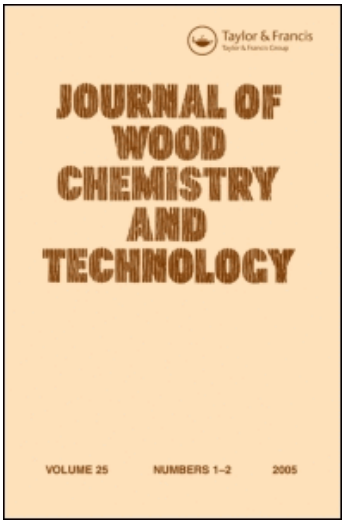

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Elder, T. J. and Worley, S. D.(1986) 'The Application of Molecular Orbital Calculations to Wood Chemistry. IV. The Formation of Methylol Derivatives', Journal of Wood Chemistry and Technology, 6: 4, 505 — 521
To link to this Article: DOI: 10.1080/02773818608085242
URL: http://dx.doi.org/10.1080/02773818608085242

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 6(4), 505-521 (1986)

THE APPLICATION OF MOLECULAR ORBITAL CALCULATIONS TO WOOD CHEMISTRY. IV. THE FORMATION OF METHYLOL DERIVATIVES.[1]

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ABSTRACT

The initial steps in the formation of phenolic resins have been studied by the performance of molecular orbital calculations. The reactions that have been examined are those occurring between formaldehyde and phenol, under basic and acidic conditions. Energies and electronic distributions were determined theoretically, and it was found the reaction is not strictly controlled by the total charge at the reactive centers, but rather seems to be influenced by the electron density in the highest occupied molecular orbital of the reactant molecules.

INTRODUCTION

As the nature of forest resources in the United States has changed, processing technology has also changed to accommodate the resource and the demands of the marketplace. An excellent example is the large segment of the forest products industry responsible for the manufacture of plywood, particleboard, and composite products. While this part of the industry is a major consumer of

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forest resources, it also consumes large amounts of adhesives that are required for the bonding of the finished products. It has been reported that the forest products industry uses 29% of all phenolic resins produced in the United States, making it the single largest consumer of these resins[2].

Since phenolic resins are of obvious importance to the forest products industry, it is not surprising that there has been extensive research into their fundamental properties [3,4] and possible alternatives to petrochemically derived phenol[5,6]. The current paper will address the formation of methylol derivatives, the first step in the polymerization of phenol and formaldehyde to produce resins. The polymerization reaction may occur under either acidic or basic conditions, forming novolak or resole resins, respectively. While the base catalyzed resoles are the resins used as adhesives in forest products application, for the sake of completeness, the acid catalyzed novolaks will also be considered. Novolaks, used to a large extent in molded articles, are linear polymers with molecular weights of about 2,000, while resoles are cross-linked polymers formed by the addition of heat to the hydroxymethyl phenol monomers[2].

Under basic conditions, the phenol is present as a phenolate ion, which adds the neutral, but polarized, formaldehyde in the ortho and para positions. The displaced proton is shifted to the oxygen of the formaldehyde, resulting in the methylol derivative (Figure 1). In contrast, the reaction leading to the novolak polymer begins by the conversion of formaldehyde, in the presence

Neglect of Diatomic Overlap), are both semi-empirical, molecular orbital techniques, and their respective capabilities have been discussed by Dewar and Ford [9]. In particular, CNDO/2 does not contain a geometry optimization procedure, as does MNDO; and CNDO/2 attempts to mimic ab initio results, while MNDO tries to reproduce experimentally determined chemical properties. In other related work, statistical mechanical calculations have been reported for polymeric phenol-formaldehyde resins[10].

METHODS

The computational procedure used in this study was developed by Dewar and Thiel [11], and is a semi-empirical, self-consistent fields method that employs modified neglect of diatomic overlap (MNDO). This procedure calculates an energetically optimized geometry, heat of formation, ionization potential (by Koopmans' theorem), dipole moments, and eigenvectors, and eigenvalues for the molecular orbitals of the molecules.

The structures that will be discussed are shown in figures 3-6 along with the numbering system that is used throughout this paper. The trial geometry for each molecule is input by specifying bond lengths, bond angles, dihedral angles, and connectivity for all atoms in the molecule. Furthermore, values for overall charge may be input for calculations on ionic species, and all variables were allowed to optimize.

As shown in the figures, the initial structures were neutral phenol for the novolak, and the phenolate anion for resole. For

each reaction, three mono-methylol derivatives and three di-methylol products were examined, along with the intermediates formed at each step. Two ortho structures were used in this study to reflect the difference that may occur in conformation of the substituent groups at the phenolic position. This logic was followed throughout this paper, such that the two ortho positions are always treated as distinct sites.

RESULTS

Novalak

The heat of formation for each structure and intermediate is shown in figures 3 and 4. Observations on the mono-methylol derivatives (Figure 3) indicate that the most stable product is formed through the para position (C-4), followed by positions C-6 and C-2. This sequence is reflected by the heats of formation (localization energy) for the preceding intermediates, but the magnitude of the negative charge at each site in the phenol ground state is found to be C-2 > C-4 > C-6. The electron density in the highest occupied molecular orbital (HOMO) at these positions in the phenol does, however, have the order C-4 > C-6 > C-2. This is consistent with the results presented in Elder and Worley[12], in which the reactions of soft electrophiles and soft nucleophiles, are controlled by the properties of the HOMO of the nucleophile and the LUMO (lowest unoccupied molecular orbital) of the electrophile.

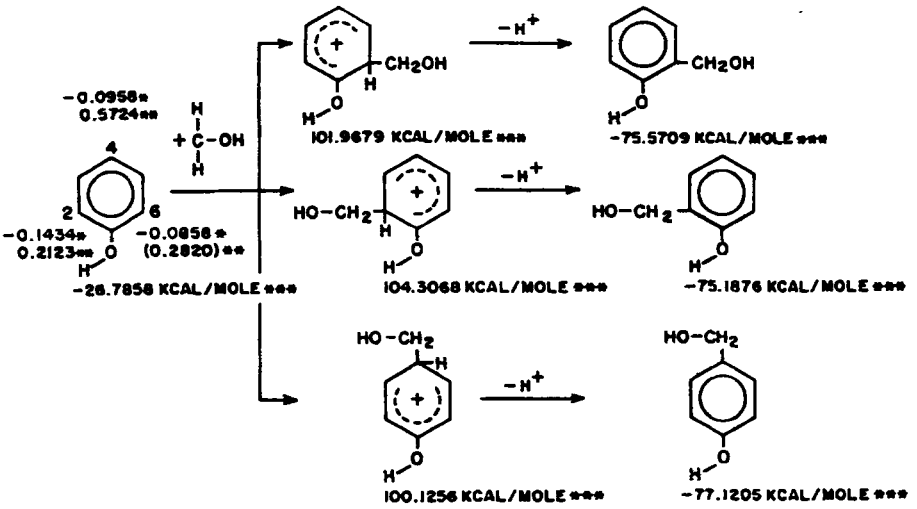

Figure 3. The formation of monomethylol intermediates and derivatives from phenol. * = Charge at each site, ** = HOMO electron density at each site, *** = Heat of formation of each structure.

The next step to be considered is the formation of di-substituted intermediates and methylols, from the mono-substituted, hydroxymethyl phenol (Figure 4). As was the case with phenol the reaction of 6-hydroxymethyl phenol (Figure 4b), and 4-hydroxymethyl phenol (Figure 4a), the reactive centers through which the lowest energy intermediates are formed, are not the positions within the neutrals that have the greatest negative charge. Rather, the HOMO electron density is again a more accurate predictor of reactivity. The reaction of the 2-hydroxymethyl phenol (Figure 4c) shows that the neutral molecule has greater magnitude in both charge and HOMO electron density at

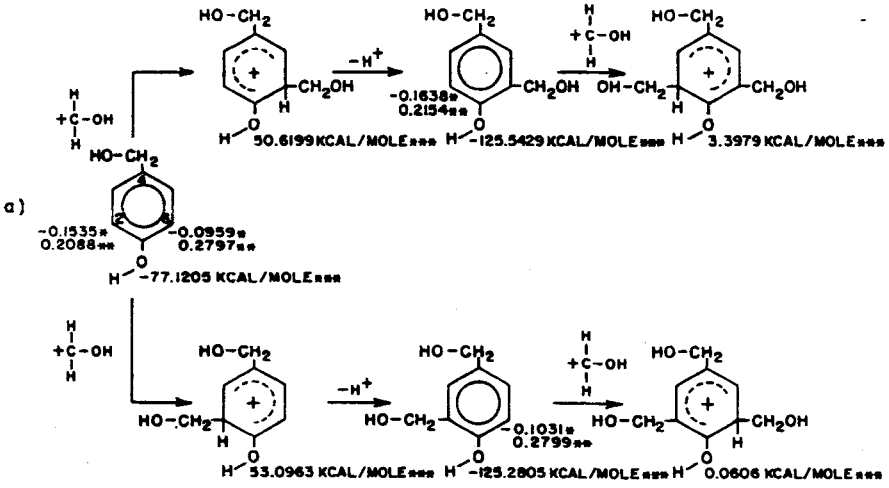

Figure 4. The formation of dimethylol intermediates, derivatives, and trimethylol intermediates from each monosubstituted methylol derivative. * = Charge at each site, ** = HOMO electron density at each site, *** = Heat of formation of each structure.

the C-4 position, through which the most stable intermediate is formed.

Finally, the disubstituted methylol derivatives and the trisubstituted intermediates will be discussed. Based on the charge distribution for the neutral di-methylol derivatives, it would be expected that attack would occur preferentially at the C-2 position of the 4-6 derivatives followed by the C-4 position of the 2-6 derivatives and the C-6 position of the 2-4 derivatives. This pattern is not, however, reflected in the energy values for the intermediates. Energetically, the intermediate formed by reaction at the position C-4 of the 2-6 derivative is the most stable followed by the C-6 position of the

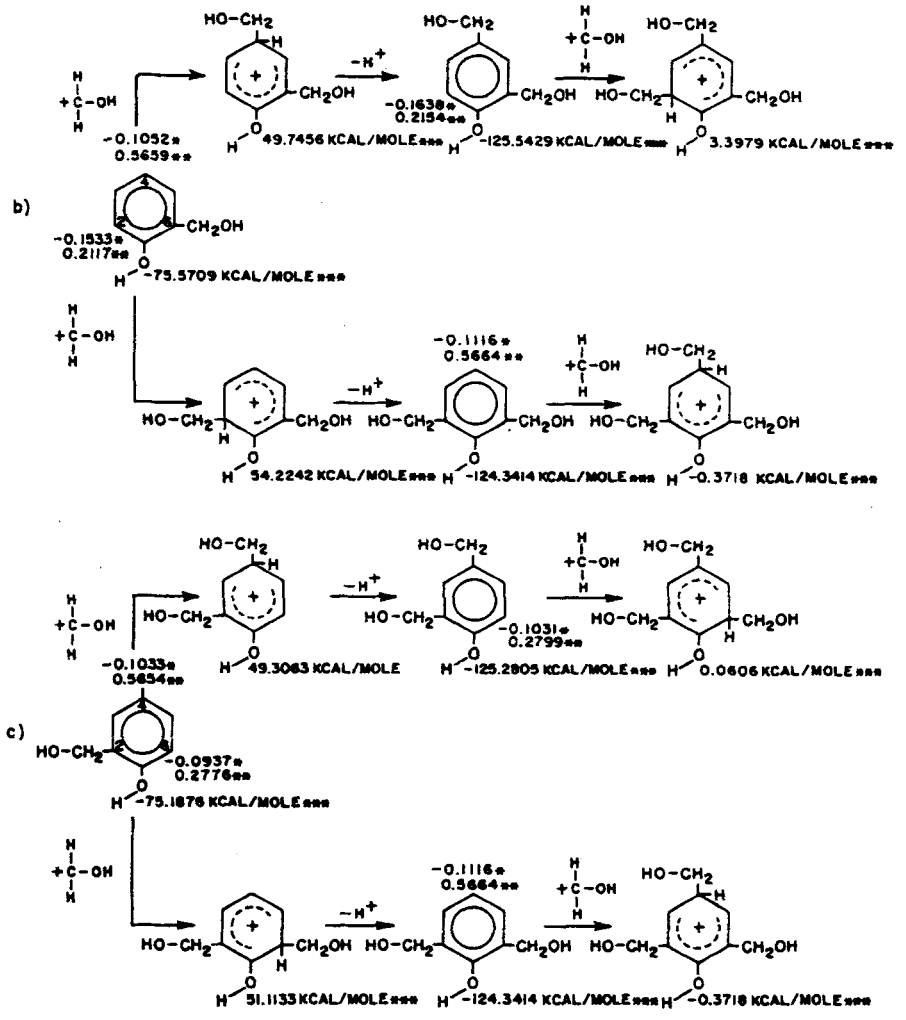

Figure 4 cont.

2-4 derivative and the C-2 position of the 4-6 derivative. Again, to rationalize these data, observations must be made on the HOMO electron density of the respective neutral ground states. It is found that this value is greatest at the C-4 position, followed by C-6 and C-2. This pattern accurately reflects the stability of the intermediates that are formed. Furthermore, it is interesting to note that if all intermediates are considered, those that are formed by attack through the C-4 position (para to the phenolic group) tend to be the most stable.

It is indicated from the lack of coulombic control of these reactions that the chemical species in question are experiencing a soft-soft reaction, under the influence of the frontier molecular orbitals[13].

Resoles

The heat of formation for each structure in the alkaline catalyzed reaction of phenol and formaldehyde was determined to be as shown in Figures 5 and 6. As before, the total charge density and HOMO electron density of the reactive sites are also shown.

The most stable mono-substituted intermediate is formed by reaction at the para position (Figure 5). While the total charge density does not differ to a large extent at any of the potentially reactive sites, the para position has the greatest HOMO electron density. In examining the next step, the transfer of the proton to the carbonyl oxygen to form the mono-methylol derivatives, the two ortho substituted products have the lowest energy values.

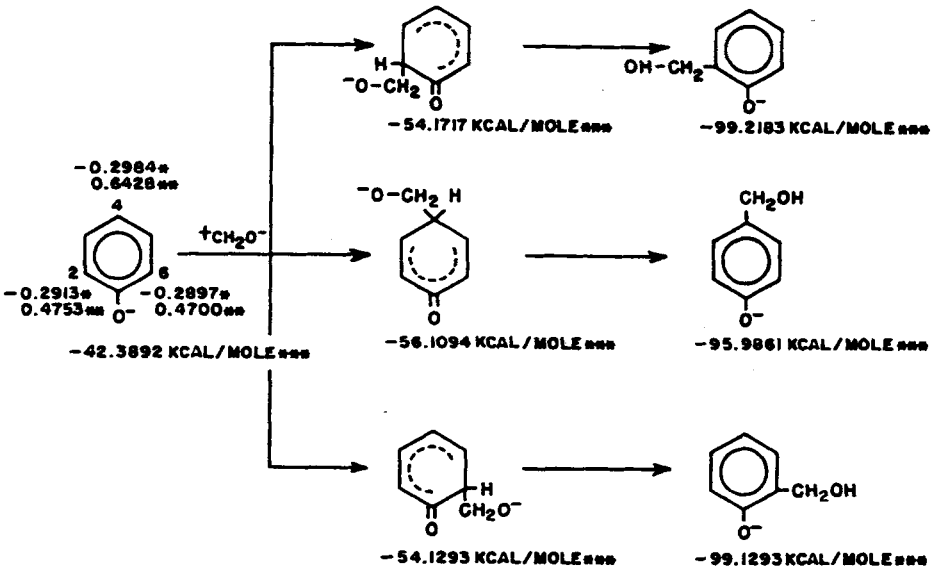

Figure 5. The formation of monomethylol intermediates and derivatives from the phenolate anion. * = Charge at each site, ** = HOMO electron density at each site, *** = Heat of formation of each structure.

This pattern continued to occur in the reactions that lead to the formation of the disubstituted methylols (Figure 6). If the para position is an open site in the mono-methylols, it is greater in both total charge density and HOMO electron density, and forms the lower energy intermediate. Upon completion of the reaction, however, products that are disubstituted at the two ortho positions are lower in energy than those that involve the para position. Finally, the reaction of the disubstituted methylols to form the trisubstituted intermediates also follows the same pattern. The para position, once again, has the greatest

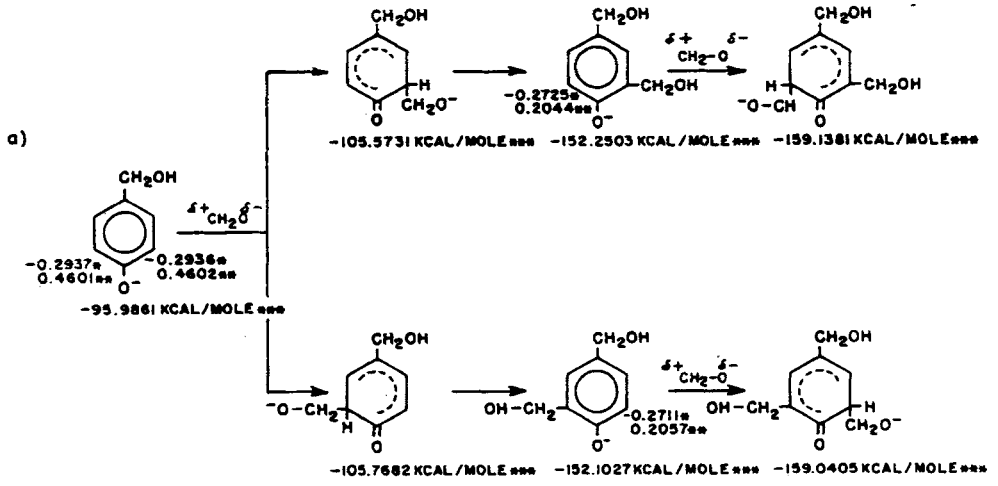

Figure 6. The formation of dimethylol intermediates, derivatives and trimethylol intermediates from each monosubstituted methylol derivative. * = Charge at each site, ** = HOMO electron density at each site, *** = Heat of formation of each structure.

concentration of negative charge, and the largest HOMO electron density, resulting in the intermediate with the lowest heat of formation.

These results illustrate the point that was made earlier with regard to the difference between kinetic stability and thermodynamic stability. The reaction indices that are reported, and energies of the intermediates, indicate that the para position is the most reactive site, but the most stable products from a thermodynamic standpoint are those that occur through one of the ortho positions. A possible explanation for this discrepancy lies in the ability of the phenolic oxygen to hydrogen bond with the

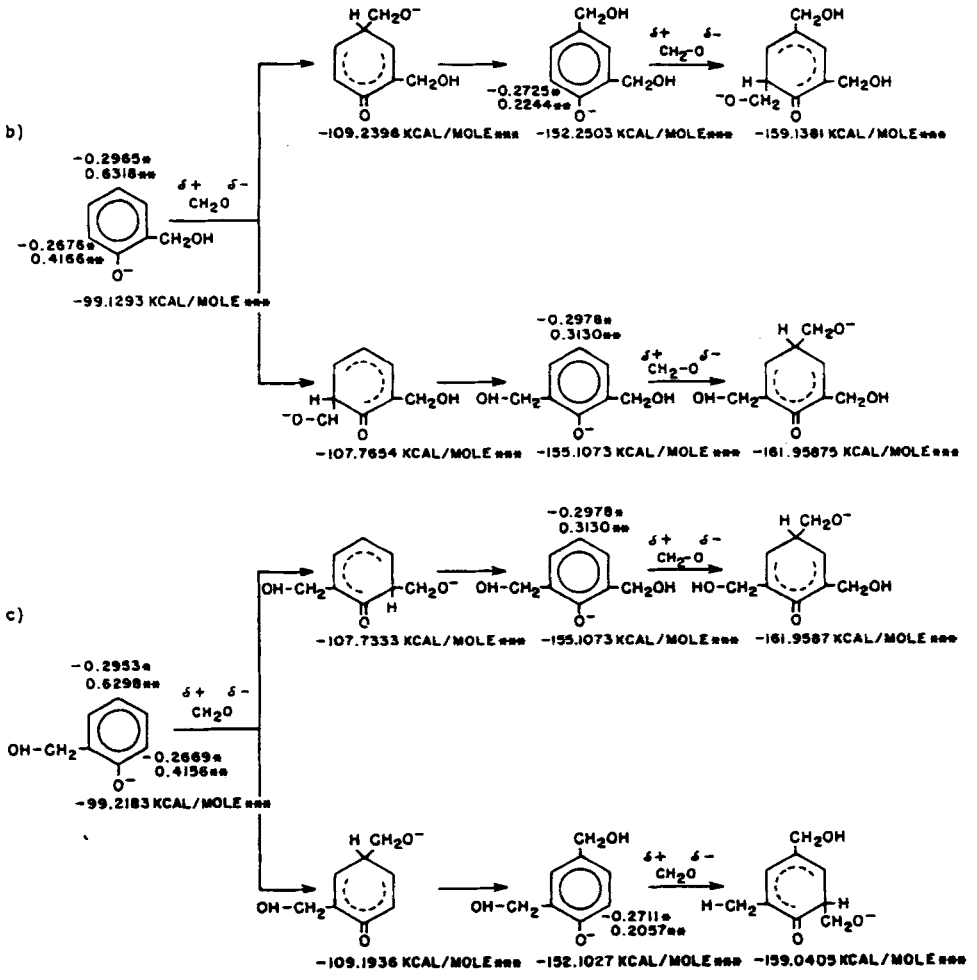

Figure 6 cont.

TABLE 1. Results from Rotation of Hydroxyl on Ortho-methylol, Relative to the Phenolic Oxygen.

Rotation	Heat of Formation (energy)
0 (equilibrium)	-99.2183 kcal/mole
45	-97.7576
90	-95.2260
135	-94.0806
180	-93.0606
225	-94.3028

hydroxyl group present on the ortho substituted methylol derivatives. This was assessed by incrementally rotating the hydroxyl group and determining the energy at a number of dihedral angles (Table 1). It was found that the most stable position was that determined by the initial optimization, in which the hydroxyl group is planar with the aromatic ring and pointing toward the phenolic oxygen. Deviations from this conformation caused an increase in the energy of the system, providing evidence that this is a hydrogen-bonded system.

It is also interesting to compare the energies calculated for the various structures and intermediates with activation energies from experimental determinations. The energies of reaction may be found by subtracting the total energy of the reactants from the energy of the product for each step. The energy of each anion is as shown in Figures 5 and 6, but in order to compare these values directly with the intermediate structures, the heat of formation of the formaldehyde must be added to that of the anion. Since the unreacted phenolate ion has a heat of formation of -42.3892

Table 2. Comparison of calculated and experimental (from reference 14) activation energies for the methylolation reaction.

Reaction	Activation Energy (kcal mole) Calculated	Experimental
Phenol -> o-methylol phenol	21.2-21.3	21.1
phenol -> p-methylol phenol	19.3	20.6
o-methylol phenol -> o,o-dimethylol phenol	24.4-24.5	20.4
o-methylol phenol -> o,p-dimethylol phenol	22.9-23.0	19.0
o,o-dimethylol phenol -> o,o,p-trimethylol phenol	26.1-26.2	21.0
o,p-dimethylol phenol -> o,o,p-trimethylol phenol	26.1	19.3
p-methylol phenol -> o,p-dimethylol phenol	23.2-23.4	19.2

kcal/mole and formaldehyde has been calculated with MNDO to have a heat of formation of -33.0 kcal/mole[14], this side of the reaction will have a total energy of -75.4 kcal/mole. The energy of the ortho substituted intermediate is -56.1094, such that the heat of reaction is found to be 19.3 kcal/mole, which compares to 20.6 kcal/mole reported in the literature[15]. The reactions of the mono- and di-substituted anions to form their corresponding intermediates are similarly calculated, and the results are shown in Table 2, along with the literature values for activation energies. Of course, it should be realized that the activation energies estimated by MNDO are minimum values because the transition state would necessarily be greater in energy than the intermediate structure which represents a minimum on the potential surface.

CONCLUSIONS

It was determined that, in general, the initial reactions of phenol and formaldehyde, whether in acidic or basic environments, are not directly charge mediated. Rather, the electron density of the highest occupied molecular orbital, at a given site is a more reliable reaction index. While this evidence is valid for formaldehyde, other cross-linking agents used in the production of phenolic resins might behave in a totally different manner, depending on their electronic structure. According to current theories of hard-soft electrophiles and nucleophiles, a system that employed a harder electrophile would be more sensitive to coulombic attraction than the formaldehyde used in this study[13].

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