 (24). Line represents first-order regression of experimental data (solid symbols) versus* Σq *using SigmaPlot (30).*

A semilog plot of relative reaction rate versus the absolute value of Σq (Fig. 3) did indicate a general correlation. However, it is clear from inspection of Figure 3 that Σq as calculated using the PM3 formalism is not a good parameter with which to correlate the reactivity of phenolic compounds with formaldehyde. Moreover, the sum of the electron density in P_z of the HOMO at these sites also did not provide a good basis for correlation of the reactivity of the phenolics.

Calculations at higher levels of theory were then performed on each phenolic compound listed in Table 1, using a combination of GAMESS (23) and Gaussian 94 (24) and a number of different methods for determining atomic charges. Σq was calculated from the atomic charges afforded by these methods, in a manner similar to that described in the previous paragraph. Table 2 presents an overview of the results from correlations of the results with the experimental kinetic data. The results in Table 2 indicate that at the higher levels of theory, the absolute value of Σq calculated from charges determined by the CHelpG and MK methods gives excellent correlations with the log of the experimental relative rate constant. Figure 4 illustrates the correlation obtained between the kinetic data of Sprung and Σq calculated at the RHF/6-31+g//RHF/6-31+g level of theory.

Although these methods give an excellent correlation between the kinetic data and Σq, this correlation was unsatisfactory in one respect. While these methods allow the kinetic data to be correlated with the sum of the charges at the respective **reactive sites,** they do not allow comparison of reactivity at individual, reactive phenolic ring positions.

Sprung's kinetic data are in the form of apparent first-order rate constants, i.e.:

$$d[F]/dT = k_{apparent} * F$$

where:

T = time
F = formaldehyde

$k_{apparent}$ = apparent first-order rate constant for the disappearance of formaldehyde

$k_{apparent}$ is related to apparent first-order rate constants (k_i) for the reaction of formaldehyde at each reaction site on the nucleus of a phenolic compound by

$$k_{apparent} = \Sigma k_i$$

Using these methods, log $k_{apparent}$ was shown to be proportional to Σq. Thus,

$$k_{apparent} \sim 10^{\Sigma q}$$

and

$$\Sigma k_i \sim 10^{\Sigma q}$$

These last two equations do not allow the apparent rate constant to be separated directly into components proportional to the charge at a particular reactive site (q_i).

TO develop a relationship between $k_{apparent}$ and individual contributions tied to the charge at a given reactive site, it was assumed that:

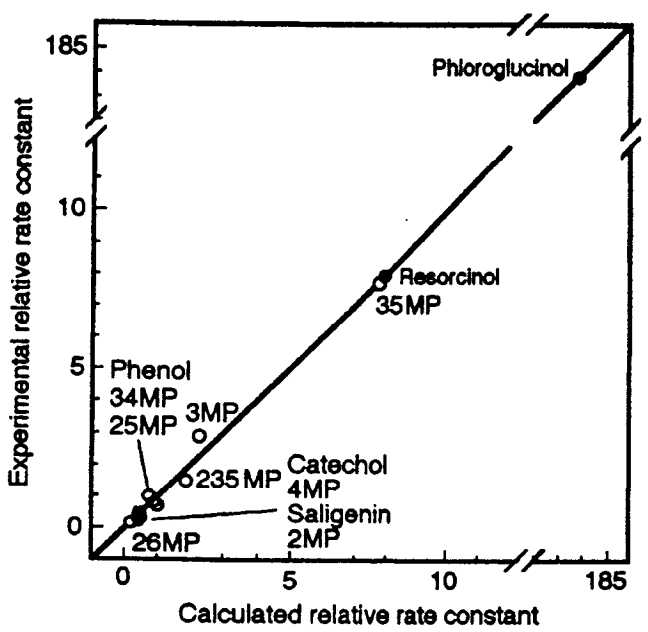

Figure 5.—*Comparison of experimental* (3) *values of relative rate constants for reaction of phenolic compounds with formaldehyde (open circles) and calculated values for catechol, resorcinol, and phloroglucinol (filled circles). The line represents a 1:1 correspondence between experimental and calcufated values for relative rate constants. CHelpG-based atomic charges used in making this correlation, as described in the text, were obtained at RHF/6-31 + g//RHF/6-31 +g level of theory.*

$$k_i \cong a + b * 10^{c*q_i}$$

where a, b, and c are constants associated with *all* reactive centers. It then follows that

$$k_{apparent} = \Sigma k_i \cong \Sigma (a + b * 10^{c*q_i})$$

$k_{apparent}$ is known experimentally and q_i is available from the chemical computations. Therefore, a, b, and c could be determined by regressing the right-hand side of the equation against the experimental data.

Figure 5 shows the relationship between the experimental relative rate constants for the reaction of formaldehyde with the phenolic compounds studied by Sprung and the relative rate constants calculated with the methods just discussed. As indicated by this figure, these methods give an excellent representation of the experimental data. In addition, Figure 5 shows the predicted rate constants for catechol, resorcinol, and phloroglucinol. The reactivity of these compounds with formaldehyde is in the order catechol < phenol < resorcinol < phloroglucinol. The methods presented here predict the relative reactivity of these compounds with formaldehyde in that order. Thus, these methods not only correlate the reactivity of the compounds studied by Sprung, they also appear to be capable of predicting the reactivity of other compounds as well.

The phloroglucinol moiety is found in many tannins. Tannins have been extensively studied as potential replacements for phenol. One problem associated with using tannins in this way is their very fast reaction with formaldehyde. It is of interest to note that this behavior could have been predicted using the methods described here. Hopefully, as these methods become better understood, they could be used to predict how materials such as tannins could be better used as a source of starting materials for adhesives.

In addition to predicting overall rate constants, these methods allow the separation of experimental rate constants into contributions that can be associated with each reactive center in proportion to the atomic charge at that reactive center and the determination of relative reactivity at each center for all the compounds studied by Sprung (Fig. **6).**

Computational methods

Semi-empirical calculations were conducted on a Gateway 2000 PC at the RHF/PM3//RHF/PM3 level of theory using HyperChem (22). All *ab initio* calculations were performed on an IBM Model 720 RISC/6000 Workstation using either GAMESS (23) or Gaussian 94 (24). The optimized structures obtained from HyperChem were used as the starting structures for calculations at the RHF/6-31g//RHF/6-31g level of theory using GAMESS. The GAMESS optimized structures were then used as the starting structures for calculating Mulliken, NBO (25), CHelp (26), CHelpG (27), and Men-Kollman/Singh (MK) (28, 29) based charges at the RHF/6-31g//RHF/6-31g, RHF/6-31+g//RHF/6-31+g, and B3LYP/6-311+g (2d,p)//B3lyp/6-311+g (2d,p) levels of theory using Gaussian 94.

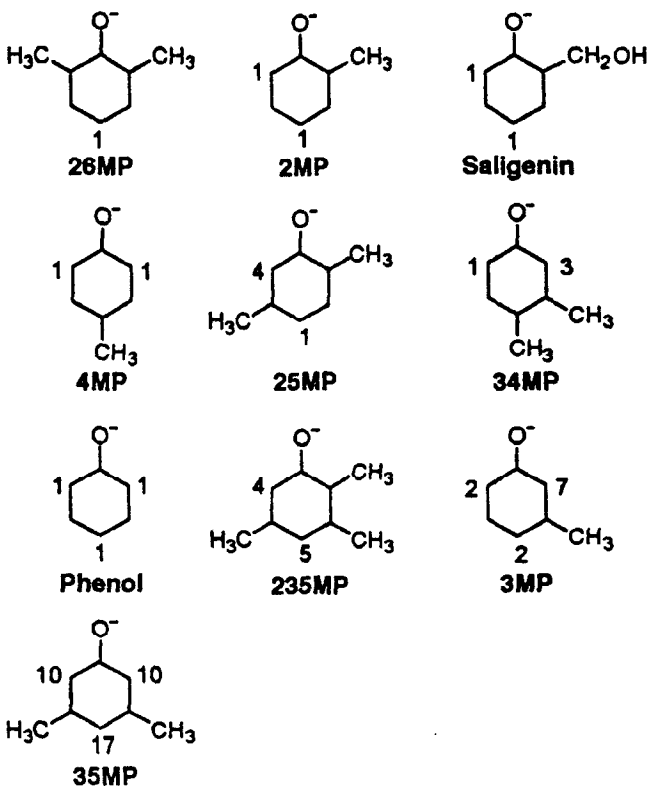

Figure 6.—*Relative reactivities with formaldehyde at reactive centers of phenolic compounds studied by Sprung (3). Relative reactivity of para position of phenol was taken as 1. Calculations were performed at RHF/6-31+g//RHF/6-31+g level of theory and charges were calculated by CHeIpG method. See Table 1 for abbreviations of compound names.*

Conclusions

The results of this study indicate that *ab initio* computational chemistry methods coupled with newer methods for calculating atomic charges can be used to explain the relative reactivities of phenolic compounds with formaldehyde. However, it should be emphasized that these results must be considered as only qualitative for the following reasons. First, the experimental kinetic data against which the computational chemistry calculations were compared were determined before the advent of such analytical techniques as NMR and HPLC. These techniques would have been able to determine whether or not reactions in addition to those needed for the formation of mono-hydroxymethyl derivatives of the phenolic compounds were responsible for the consumption of formaldehyde. Second, only gross steric hindrances to reaction (i.e., the presence of a substituent on a potential reactive site) were considered. More subtle steric hindrances from neighboring groups are probably also important. Finally, the experimental data were obtained for reactions in nonaqueous conditions and may not be directly applicable to aqueous conditions. Experiments to address these and other potential concerns are being undertaken. In addition, calculations are being conducted using other data available in the extant literature.

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