Predicting the Reactivity of Phenolic Compounds with Formaldehyde Under Basic Conditions: An *Ab Initio* Study

ANTHONY H. CONNER

USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53705-2398

Received 14 September 1999; accepted 22 November 1999
Published online 24 July 2000

ABSTRACT: A method is needed to predict which compounds, from the many alternative phenolic compounds, might be best for making polymeric phenolic systems. Kinetic data for the reaction of a series of phenolic compounds with formaldehyde using a base catalysis are available in the literature. Semiempirical calculations, using RHF/PM3, and *ab initio* calculations, using RHF/6-31G, RHF/6-31+G, and B3LYP/6-311+G(2d,p), were performed on the series of phenolic compounds to determine their relative reactivities. Atomic charges were determined for the phenolate anions. For each compound, I summed the absolute value of the calculated, negative charges residing on carbon atoms of the phenolic ring at which the HOMO was located and at which no substituent was present to cause steric interference with the reaction. The sum of the charges for each compound was then regressed against the log of the relative reaction rate for that compound. The sum of charges from PM3-based calculations gave poor correlation with reactivity. The sums of charges calculated by the CHelpG and Merz-Kollman/Singh methods at the *ab initio* levels of theory give excellent correlations with reactivity of the phenolics toward formaldehyde. Based on the calculated charges, estimates of the relative reactivity at each of the reactive sites on each of the phenolic compounds were determined. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 355-363, 2000

Key words: chemical computation; *ab initio;* semiempirical; phenol; formaldehyde; adhesive

INTRODUCTION

Adhesives constitute an important component in the manufacture of a wide array of composite products produced by the forest products industry and used by the consumer. Approximately 57% of all phenolics are used for the production of wood adhesives and binders.[1] From time to time during recent decades, various political and economic factors have caused the price of phenol to increase, which caused a concomitant marked increase in the price of wood adhesives. This situation has led to recognition of the importance of research on alternate sources of starting materials for the production of adhesives.[2]

In general, materials are chosen for study as alternative sources of feedstocks for the production of adhesives because they are structurally similar to materials already employed for this purpose. For example, tannins[3] and lignins[4] 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

The use of trade or firm names in this publication is for reader information and does not imply endorsement by the US. Department of Agriculture of any product or service.

The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright.

Journal of Applied Polymer Science, Vol. 78, 355-363 (2000)
© 2000 John Wiley & Sons, Inc.

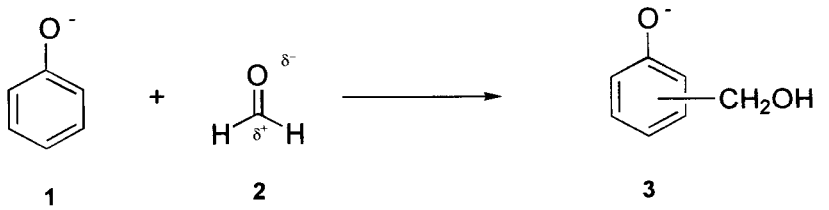

Figure 1 Reaction of phenol with formaldehyde.

structure of a given component. To select the best starting materials from an array of alternatives, one must produce adhesive formulations using all the alternatives in various proportions and then conduct experiments to assess the efficacy of each of those formulations 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 having to test all possible materials, one would be able to eliminate a number of less likely candidate materials at the outset.

The reactions of phenolic compounds with formaldehyde to form polymeric systems can be either acid- or base-catalyzed. Resins made using an acid catalyst and a phenol-to-formaldehyde ratio greater than 1 are referred to as novolaks. Novolaks require the addition of another reactive component to effect cure. Resins made using a basic catalyst and a phenol-to-formaldehyde ratio less than 1 are referred to as resoles. Resoles contain reactive hydroxymethyl end-groups that can further react to form the cured state. Almost all phenolic adhesive systems used to bond wood are base-catalyzed resole resins.

In resole resins, 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. To determine a method to predict the reactivity of phenolic compounds, this study investigated the formation of hydroxymethyl derivatives under basic conditions on reacting formaldehyde with phenolic compounds using computational chemistry methods. The results of those computational chemistry calculations are compared with experimental data reported in the literature.

RESULTS AND DISCUSSION

There is a large amount of literature on the general reactivity of aromatic compounds, especially correlation of reactivity with Hammett activity coefficients[5] localization energy,[6] and frontier molecular orbitals.[7] Many experimental kinetic studies have been conducted on the reactivity of phenolic compounds (especially phenol) with formaldehyde, [8–20] but few systematic studies have been conducted that compare the reactivity of different phenolic compounds with formaldehyde, especially under the same reaction conditions.

A particularly extensive study was conducted by Sprung,[8] who reported data for the reactivities of a variety of phenolics under the same set of reaction conditions. The reactions were carried out under anhydrous conditions rather than under the aqueous reaction conditions typically employed for the preparation of phenolic adhesives. Sprung did note, however, that the kinetic courses of the reactions were similar to those found 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, the data are useful for both qualitative assessments and for testing the use of computational methods to predict the reactivity of phenolics.

The reaction of phenolics (e.g., phenol) with formaldehyde (Fig. 1) corresponds to an electrophilic aromatic substitution.[21] 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 at the *ortho*- and *para*-positions can then occur with the partial positive charge on the carbon of formaldehyde.

Total electron density calculations at carbons of the phenol ring[22,23] using CNDO/2[24] and MNDO[25] have been used to explain the fact that

Table I Relative Reaction Rates of Formaldehyde with Various Phenols at 90°C Under Anhydrous Conditions[8]

Compound	Abbreviation	Relative Rate
3,5Xylenol	35MP	7.75
m-Cresol	3MP	2.88
2,3,5-Trimethylphenol	235MP	1.49
Phenol	—	1.00
3,4-Xylenol	34MP	0.83
2,5-Xylenol	25MP	0.71
p-Cresol	4MP	0.35
Saligenin	—	0.34
o-Cresol	2MP	0.26
2,6-Xylenol	26MP	0.16

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 was best explained by the electron density in the HOMO of the reactant molecules.[23] Recently, charges calculated by *ab initio* methods were used to explain the copper-catalyzed oxidative phenol coupling reaction.[26] While 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.

Table I lists those phenolic compounds for which Sprung obtained kinetic data on reactivity with formaldehyde. The relative reaction rates of the phenolic compounds with formaldehyde cover a wide range. This wide range in reactivity illustrates the subtle effect that chemical structure has on reactivity. Because of their wide range of kinetic rate constants and the large number of compounds studied under the same reaction conditions, Sprung's data were ideal for comparing with computational data. At the conditions employed for the reactions, only mono-addition reactions were thought to have occurred to any significant extent.' Sprung obtained first-order, apparent kinetic rate constants by following the disappearance of formaldehyde. Thus, the rates are overall rates that account for reaction of formaldehyde at all possible reactive sites on the phenolic ring.

For purposes of determining reactivity by computational means, three criteria were considered necessary for reaction to take place: Reaction of formaldehyde with a given phenolic compound would occur only 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. These criteria are, in effect, a reflection of the Klopman and Salem equation[7] for estimating chemical reactivity.

Semiempirical Calculations

Initial calculations were conducted on the phenolate anions at the restricted Hartree–Fock level of theory using PM3. These calculations afforded information on the molecular orbitals and the charge at each of the atomic nuclei. 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 charges at those atomic sites of the phenolic ring on which the HOMO was located and on which no substituent (other than hydrogen) was present were summed to give the quantity Σq (Table II). The charges at those sites with substituents were eliminated from Σq as an incomplete means of accounting for steric interactions that would interfere with the approach of the formaldehyde molecule. A plot of the absolute value of Σq calculated for each phenolic compound versus the relative reaction rate for that phenolic compound did not indicate a linear relationship. A semilog plot of the absolute value of Σq versus the relative reaction rate (Fig. 3) did indicate a general correlation. However, it is clear from Figure 3 that Σq as calculated using the PM3 formalism is not a good parameter upon which to correlate the reactivity of phenolic compounds with formaldehyde. The sum of the electron density in P_z of the HOMO at these sites also was not a good basis for correlation of the reactivity of the phenolics.

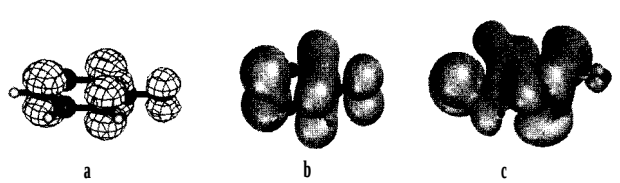

Figure 2 HOMO of the phenolate anion calculated at (a) RHF/PM3, (b) RHF/6-31+G, and (c) B3LYP/6-311+G(2d,p). Calculations were conducted with (a) HyperChem[27] and (b,c) Gaussian 98.[28]

Table II Calculation of S*q* from Charges Calculated at RHF/PMS for the Various Phenolic Compounds

	Charges at Each Reactive Center			
Compound[a]	C2	C4	C6	Σq[b]
26MP	−0.33	−0.35	−0.33	−0.35
2MP	−0.34	−0.35	−0.36	−0.71
Saligenin	−0.36	−0.35	−0.35	−0.70
4MP	−0.36	−0.34	−0.36	−0.72
25MP	−0.34	−0.35	−0.34	−0.69
34MP	−0.36	−0.33	−0.36	−0.72
Phenol	−0.36	−0.36	−0.36	−1.08
235MP	−0.33	−0.34	−0.34	−0.68
3MP	−0.35	−0.35	−0.36	−1.06
35MP	−0.36	−0.34	−0.35	−1.05

[a] See Table I for definition of abbreviations for the compounds.
[b] Σq represents the sum of the charges on the unsubstituted reactive centers (outlined) at C2, C4, and C6 of the phenolic nucleus.

Ab Initio Calculations

Ab initio calculations were then made on each of the phenolic compounds listed in Table I using Hartree-Fock and density functional theory methods and a variety of methods to determine atomic charges. Σq was calculated from the atomic charges afforded by these methods in a manner similar to that described above. Table III presents an overview of the correlation of these results with the experimental kinetic data. It can be seen from the results in Table III that the absolute value of Σq calculated from charges determined by the CHelpG and Merz-Kollman/Singh (MKS) methods give excellent correlation with the log of the experimental relative-rate constants. Figure 4 illustrates the excellent correlation obtained between Σq calculated at RHF/6-31+G and the kinetic data of Sprung.

Because of the additional orbitals on all heavy atoms, the HOMOs calculated at B3LYP/6-311+G(2d,p) were not as cleanly centered on the *ortho* and *para* carbon atoms of the phenolic rings as were the HOMOs calculated with the other model chemistries (Fig. 2). For purposes of calculating Σq at B3LYP/6-311+G(2d,p), only those charges at the same atoms used in the calculations at the other model chemistries were used. However, from the data presented in Table III, this method clearly also gives excellent correlation between Σq and the experimental reaction rates.

Reactivity at Individual Reaction Sites

Although the *ab initio* methods discussed above give an excellent correlation between Σq and Sprung's kinetic data, this correlation was unsatisfactory in one regard: While this method allowed correlation of the kinetic data with the sum of the charges at the respective reactive sites, it did not allow the reactivity at individual, reactive phenolic ring positions to be compared.

A crude estimate of the reactivity at individual reaction sites for each phenolic compound studied by Sprung can be obtained by dividing the relative kinetic rate constant for that phenolic compound by the number of reactive sites in that compound. This affords an average relative rate constant for each compound. A semilog plot of the average relative rate constants versus the average atomic charge (i.e., Σq divided by the number of reactive sites) gives a linear relationship (Fig. 5), confirming the fact that the rate of reaction

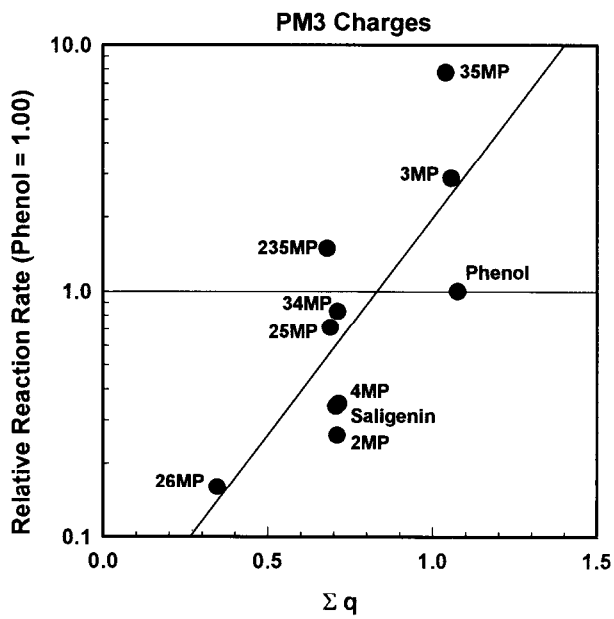

Figure 3 Semilog plot of the absolute value of Σq versus relative reaction rate for reaction of the phenols with formaldehyde. Charges were calculated at RHF/PM3 using HyperChem.[27] The line represents the first-order regression of the data using SigmaPlot.[29]

Table III Correlation of Σq with the Experimental Kinetic Data of Sprung[8a]

	Correlation Coefficient (R^2)			
Atomic Charge Method	RHF/PM3	RHF/6-31G	RHF/6-31+G	B3LYP/6-311+G(2d,p)
Mulliken	0.60	0.77	0.30	0.49
HOMO P_z electron density	0.62	—	—	—
NBO	—	0.66	0.66	0.64
CHelp	—	0.77	0.80	0.80
CHelpG	—	0.94	0.96	0.98
MKS	—	0.97	0.98	0.95

[a] Σq was determined with various computational methods using several methods of calculating atomic charges as indicated. The correlation coefficients were determined from a first-order regression of Σq against the log of the relative kinetic rate constants for reaction between formaldehyde and the phenolic compounds studied by Sprung[8] using SigmaPlot.[29]

(k_i) at an individual site (i) on a given phenolic compound appears to be correlated with the calculated atomic charge (q_i) at that site. Thus,

$$k_i \sim 10^{(q_i)}$$

The correlation between average relative kinetic rate constants and average charge for a given phenolic compound is not as good (Table IV) as that for the correlation previously discussed. Again, the CHelpG and MKS methods of calculating atomic charge appear to give stronger correlations.

To further explore the relationship between k_i and an individual contribution tied to the charge at a given reactive site, it was assumed that

$$k_i \simeq a + 10^{(b \times q_i + c)}$$

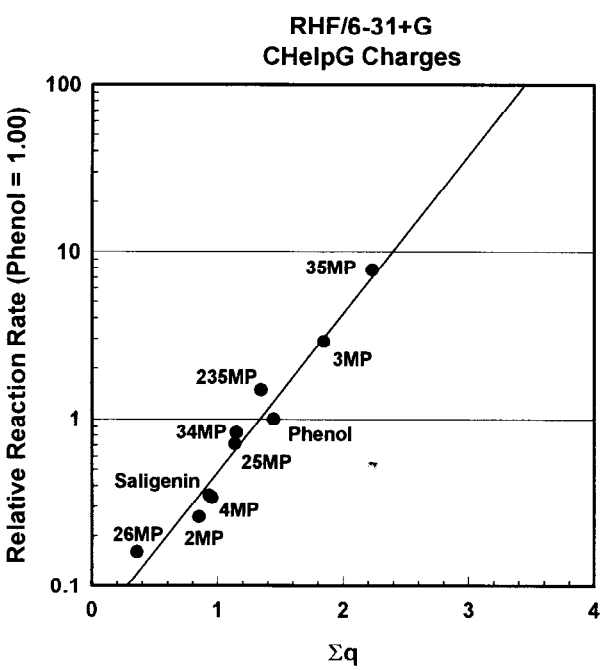

Figure 4 Semilog plot of the absolute value of Σq versus relative reaction rate for reaction of the phenols with formaldehyde. CHelpG-based charges were calculated at RHF/6-31+G using Gaussian 98.[28] The line represents the first-order regression of the experimental data versus Σq using SigmaPlot.[29]

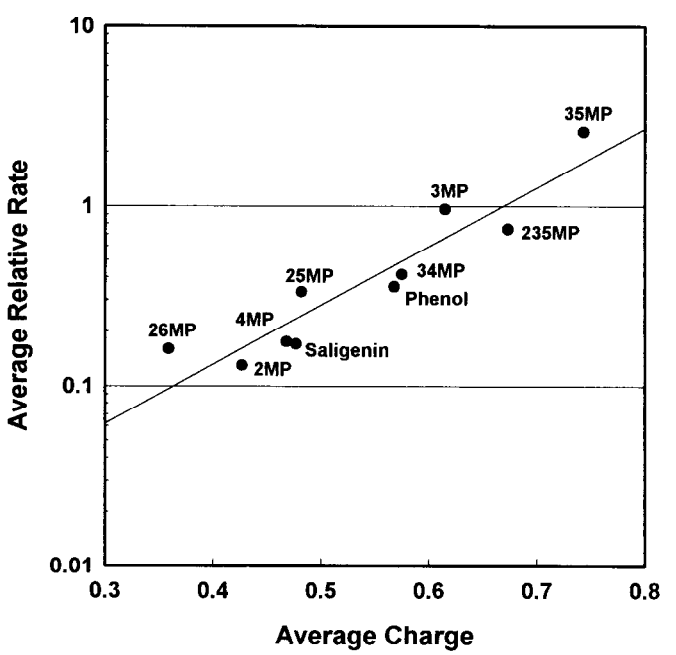

Figure 5 Semilog plot of the absolute value of the average atomic charge versus average relative reaction rate for reaction of the phenols with formaldehyde. CHelpG-based atomic charges were calculated at RHF/6-31+G using Gaussian 98.[28] The line represents the first-order regression of the data using SigmaPlot.[29]

Table IV Correlation of Average Charge at the Reactive Sites with the Average Kinetic Rate Constants for Those Reactive Sites[a]

	Correlation Coefficient (R^2)		
Atomic Charge Method	RHF/6-31g	RHF/6-31+G	B3LYP/6-311+G(2d,p)
CHelp	0.23	0.29	0.31
CHelpG	0.85	0.87	0.86
MKS	0.79	0.80	0.72

[a] Charge was determined with various computational methods as indicated. The correlation coefficients were determined from a first-order regression of average charge against the log of the average relative kinetic rate constants for reaction between formaldehyde and the phenolic compounds studied by Sprung[8] using SigmaPlot.[29]

where *a*, *b*, and c are constants associated with all reactive centers on all phenolic compounds. It then follows that Sprung's apparent rate constant (k_{apparent}) for the reaction of a given phenolic compound with formaldehyde can be formulated as

$$k_{\text{apparent}} = \sum k_i \simeq \sum [a + 10^{(b \times q_i + c)}]$$

k_{apparent} is known experimentally from Sprung's data, and q_i at each reactive site is available from the chemical computations. Therefore, *a*, *b*, and c can be determined by regressing the right side of the equation against the experimental data using nonlinear methods (Table V). This method allows the experimental rate constants to be separated into contributions that can be attributed to each reactive center in proportion to the atomic charge at that reactive center (Table VI).

Figure 6 illustrates the relative magnitudes of the reactivity at each of the reactive centers for all the compounds studied by Sprung based upon CHelpG charges calculated at RHF/6-31+G. However, the predictions of positional reactivity (Table VI) depend upon the computational methods that were used for the calculation. Thus, for example, use of CHelpG-based charges led to the prediction that the reactivity of 35MP is due to reactions at C2, C4, and C6, whereas, use of MKS-based charges led to the prediction that the reactivity of 35MP is due predominately to reaction at C4. Also, there are differences depending on whether Hartree-Frock or density functional theory methods were used to compute the charges. Unfortunately, Sprung's experimental data do not include information on the reactivity of formaldehyde at individual phenolic sites. In the absence of experimental data on the reactivity of formaldehyde at the individual positions of the phenolic compounds, it is not possible to determine which computational method might provide the best predictions of positional reactivity. Experiments are underway to obtain the data needed for comparison.

COMPUTATIONAL METHODS

Structure optimizations as well as energies and charges for each of the compounds were calculated with the same level of theory and basis set.

Table V Constants Obtained by Nonlinear Regression of the Experimental Relative Rates Determined by Sprung and the Positional Charges That Were Calculated by the Methods Indicated[a]

Computational Method	Atomic Charge Method	*a*	*b*	*c*
RHF/6-31G	CHelpG	0.21 ± 0.07	-19.5 ± 3.3	-13.1 ± 2.3
	MKS	0.43 ± 0.11	-108.5 ± 56.4	-91.0 ± 47.6
RHF/6-31+G	CHelpG	0.21 ± 0.09	-16.4 ± 3.0	-11.4 ± 2.3
	MKS	0.42 ± 0.12	-31.6 ± 11.1	-29.5 ± 10.9
B3LYP/6-311+G(2d,p)	CHelpG	0.30 ± 0.15	-16.3 ± 5.6	-9.1 ± 3.5
	MKS	0.43 ± 0.12	-27.6 ± 11.3	-23.3 ± 10.2

[a] The values of the constants are shown ± standard error.

Table VI Calculated Relative Rates (CRR) for the Reaction of Various Phenolic Compounds with Formaldehyde[a]

		Relative Rate at Each Reactive Center[c]		
Compound[b]	CRR	C2	C4	C6
		CHelpG charges		
26MP	0.21/0.22/0.31	0.00/0.00/0.00	0.21/0.22/0.31	0.00/0.00/0.00
2MP	0.46/0.47/0.64	0.00/0.00/0.00	0.21/0.22/0.31	0.25/0.25/0.33
Saligenin	0.49/0.49/0.63	0.00/0.00/0.00	0.22/0.23/0.31	0.26/0.26/0.32
4MP	0.47/0.47/0.64	0.23/0.24/0.32	0.00/0.00/0.00	0.23/0.24/0.32
25MP	1.00/0.99/1.23	0.00/0.00/0.00	0.24/0.24/0.36	0.77/0.74/0.87
34MP	0.84/0.90/0.88	0.59/0.64/0.55	0.00/0.00/0.00	0.25/0.26/0.33
Phenol	0.75/0.77/1.00	0.27/0.28/0.34	0.22/0.22/0.32	0.27/0.28/0.34
235MP	1.74/1.87/2.11	0.00/0.00/0.00	0.81/1.04/1.37	0.93/0.84/0.74
3MP	2.37/2.24/1.47	1.73/1.56/0.67	0.31/0.34/0.43	0.33/0.34/0.36
35MP	7.80/7.79/7.67	2.59/2.09/1.37	2.63/3.61/4.93	2.59/2.09/1.37
		MKS charges		
26MP	0.43/0.42/0.43	0.00/0.00/0.00	0.43/0.42/0.43	0.00/0.00/0.00
2MP	0.86/0.83/0.85	0.00/0.00/0.00	0.43/0.42/0.43	0.43/0.42/0.43
Saligenin	0.86/0.83/0.85	0.00/0.00/0.00	0.43/0.42/0.43	0.43/0.42/0.43
4MP	0.86/0.83/0.85	0.43/0.42/0.43	0.00/0.00/0.00	0.43/0.42/0.43
25MP	0.86/0.85/0.88	0.00/0.00/0.00	0.43/0.42/0.43	0.43/0.43/0.46
34MP	0.86/0.84/0.85	0.43/0.42/0.43	0.00/0.00/0.00	0.43/0.42/0.43
Phenol	1.29/1.25/1.28	0.43/0.42/0.43	0.43/0.42/10.43	0.43/0.42/0.43
235MP	1.51/1.69/1.55	0.00/0.00/0.00	0.47/0.92/0.99	1.04/0.76/0.55
3MP	1.29/1.30/1.29	0.43/0.47/0.44	0.43/0.42/0.43	0.43/0.42/0.43
35MP	7.75/7.74/7.75	0.46/0.49/0.44	6.42/6.59/6.84	0.87/0.66/0.47

[a] The calculated relative rates were partitioned into relative rates for reactions at each reactive center on the phenolic compound using the methods discussed in the text.
[b] See Table I for definition of abbreviations for the compounds and for listing of experimental relative rates.
[c] The first value was obtained with RHF/6-31G; the second, with RHF/6-31+G; and the third, with B3LYF'/6-311+G(2d,p).

Semiempirical calculations were conducted on a Gateway 2000 PC at RHF/PM3[30] using HyperChem. All *ab initio* calculations were performed on an IBM Model 720 RISC/6000 Workstation with GAMESS[31] and on a 400-MHz Pentium II based PC with Gaussian 98.[28] The optimized structures obtained from HyperChem were used as the starting structures for calculations at RHF/6-31G using GAMESS. The GAMESS-optimized structures were used for optimizing structures and calculating Mulliken-, NB0-,[32] CHelp-,[33] CHelpG-,[34] and Merz-Kollman/Singh[35,36] -based charges at RHF/6-31G, RHF/G-31+G, and B3LYP/6-311+G(2d,p) using Gaussian 98.

CONCLUSIONS

The results presented above indicate that *ab initio* computational chemistry methods coupled with newer methods to calculate atomic charges can be used to explain the relative reactivities of phenolic compounds with formaldehyde. However, these results are only qualitative. The experimental kinetic data with which the computational chemistry calculations were compared were determined before the advent of such analytical techniques as NMR and HPLC. These techniques would be able to determine whether or not reactions in addition to those needed for the formation of monohydroxymethyl derivatives of the phenolic compounds were responsible for the consumption of formaldehyde. However, these are the only available data that cover a wide range of phenolic compounds reacted with formaldehyde at the same conditions. Also, 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 neigh-

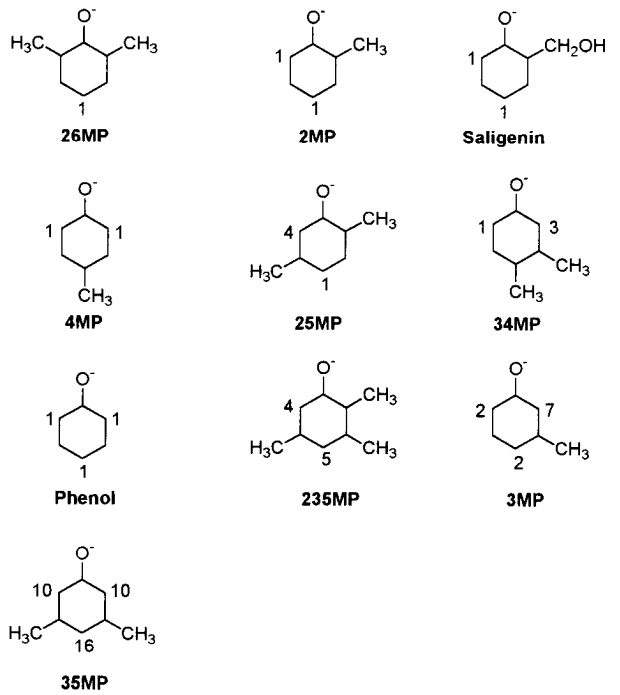

Figure 6 Relative reactivities with formaldehyde at the reactive centers of the phenolic compounds studied by Sprung[8] based upon CHelpG-based charges calculated at RHF/6-31+G. The relative reactivity of the *para*-position of phenol is taken as 1 (See Table I for abbreviations of compound names).

boring groups probably are also important. 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 using other data available in the extant literature are being conducted.

I thank Dr. Steve Verrill of the Forest Products Laboratory for his assistance in conducting statistical analyses and nonlinear regressions on the data.

REFERENCES

1. White, J. T. In Wood Adhesives 1995; Christiansen, A. W.; Conner, A. H., Eds.; Forest Products Society: Madison, WI, 1996; pp 3–8.
2. Lambuth, A. L. In Adhesives from Renewable Resources; Hemingway, R. W.; Conner, A. H., Eds.; ACS Symposium Series 385; American Chemical Society: Washington, DC, 1989; pp 1–10.
3. Pizzi, A. In Handbook of Adhesive Technology; Pizzi, A.; Mittal, K. L., Eds.; Marcel Dekker: New York, 1994; pp 347–358.
4. Pizzi, A. In Handbook of Adhesive Technology; Pizzi, A.; Mittal, K. L., Eds.; Marcel Dekker: New York, 1994; pp 359–368.
5. Hansch, C.; Leo, A. Exploring QSAR: Fundamentals and Applications in Chemistry and Biology; American Chemical Society: Washington, DC, 1995.
6. Higasi, K.; Baba, H.; Rembaum, A. Quantum Organic Chemistry; Interscience: New York, 1965.
7. Fleming, I. Frontier Orbitals and Organic Chemical Reactions; Wiley: New York, 1976.
8. Sprung, M. M. J Am Chem Soc 1941, 63, 334.
9. De Jong, J. I.; De Jong, J. Rec Trav Chim 1953, 72, 497–509.
10. Freeman, J. H.; Lewis, C. W. J Am Chem Soc 1954, 76, 2080–2087.
11. Dijkstra, R.; De Jong, J.; Lammers, M. F. Rec Trav Chim 1962, 81, 285–296.
12. Zavitsas, A. A.; Beaulieu, R. D.; LeBlanc, J. R. J Polym Sci Part A-1 1968, 6, 2541–2559.
13. Aldersley, J. W.; Hope, P. Angew Makromol Chem 1972, 24, 137–153.
14. Troughton, G. E. Holzforschung 1972, 26(5), 170–173.
15. Sebenik, A.; Lapanje, S. Angew Makromol Chem 1977, 63, 139–156.
16. Sebenik, A.; Lapanje, S. Angew Makromol Chem 1978, 70, 59–70.
17. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P. Polymer 1994, 35, 3046–3054.
18. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P. Polymer 1996, 37, 939–953.
19. Grenier-Loustalot, M.-F.; Larroque, S.; Grande, D.; Grenier, P. Polymer 1996, 37, 1363–1369.
20. Higuchi, M.; Nohno, S.; Morita, M.; Tohmura, S.-I. In International Contributions to Wood Adhesion Research; Christiansen, A. W.; Pilato, L. A., Eds.; Forest Products Society: Madison, WI, 1999; pp 101–107.
21. Knop, A.; Scheib, W. Chemistry and Application of Phenolic Resins; Springer-Verlag: New York, 1979.
22. Knop, J. V.; Knop, A. Reported in Knop, A.; Scheib, W. Chemistry and Application of Phenolic Resins; Springer-Verlag: New York, 1979.
23. Elder, T. J.; Worley, S. D. J Wood Chem Technol 1986, 6, 505–521.
24. Pople, J. A.; Santry, D. D.; Segal, G. A. J Chem Phys 1965, 43, 129.
25. Dewar, M. J. S.; Thiel, W. J Am Chem Soc 1977, 99, 4907.
26. Baesjou, P. J.; Driessen, W. L.; Challa, G.; Reedijk, J. J Am Chem Soc 1997, 119, 12590–12594.
27. HyperChem 4.5; Hypercube: Waterloo, Ont., Canada.
28. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.;

Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.6; Gaussian: Pittsburgh, PA, 1998.

29. SigmaPlot Version 4.0. SPSS: Chicago, IL.
30. Stewart, J. J. P. J Comput-Aided Mol Des 1990, 4, 1–105.
31. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J Comput Chem 1993, 14, 1347–1363.
32. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1; Theoretical Chemistry Institute: University of Wisconsin, Madison, WI.
33. Chirlian, L. E.; Francl, M. M. J Comp Chem 1987, 8, 894.
34. Breneman, C. M.; Wiberg, K. B. J Comp Chem 1990, 11, 361–373.
35. Besler, B. H.; Merz, K. M., Jr.; Kollman, P. A. J Comp Chem 1990, 11, 431.
36. Singh, U. C.; Kollman, P. A. J Comp Chem 1984, 5, 129.