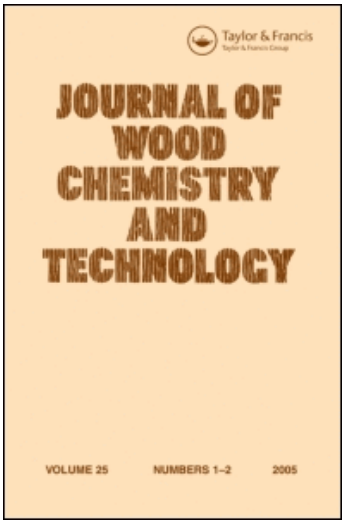

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THE BLEACHING AND PHOTOSTABILIZATION OF HIGH-YIELD PULP BY SULFUR COMPOUNDS. I. REACTION OF THIOGLYCEROL WITH MODEL QUINONES

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ABSTRACT

The reaction of thioglycerol with quinones selected to model the chromophores present in high-yield pulp has been investigated. The reaction is rapid and complex, involving initial Michael addition, aromatization of the adducts to hydroquinones, and reoxidation of those hydroquinones to new chromophores. The Michael addition is responsible for the bleaching effect of thioglycerol upon pulp, and the reoxidation is responsible for the eventual development of more intense color by treated pulp. Semi-empirical and *ab initio* molecular orbital calculations have been used as an aid to rationalizing the experimental results.

INTRODUCTION

In the past, high-yield pulps could be used only for newsprint and magazine papers because their low quality severely limited their ability to compete in higher quality papers, such as printing and writing grades.

Today, state-of-the-art pulp mills are producing high-yield pulps with smoothness, formation, and bonding characteristics suitable for fine papers. Thus, the only remaining obstacle inhibiting wide use of high-yield pulps is their tendency to turn yellow upon exposure to light or heat. Thermally-induced brightness reversion usually results in only 2-5 points loss in brightness, whereas photo-induced reversion of high-yield pulps can cause more than 30 points in brightness loss. For reference, photo-induced reversion causes a loss of approximately 3 brightness units during the lifetime of a typical bleached kraft pulp[1]. Therefore, inhibition of photo-induced reversion is critical for the use of high-yield pulps in printing and writing grades of paper. Recently, the investigation of brightness and brightness reversion of high-yield pulps was identified as a high priority research area by a group of industrial executives and academic researchers in the pulp and paper field[2].

A promising method of brightness stabilization originally was studied by Cole and Sarkanen at the University of Washington[3,4]. In this investigation, several sulfur-containing compounds, including thiols and sulfides, were found to be effective inhibitors of photo-induced yellowing in high-yield pulps. Furthermore, thiols provided the additional benefit of an initial bleaching effect on the pulp. Thioglycerol, for example, initially brightened the pulp; over time, the brightness decayed to near its original value. Then, much more slowly than untreated pulp, the thioglycerol-treated material lost brightness until ultimately in some cases becoming darker than untreated pulp. Both the initial bleach and the stabilizing activity of the sulfur compounds were strongly dependent on molecular structure. Functional group composition, and molecular size and shape appeared to be very important. For example, glycol dimercaptoacetate ($CH_2CH_2(OOCCH_2SH)_2$) and pentaerythritol tetrathioglycolate ($C(CH_2OOCCH_2SH)_4$) had strikingly different effects on stabilization even though the same functional groups are present[5]. Most of these structure-related issues remain unexplained.

The initial results of Cole and Sarkanen, particularly with thioglycerol, have been reproduced repeatedly by numerous scientists throughout the world[6-10]. Although no definitive mechanistic studies have been performed, these workers generally have agreed with Cole and Sarkanen in proposing that these compounds behave as antioxidants, competing with the free phenolic hydroxyl groups in lignin as hydrogen donors. Similarly, the original suggestion that free thiol groups might undergo addition reactions with pre-existing chromophoric quinoidal or stilbenoid structures, thereby converting them to colorless compounds and "bleaching" the pulp, has received support[11-15]. While the extent to which quinones are responsible for the yellow color of aged high-yield pulps is still being debated, many studies support their significant contribution to photochemical and thermal reversion[16-21].

In this paper, we report that a combination of experimental investigations and molecular modeling has confirmed the addition reaction of thioglycerol with chromophoric quinoid structures, and provided a rational explanation for the subsequent redevelopment of color[22]. In subsequent papers of the series, we will report the application of this fruitful combination to the more significant ability of thioglycerol and its cogeners to stabilize high-yield pulp against photo-yellowing.

RESULTS

The five *o*- and *p*-benzoquinones **1** - **5** (Figures 1 - 4) were selected as models for some of the pre-existing chromophores in high-yield pulp. They were prepared and purified as described in the Experimental Section. Each was reacted with thioglycerol (**6**) in methanol solution. Crude product mixtures were acetylated with acetic anhydride and pyridine. Acetylated products were isolated by preparative TLC or HPLC and characterized by ^{1}H nmr, infrared spectroscopy, and elemental

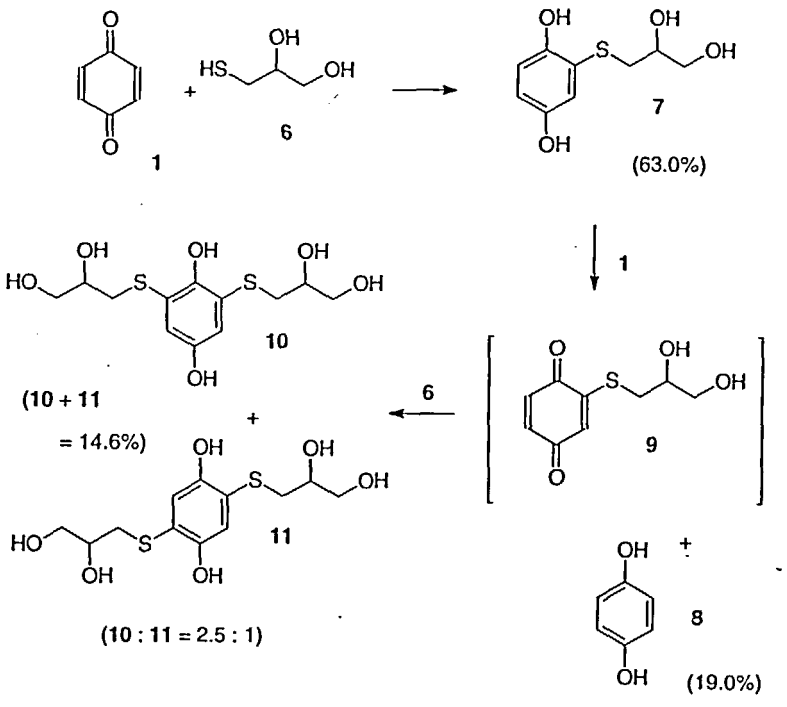

Figure 1: Reaction of thioglycerol with *p*-benzoquinone.

analysis. Details of characterization are provided in the Experimental Section. Acetylated reaction mixtures were quantitated by analytical HPLC using authentic samples from the preparative experiments for identification of peaks. This methodology allowed us to account for 70-95% of the original quantity of quinones brought into reaction; the lesser yields were obtained from the *o*- quinones, the instability of which led to significant formation of unimolecular decomposition products. That is, the results described below clearly represent the major reaction pathways of the quinones.

The acetylation of the reaction mixtures not only facilitated analysis, it stabilized the thioglycerol-quinone adducts against air

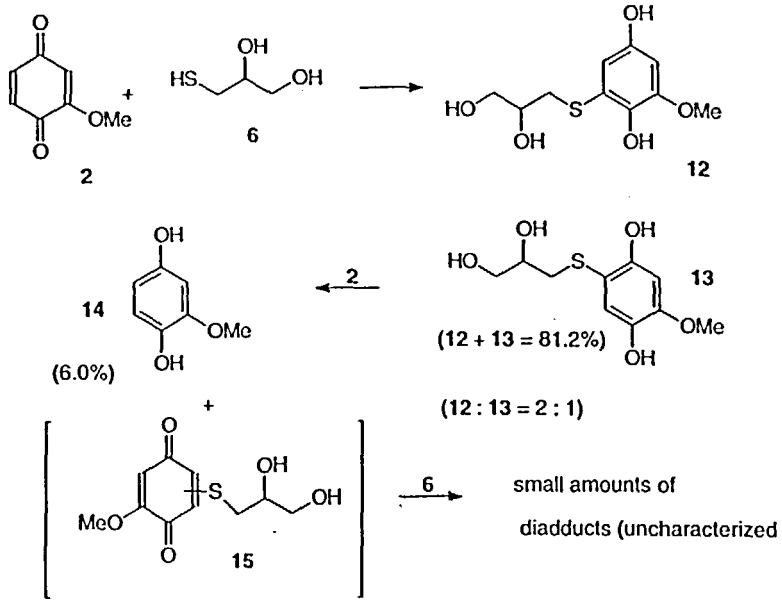

Figure 2: Reaction of thioglycerol with 2-methoxy-1,4-benzoquinone.

oxidation to sulfur-substituted quinones, a process that led to significant color redevelopment during early efforts to separate the reaction mixtures.

The behavior of **1**, shown in Figure 1, is typical of our results. The quinone reacts rapidly with thioglycerol by a Michael addition to give the hydroquinone **7**, which is the principal product observed. Compound **7** then enters into a redox couple with unreacted **1**, producing hydroquinone (**8**) and the thioglycerol-substituted quinone **9**. Such behavior is well-established for reactions of simple thiols with quinones.[23] This new quinone is more reactive toward nucleophilic addition than benzoquinone, and itself enters into reaction with thioglycerol, leading to the mixture of disubstituted hydroquinones **10** and **11**.

Support for this mode of formation of **10** and **11** is found in the near-equivalent yields of **8** (19%) and **10/11** (15%), as well as in the

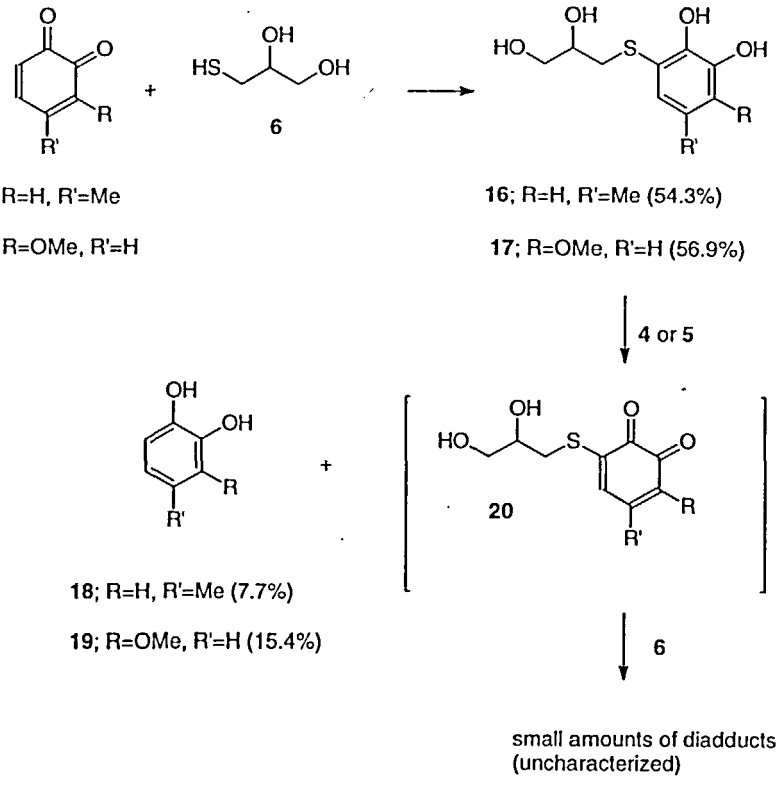

Figure 3: Reaction of thioglycerol with *o*-quinones.

observation that if **1** is reacted with a large excess of thioglycerol, so that all **1** is rapidly converted to **7**, no **8** or **10/11** are formed.

Similar behavior was observed for **2**, **4**, and **5** (Figures 2 and 3), with the exception that these quinones gave much less redox chemistry and multiple substitution. With disubstituted quinone **3**, a second kind of redox chemistry appears, evidenced by the formation of the disulfide of thioglycerol (Figure 4). (The possibility that disulfide **22** is formed by air oxidation of thioglycerol is excluded by our observation that it does not form under these conditions if **3** is omitted from the reaction mixture, as

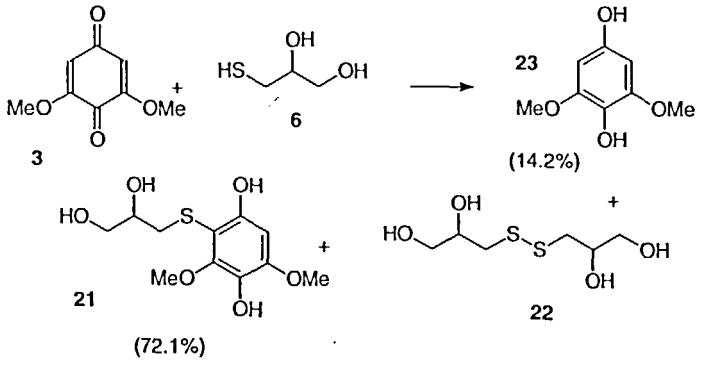

Figure 4: Reaction of thioglycerol with 2,6-dimethoxy-1,4-benzoquinone.

well as by its absence from all other reactions carried out under these same conditions.) Although the major reaction pathway continues to be Michael addition, as also observed by Hirashima and Sumimoto[11] (who found no disulfide!), the direct redox reaction between the quinone and thioglycerol becomes an important reaction channel.

As judged qualitatively by the time required for complete reaction, the relative reactivities of the model quinones toward addition of thioglycerol fell in the order: **1** > **4** > **5** > **2** > **3**. Only quinone **3** yielded any disulfide formation, so that relative reactivities for this process could not be judged.

DISCUSSION

To provide a more detailed understanding of the interaction of thioglycerol and the model quinones, we sought to apply molecular modeling techniques to three aspects of the chemistry described above: (1) the relative reactivities of the quinones toward Michael addition; (2) the regioselectivity of the addition; and (3) the redox reaction between the initial Michael adducts and unreacted quinones.

Frontier molecular orbital (FMO) theory[24] has been applied successfully to prediction of the behavior of a wide variety of organic molecules. For the specific case of nucleophilic addition to quinones[25], the theory suggests that the relative reactivity of quinones will be related to the difference in energy between the highest occupied molecular orbital (HOMO) of the nucleophile and the lowest unoccupied molecular orbital (LUMO) of the quinone. Furthermore, if the reaction is subject to kinetic control (*i.e.*, it is not reversible under the reaction conditions), then the relative proportions of isomeric products from a given quinone (the regioselectivity) should be related to the squares (to obviate consideration of phase signs) of the coefficients of the various reaction centers in the quinone LUMO. Larger coefficients imply more effective overlap with the attacking nucleophile.

The size of some of the molecules we wished to treat precluded application of *ab initio* methods to all structures. Hence, we resorted to semi-empirical calculations employing the AM1 Hamiltonian. To gain more confidence in our results, however, we did apply *ab initio* methods to several of the smaller molecules, and showed that total energies, HOMO energies, and LUMO energies, while different in absolute magnitude, were directly proportional between AM1 semi-empirical and 3-21G(*) *ab initio* calculations. For example, a plot of the 3-21G(*) LUMO/HOMO energies of compounds **1** - **6** *vs* the AM1 energies is linear, with a correlation coefficient of 0.999.

Tables 1 and 2 contain results of AM1 semi-empirical calculations on thioglycerol, the model quinones, and a number of derived quinones and hydroquinones. The HOMO of thioglycerol, which is composed almost entirely of an unshared pair on sulfur, lies at about -8.88 ev. Closest to it in energy, with one exception, are the unsubstituted *o*- and *p*-benzoquinones. Attachment to the quinones of π-donor methyl and methoxyl substituents, as expected from simple perturbation theory,

TABLE 1

Computed Properties of Thioglycerol and Quinones

Compound	ΔH_f, kcal/mol	E_{HOMO}, ev	E_{LUMO}, ev	E_o, kcal/mol
1	-25.1	-10.88	-1.74	55.8
2	-63.3	-10.26	-1.63	76.8
3	-100.7	-10.18	-1.52	97.7
4	-31.0	-10.11	-1.60	73.2
5	-59.9	-9.57	-1.56	76.6
6	-108.3	-8.88	0.931	70.3
9	-128.7	-8.96	-1.87	116.3
25	-167.5	-8.96	-1.78	137.0
26	-166.3	-8.96	-1.81	137.0
27	-134.3	-8.76	-1.77	133.3
28	-130.9	-9.18	-1.83	133.9
29	-161.0	-8.56	-1.80	136.6
30	-163.3	-8.99	-1.70	137.1

TABLE 2

Computed Properties of Hydroquinones

Compound	ΔH_f, kcal/mol	E_{HOMO}, ev	E_{LUMO}, ev	E_o, kcal/mol
8	-65.7	-8.73	0.22	69.9
7	-167.0	-8.76	-0.38	129.9
12	-205.3	-8.24	-0.092	150.9
13	-204.0	-8.04	-0.083	150.9
14	-100.1	-8.48	-0.20	90.7
16	-177.2	-8.96	-0.41	147.4
17	-203.4	-9.04	-0.43	150.7
18	-73.8	-8.72	0.34	87.1
19	-104.3	-8.87	0.35	90.7
21	-236.9	-8.01	-0.20	171.6
23	-137.9	-8.40	0.25	111.5
24	-208.0	-8.25	-0.02	150.8
31	-175.5	-8.60	-0.32	147.5

raises the energy of the LUMO, which should make the quinone less reactive. This is precisely our observed reactivity pattern.

The one exception among the more reactive quinones is the one bearing a thioglycerol substituent, compound **9**. For the sulfur of the thioglyceryl group to be a π-donor would require 3p-2p orbital overlap, which is inefficient; hence the electronegativity of sulfur makes this group electron-attracting, *lowering* the energy of the HOMO. The thioglyceryl substituent makes the quinone *more* reactive than unsubstituted *p*-benzoquinone.

The success of FMO theory in helping us understand the reactivity of the quinones is not repeated for rationalizing the regioselectivity of addition. Figure 5 shows the squares of the LUMO coefficients for the four unsymmetrical quinones we examined. These coefficients essentially describe the extent of contribution of a carbon $2p_y$ orbital at each site to the LUMO. In only one case does the largest coefficient correspond to the principal observed product, and in that case (compound **2**), the prediction is certainly equivocal.

In part, the failure of the correlation may result from the relatively small differences calculated; altogether, however, we believe it implies that the initial attack of thioglycerol on the quinone is reversible. If this is so, then the product composition should be determined by the relative stabilities of the initial Michael adducts, prior to aromatization to hydroquinones. This possibility was examined with the aid of the calculated enthalpies of formation for the Michael adducts (Table 3).

Figure 6 shows an example of this analysis. Attack of thioglycerol on methoxyquinone **5** can produce either **17a**, which tautomerizes to the observed product **17**, or **24a**, which would tautomerize to **24**, predicted by FMO theory to be more important, but not observed among the products of this reaction. The calculated ΔH_f of **17a** is -187.9 kcal/mol, whereas that of **24a** is -184.9 kcal/mol. If **17a** and **24a** were actually to reach

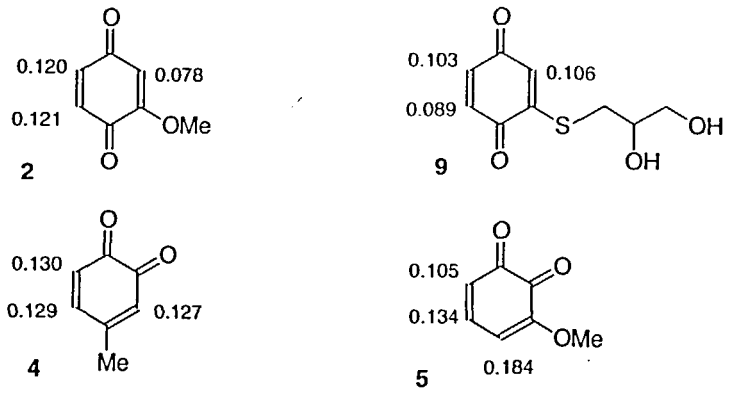

Figure 5: Squares of LUMO coefficients for unsymmetrical quinones.

TABLE 3

Computed Properties of Michael Adducts

Compound	ΔH_f, kcal/mol	E_o, kcal/mol
10a	-254.0	190.6
11a	-251.9	190.3
12a	-186.9	150.9
13a	-188.8	150.9
16a	-158.1	147.4
17a	-187.9	150.8
24a	-184.9	150.9
31a	-155.9	147.5

equilibrium with each other, the 3.0 kcal/mol difference would correspond to an equilibrium constant of about 100 favoring **17a** (assuming, of course, that ΔS_f is similar for both). The greater stability of **17a** is undoubtedly related to its being linearly conjugated, whereas **24a** is cross-conjugated.

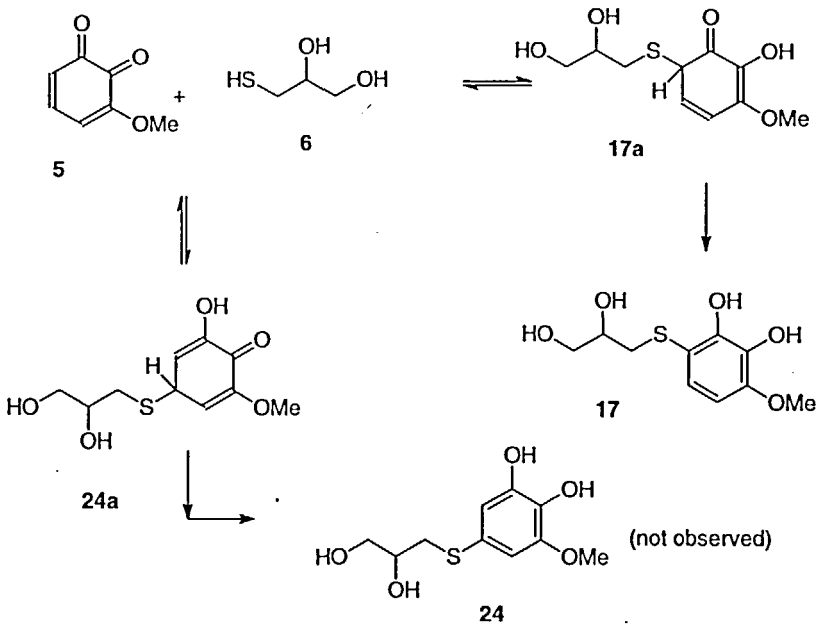

Figure 6: Intermediates in the reaction of thioglycerol with 3-methoxy-1,2-benzoquinone.

For methylquinone **4**, the adduct leading to observed product **16** is calculated to have ΔH_f = -158.1 kcal/mol; the adduct that would lead to the unobserved FMO product has ΔH_f = -155.9 kcal/mol. Again, the difference probably lies in cross- *vs* linear conjugation. A similar pattern is seen for addition of a second thioglyceryl residue to quinone **9**. The observed principal product is formed from an intermediate having ΔH_f = -250.6 kcal/mol as compared to -248.3 kcal/mol for the intermediate leading to the minor, FMO theory-predicted, product. Addition of thioglycerol to **2**, however, gives predominantly **12** via an intermediate of ΔH_f = -186.9 kcal/mol. The lesser product **13** is formed from an intermediate having ΔH_f = -188.8 kcal/mol. That is, the FMO predicted intermediate is also the

more stable one, yet the product from the other intermediate is predominant. We have no entirely satisfactory explanation for this result at present.

Nonetheless, a possible solution is available in the third area to which we applied molecular modeling techniques: the redox reaction between the initially formed thioglycerol-substituted hydroquinone and remaining unreacted quinone. *A priori*, these reactions might be analyzed either thermodynamically, by computing ΔH for each reaction from ΔH_f of the reactants and products, or by FMO theory, arguing that the reaction will proceed most readily for that quinone-hydroquinone pair having the smallest LUMO-HOMO gap. In Figure 7, we summarize both of these approaches as applied to the regioisomeric adducts from **2**.

As above, enthalpies of formation calculated with the AM1 semi-empirical Hamiltonian are employed. We see that adduct **13**, predicted by FMO theory to be the principal product, as well as forming *via* the more stable Michael adduct, is predicted to react slightly exothermically (0.3 kcal/mol) with **2**. The isomeric product, **12**, which is found to be the major product, is predicted to react *endo*thermically with **2**. Examination of the quinone LUMOs and hydroquinone HOMOs results in a similar prediction. The LUMO of **2** (-1.625 ev) and the HOMO of **13** (-8.036 ev) are separated by 6.411 ev, whereas the LUMO of **2** and the HOMO of **12** (-8.237 ev) are separated by 6.612 ev. That is, **13**, by either measure, should be destroyed by oxidation to the corresponding quinone more readily than **12**. This may account, at least in part, for its relatively small proportion of the observed product mixture.

Similar analyses suggest that the redox reaction of **1** with **7**, which is observed to be a major contributor to product formation (Figure 1) should be exothermic by 1.8 kcal/mol. Redox reactions involving **4** and its addition products **16** and **31** are both found to be endothermic (0.1 and 1.8 kcal/mol, respectively), which may be why **4** produces the smallest

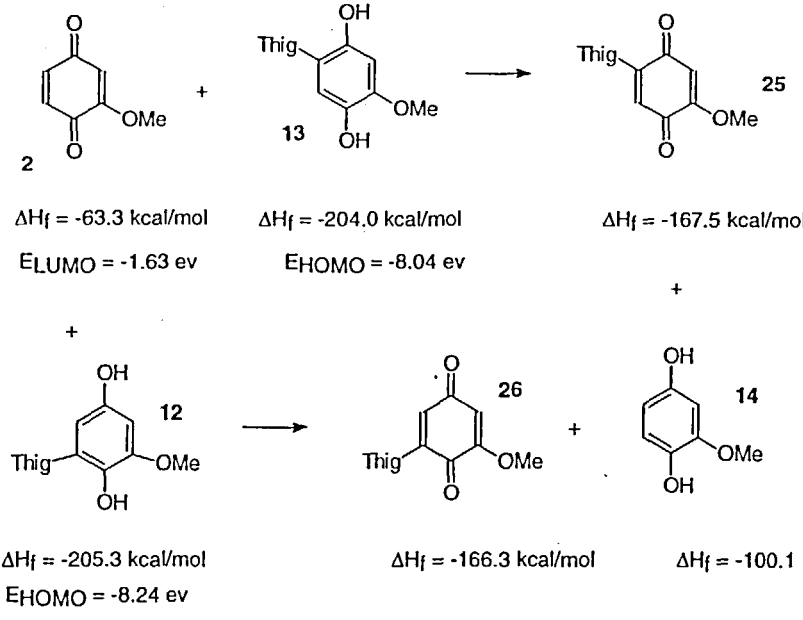

Figure 7: Redox reactions of Michael adducts (Thig = thioglyceryl).

amounts of diaddition products. Reaction of **5** with **17** is exothermic (2.0 kcal/mol), whereas its reaction with **24** is slightly endothermic, again suggesting a perturbation of product ratios determined by the stability of the intermediate Michael adduct.

Thus the overall product composition in the reaction of thioglycerol with quinones appears to be a complicated function of the nature of the frontier orbitals, the thermodynamic stability of the initial Michael adduct, and the ease of reoxidation of the hydroquinone to which the Michael adduct is transformed.

Nonetheless, the overall form of the results provides an excellent picture of the bleaching aspect of the behavior of high-yield pulp upon treatment with thioglycerol. The initial bleach is produced by Michael

addition of the thiol functionality to chromophoric quinones (and possibly quinonemethides) produced in the pulping process. The resulting substituted hydroquinones are colorless. Almost immediately, however, the adducts react in a redox couple with unreacted quinones, converting a portion of the adducts to quinones bearing thioglyceryl substituents, which are colored. Some color therefore redevelops in the pulp. Over the long term, although the treated pulp is protected against further degradation of its lignin content (by a mechanism we now are exploring), slow air oxidation of the remaining thioglyceryl-substituted hydroquinones ultimately results in the development of thioglyceryl-substituted quinones, which are more intensely colored than the chromophores produced by lignin degradation.

COMPUTATIONAL METHODOLOGY

Ab initio calculations were carried out with the SPARTAN[26] 3.1 suite of programs running on an SGI Indigo workstation. Semi-empirical calculations employed either SPARTAN, or MOPAC 6.0[27] running on a Gateway 486 DX2 PC. Molecular mechanics calculations were performed with PCModel[28] on the PC. Visualization of molecular structures was accomplished with either the Spartan graphical interface or Xmol, a program developed at the Minnesota Supercomputer Center. All structures were subject to full geometry optimization within an appropriate symmetry group, and all calculated vibrational frequencies were real. Molecules having a significant degree of conformational freedom (those bearing thioglyceryl side chains) were examined with molecular mechanics calculations, employing full torsional and vibrational annealing, to locate the global minimum, which was used as a starting point for the semi-empirical calculations. All calculations involving enthalpies of formation were corrected for differences in zero-point vibrational energies,

which in most cases were negligible. Further details of the computational methodology or copies of full output data are available upon request from the authors.

EXPERIMENTAL

Benzoquinone (Aldrich) was recrystallized from chloroform; other commercial chemicals were used without purification. HPLC analyses were performed on a Hewlett-Packard 1090 Series II Liquid Chromatograph, equipped with an AllTech analytical silica column (4.7 x 250 mm). The mobile phase was ethyl acetate/hexane (40/60). Preparative separations were accomplished with a Waters 510 HPLC or AllTech silica gel (1 mm) TLC plates. Yields were determined from calibration curves prepared using authentic samples. Melting points are uncorrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ. ^{1}H nmr spectra were obtained with Varian XL-200 and Varian Gemini 300 spectrometers; infrared spectra were obtained with a Bio-Rad FTS-60 ft-ir spectrophotometer.

2-Methoxy-1,4-benzoquinone. (a) 2-methoxy-1,4-hydroquinone. The method of Bailey and Dence[29] was applied to 15:2 g (0.1 mol) of vanillin, 100 mL of 1 N NaOH, and 142 mL of 3% H_2O_2. A dark brown oil was received, which crystallized on standing for a few hours. Yield: 35%, mp 87-89 °C (lit.[26] 88-88.5 °C). **(b)** A modification of the method of Willstatter and Muller[27] was used: 140 mg (1 mmol) of the hydroquinone was dissolved in 10 mL of ether, and ca. 30 mg of anhydrous $MgSO_4$ was suspended in the solution. To this mixture 475 mg of Ag_2O was added with stirring. After 45 min., the mixture was filtered, and the solids were washed with $CHCl_3$. The combined filtrate and washes were concentrated on a rotary evaporator. The quinone crystallized from the residue. Yield: 84%, mp 142-144 °C (lit.[29] 143-144 °C).

2,6-Dimethoxy-1,4-hydroquinone was prepared by H_2O_2 oxidation of syringaldehyde as described above. Yield: 40%, mp 153-155 °C (lit.[11] 153.5-154.5 °C).

2,6-Dimethoxy-1,4-benzoquinone was prepared by oxidizing the hydroquinone with Ag_2O as described above. The solvent was acetone and the reaction time was 60 min. Yield: 80%, mp 257-258 °C (lit.[11] 256-257 °C).

4-Methyl-1,2-benzoquinone and **3-methoxy-1,2-benzoquinone** were prepared by Ag_2O oxidation of the corresponding catechols as described above. Yields were 60% and 85%, respectively, and mps were 76-77 °C (lit.[29] 76-78 °C) and 107-109 °C (lit.[31] 107-110 °C).

$(HOCH_2CHOHCH_2S)_2$ (Disulfide of thioglycerol). Thioglycerol (200 mg; 185 mmol) was dissolved in 2 mL of methanol. To this solution, solid I_2 was added until the brown color persisted. The mixture was stirred for 60 min., and Ag_2CO_3 was added portionwise until a heavy precipitate of AgI formed. The mixture was filtered and the residue washed three times with methanol. The combined filtrate and washings were dried over anhydrous $MgSO_4$ overnight. Concentration of the solution on a rotary evaporator, followed by drying *in vacuo* yielded a thick oil. Yield: 65%. The ^1H nmr spectrum clearly shows the oil to be a mixture of the *meso*- and *racemic* diastereomers; absorptions are found at: 2.70, 2.92 (4H, dd, $SC\underline{H}_2$); 3.37 (4H, m, $C\underline{H}_2OH$); 3.65 (2H, m, $C\underline{H}OH$); 4.68 (2H, t, $CH_2O\underline{H}$); and 4.92 (2H, d, $CHO\underline{H}$) ppm.

General Method for Acetylation. The substrate (hydroquinone, disulfide, or reaction mixture) was suspended in excess acetic anhydride. Pyridine was added slowly with stirring until all the substrate dissolved. The mixture was allowed to stand overnight at room temperature; then excess acetic anhydride, acetic acid, and pyridine were distilled out under vacuum.

Reaction of *p*-benzoquinone with thioglycerol. Benzoquinone (108 mg; 1.0 mmol) was dissolved in 10 mL of methanol. To this solution was

added with stirring 115 mg (1.0 mmol, 95% pure) of thioglycerol dissolved in 2 mL of methanol. The mixture immediatly darkened to brown, and turned clear in about 10 min. After stirring for 2 hr., the mixture was concentrated on a rotary evaporator, and the residue was acetylated as described above. From the acetylation residue, the following compounds were isolated by preparative TLC: (1) hydroquinone diacetate, 19.0%, ^{1}H nmr, 2.29 (6H, s, OCOC$\underline{H}_3$) and 7.10 (4H, s, aryl H) ppm (identical to spectrum of an authentic sample); (2) 2-(thioglyceryl)-1,4-hydroquinone tetraacetate (tetraacetate of **7**), 63.0%, ^{1}H nmr, 2.01, 2.06, 2.24, 2.30 (12H, s, OCOC$\underline{H}_3$), 3.07, 3.14 (2H, dd, SC$\underline{H}_2$), 4.21, 4.34 (2H, dd, C$\underline{H}_2$OAc), 5.13 (1H, m, C$\underline{H}$OAc), 7.00 (1H, dd, aryl H), 7.08 (1H, d, aryl H), 7.28 (1H, d, aryl H) ppm; IR, 3092, 2964, 1772, 1749, 1732, 1600, 1489, 1440, 1373, 1245, 1205, 1174 cm^{-1}; Anal., calcd. for $C_{17}H_{20}SO_8$, C = 53.12%, H = 5.24%, found, C = 53.29%, H = 5.14%; (3) mixture of the hexaacetates of **10** and **11**, 14.6%, Anal., calcd. for $C_{24}H_{31}S_2O_{12}$, C = 50.17%, H = 5.26%, found, C = 49.82%, H = 5.13%. This mixture was separated by preparative HPLC (silica gel, 40/60 ethyl acetate/hexane). The ratio of **10** : **11** was 2.5 : 1. The chromatogram also gave indication of small amounts of unidentified material, which, from its retention time, could be a triadduct. ^{1}H nmr of **10**: 2.03, 2.07, 2.32, 2.37 (18H, s, OCOC$\underline{H}_3$), 3.05, 3.15 (4H, dd, SC$\underline{H}_2$), 4.19, 4.34 (4H, dd, C$\underline{H}_2$OAc), 5.12 (2H, m, C$\underline{H}$OAc), 7.16 (2H, s, aryl H) ppm. ^{1}H nmr of **11**: 2.02, 2.06, 2.35 (18H, s, OCOC$\underline{H}_3$), 3.03, 3.12 (4H, dd, SC$\underline{H}_2$), 4.19, 4.33 (4H, dd, C$\underline{H}_2$OAc), 5.12 (2H, m, C$\underline{H}$OAc), 7.16 (2H, s, aryl H) ppm.

Inverse addition of *p*-benzoquinone to thioglycerol. Benzoquinone (108 mg, 1 mmol) was dissolved in 10 mL of methanol, and this solution was added to a solution of thioglycerol (345 mg, 3 mmol) in 2 mL of methanol. The reaction mixture was worked up and acetylated as above; HPLC analysis indicated 2-(thioglyceryl)-1,4-hydroquinone tetraacetate to be the only product.

Reaction of 2-methoxy-1,4-benzoquinone (2) with thioglycerol. Reaction was conducted exactly as for *p*-benzoquinone (above) with 69 mg (0.5 mmol) of methoxybenzoquinone, 57 mg (0.5 mmol) of thioglycerol, and 8 mL of methanol. Products isolated from the acetylated reaction mixture were: (1) 2-methoxy-1,4-hydroquinone diacetate (diacetate of **14**), 6.0%, ^{1}H nmr, 2.29, 2.30 (6H, s, OCOC$\underline{H}_3$), 3.81 (3H, s, OC$\underline{H}_3$), 6.58, 7.02 (2H, d, aryl H), 6.72 (1H, dd, aryl H) ppm (identical to spectrum of an authentic sample); (2) a mixture of the tetraacetates of **12** and **13**, 81.2%, Anal., calcd. for $C_{18}H_{22}SO_9$, C = 52.17%, H = 5.35%, found, C = 52.42%, H = 5.31%. The mixture was separated by HPLC as above, giving the ratio **12** : **13** = 2 : 1. Also seen in the chromatogram was a small amount of material having a retention time appropriate to a diadduct. ^{1}H nmr of **12**: 2.02, 2.06, 2.30, 2.34 (12H, s, OCOC$\underline{H}_3$), 3.05, 3.12 (2H, dd, SC$\underline{H}_2$), 3.80 (3H, s, OC$\underline{H}_3$), 4.20, 4.34 (2H, dd, C$\underline{H}_2$OAc), 5.12 (1H, m, C$\underline{H}$OAc), 6.63, 6.85 (2H, d, aryl H) ppm. ^{1}H nmr of **13**: 2.01, 2.05, 2.31, 2.35 (12H, s, OCOC$\underline{H}_3$), 3.00 (2H, d, SC$\underline{H}_2$), 3.81 (3H, s, OC$\underline{H}_3$), 4.19, 4.32 (2H, dd, C$\underline{H}_2$OAc), 5.12 (1H, m, C$\underline{H}$OAc), 6.72 (1H, s, aryl H), 7.26 (1H, s, aryl H) ppm.

Reaction of 2,6-dimethoxy-1,4-benzoquinone (3) with thioglycerol. Dimethoxybenzoquinone (**3**) (10.5 mg, 0.063 mmol) was dissolved in 12 mL of methanol. To this solution was added with stirring 7.1 mg (0.063 mmol) of thioglycerol in 1 mL of methanol. The mixture was stirred for 142 hr. and concentrated on a rotary evaporator. Acetylation and analysis showed that only a very small amount of reaction had occurred. The procedure was repeated with 35.5 mg of thioglycerol and a reaction time of 144 hr. Acetylation and analysis identified the following products: (1) 2,6-dimethoxy-1,4-hydroquinone acetate (acetate of **23**), 14.2%, ^{1}H nmr, 2.29, 2.33 (6H, s, OCOC$\underline{H}_3$), 3.79 (6H, s, OC$\underline{H}_3$), 6.39 (2H, s, aryl H) ppm (identical to the spectrum of an authentic sample); (2) tetraacetate of **21**, 72.1%, ^{1}H nmr identical to that in the literature[11]; (3) tetraacetate of

thioglycerol disulfide (tetraacetate of **22**), 9.55 mg, ^{1}H nmr, 2.08 (6H, s, $CH_2OCOC\underline{H}_3$), 2.09, 2.10 (6H, s, $CHOCOC\underline{H}_3$), 2.94 (4H, dd, $SC\underline{H}_2$), 4.16, 4.38 (4H, dd, $C\underline{H}_2OAc$), 5.30 (2H, m, $C\underline{H}OAc$) ppm, identical to that of an authentic sample prepared as described above.

Reaction of 4-methyl-1,2-benzoquinone (4) with thioglycerol. The same procedure as for benzoquinone was followed, with 61 mg (0.5 mmol) of **4**, and 56.9 mg (0.5 mmol) of thioglycerol in 7 mL of methanol for 4 hr. Acetylation and analysis identified the following products: (1) acetate of 4-methylcatechol (acetate of **18**), 7.7%, ^{1}H nmr, 2.27, 2.28 (6H, s, $OCOC\underline{H}_3$), 2.34 (3H, dd, aryl CH_3), 6.99 (1H, m, aryl H), 7.05 (2H, d, aryl H) ppm (identical to spectrum of an authentic sample; (2) tetraacetate of **16**, 54.0%, ^{1}H nmr, 2.02, 2.06, 2.27, 2.33 (12H, s, $OCOC\underline{H}_3$), 2.35 (3H, dd, aryl CH_3), 3.05, 3.14 (2H, dd, $SC\underline{H}_2$), 4.20, 4.33 (2H, dd, $C\underline{H}_2OAc$), 5.12 (1H, m, $C\underline{H}OAc$), 6.91, 7.22 (2H, dq incompletely resolved, aryl H) ppm; IR, 2932, 1769, 1740, 1596, 1587, 1471, 1430, 1369, 1208, 1176, 1114, 1041, 1016 cm^{-1}; Anal., calcd. for $C_{18}H_{22}SO_8$, C = 54.26%, H = 5.56%, found, C = 54.45%, H = 5.73%.

Reaction of 3-methoxy-1,2-benzoquinone (5) with thioglycerol. . The same procedure as for benzoquinone was followed, with 28.3 mg (0.205 mmol) of **5**, and 23.3 mg (0.205 mmol) of thioglycerol in 6 mL of methanol for 4 hr. Acetylation and analysis identified the following compounds: (1) acetate of 3-methoxycatechol (acetate of **19**), 15.4%, ^{1}H nmr, 2.28, 2.30 (6H, s, $OCOC\underline{H}_3$), 3.83 (3H, s, $OC\underline{H}_3$), 6.78, 6.86 (2H, dd, aryl H), 7.11 (1H, dd, inc. res., aryl H) ppm (identical to that of an authentic sample; (2) tetracetate of **17**, 56.9%, ^{1}H nmr, 2.02, 2.05, 2.30, 2.35 (12H, s, $OCOC\underline{H}_3$), 2.98 (2H, d, $SC\underline{H}_2$), 3.84 (3H, s, $OC\underline{H}_3$), 4.17, 4.33 (2H, dd, $C\underline{H}_2OAc$), 5.04-5.16 (1H, m, $C\underline{H}OAc$), 6.86, 7.44 (2H, d, aryl H); IR, 2946, 2845, 1776, 1736, 1491, 1438, 1373, 1290, 1209, 1174, 1082 cm^{-1}; Anal., calcd. for $C_{18}H_{22}SO_9$, C = 52.17%, H = 5.35%, found, C = 52.48%, H = 5.31%.

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