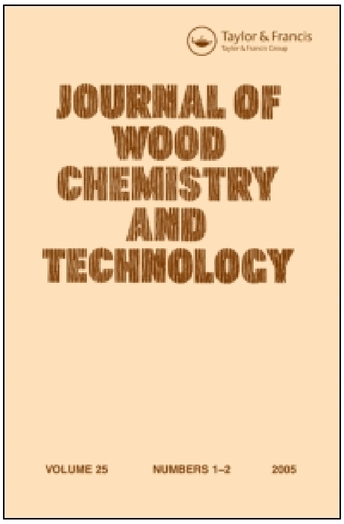

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ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VI): ALCOHOL BISULFITE PULPING

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ABSTRACT

Compound 1, which incorporates a hex-5-enyl group on a quinone methide precursor, has been used to demonstrate that $NaHSO_3$ in 50% isopropyl alcohol exhibits electron transfer reactions. There is a significant solvent effect associated with this system since $NaHSO_3$ in aq. NaOH showed very few products typical of an electron transfer system, while 50% isopropyl alcohol by itself at 150°C provided some of the typical products. The electron transfer ability of the 50% isopropyl alcohol/$NaHSO_3$ system increases with increasing temperature but is less than that of aqueous anthrahydroquinone at similar temperatures.

INTRODUCTION

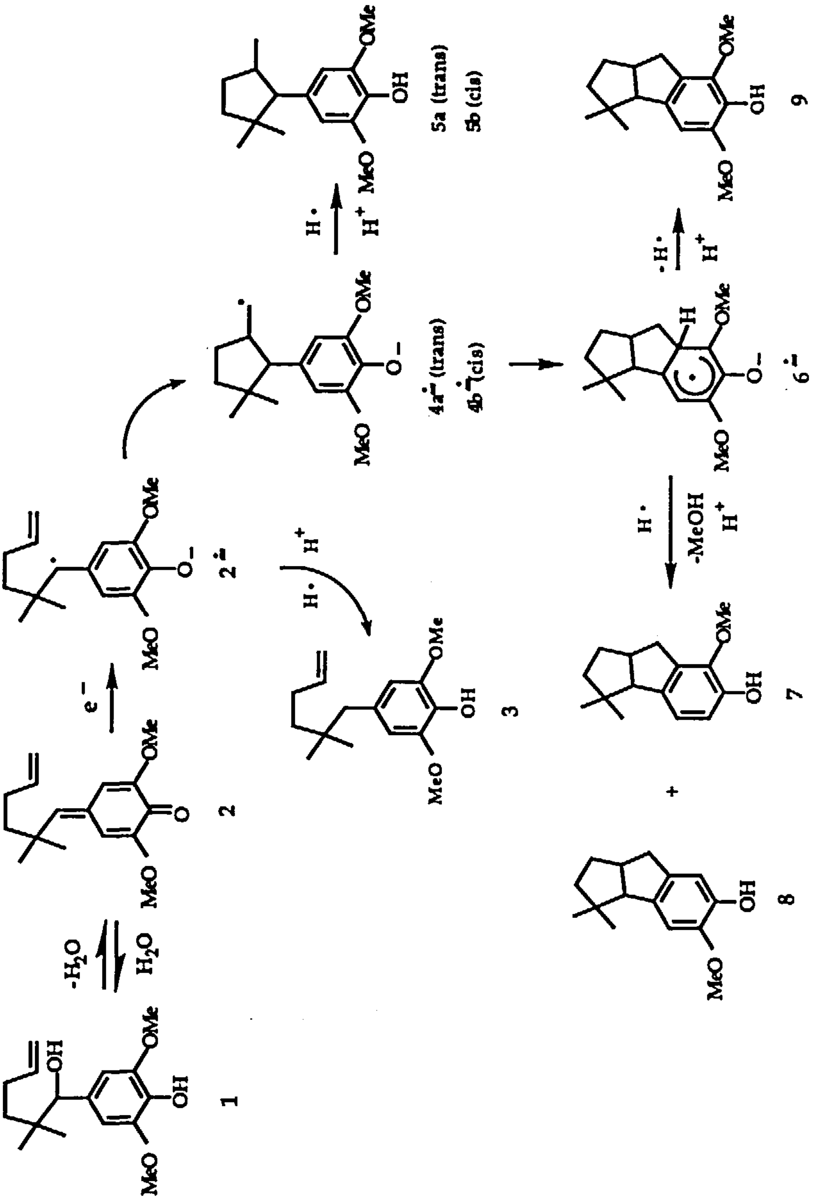
Previous studies in our laboratory have been directed at demonstrating the importance of electron transfer reaction mechanisms for certain pulping systems. One of these studies[3] employed 5,5-dimethyl-6-hydroxy-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene, commonly referred by us as the "electron transfer detector" (ETD) compound. Under aqueous alkaline reactions conditions, anthrahydroquinone and glucose showed the ability to transfer electrons, while sodium sulfide and sodium sulfite (the principal reagents in kraft and sulfite pulping processes) did not transfer electrons to ETD.

The reactions of ETD (1) are outlined in Scheme 1. At high temperature ETD is transformed to a quinone methide (2); quinone methides are key intermediates in pulping reactions.[4] Electron transfer to 2 leads to the quinone methide radical anion $2^{\dot{-}}$. Reduction of the radical anion directly produces 3 and after cyclization produces 5, 7-9. The ratio of cyclic (7-9) to acyclic (5) products formed depends on the relative rates of hydrogen atom transfer by the radical intermediates; a medium which readily supplies hydrogen atoms will give a larger amount of acyclic product, since intermediate $2^{\dot{-}}$ will be reduced before cyclization can occur. The occurrence of five-membered cyclic compounds in the product mixture is evidence that the quinone methide radical anion $2^{\dot{-}}$ had formed, and electron transfer reactions had occurred.

Sakai and co-workers have been examining the chemistry of alcohol bisulfite pulping.[5-7] They have suggested that the 50% alcohol sodium bisulfite system may be reacting by an electron transfer mechanism or a homolysis reaction mechanism.[7] We decided to examine these reaction conditions with the ETD compound and look for the production of five-membered ring cyclic products. The goal of this research was to verify whether the alcohol bisulfite cooking process involves single electron transfer reactions.

RESULTS AND DISCUSSION

Table 1 lists the results of the reactions of ETD compound with $NaHSO_3$ in 1 M NaOH in water and in 50% isopropyl alcohol (IPA), along with comparisons to reactions in 1 M NaOH, glucose and Na_2SO_3 in 1 M NaOH, and 50% isopropyl alcohol. Glucose is an electron transfer reagent which shows a large amount of cyclized products. The product ratios are somewhat dependent on reaction temperature; therefore, two temperatures were examined, 135°C (where much of our earlier results[1] were obtained) and 150°C. The structural assignments were based on comparing GC/MS results to the known mixture from the glucose reaction and available compounds.



Scheme 1. Reactions of ETD[3]

Table 1. Product Distributions[a] for the Reactions[b] of ETD (1)

	glucose		$NaHSO_3$ in IPA[d]		Na_2SO_3		$NaHSO_3$		IPA[d]		1 M NaOH	
product[c]	135°C	150°C	135°C	150°C[e]	135°C	150°C	135°C	150°C	135°C	150°C	135°C	150°C
syringol	5.2	6.5	0.2		8.1	15.9	9.3	18.8		1.0	10.8	10.4
syringaldehyde						11.0		13.4				39.3
7	10.3	5.8	1.2	0.8	2.9		0.4				1.8	
8	7.5	5.1	0.7	0.5	2.6		2.6			0.2	1.8	
5a	52.0	46.2	10.9	46.5	6.0	0.4				30.8	6.0	0.2
5b	2.8	9.7	3.9	7.1						0.8		
3	1.8	4.9	8.1	9.6								
unknown[f]			4.9	2.9					18.0	19.2		
9	5.2	16.0	3.6	13.7						13.0		
1 (ETD)	12.2	0.2	43.9	1.6	77.5	66.7	84.5	65.2	78.6	13.8	79.6	43.4
others	2.9	5.6	22.6	17.1	2.9	6.0	3.2	2.6	3.4	21.2		6.6

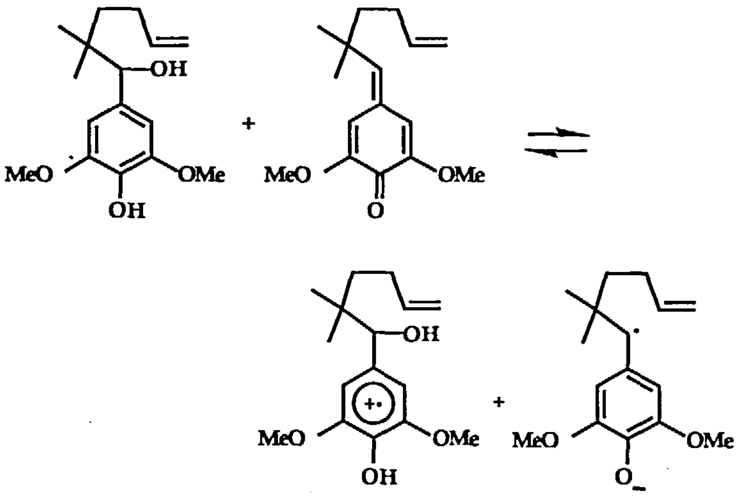
[a] Yields are based on relative integrated signal areas, expressed as a %, for those gas chromatography signals between 3-20 min retention time. [b] Unless noted differently the solvent was 1 M aqueous NaOH. The 150°C reaction time was 24 hr; the 135°C reaction time was 18 hr. [c] Listed in order of GC elution time. [d] Isopropyl alcohol, 50% with water, no added NaOH. [e] Reaction time of 21 hr. [f] GC/MS apparent mol. ion of 262.

There are several interesting results indicated by the data in Table 1. First and foremost is that $NaHSO_3$ in IPA gives rise to both cyclic and acyclic reduction products, indicating that electron transfer reactions are occurring under these conditions. In fact, $NaHSO_3$/IPA generates products similar in type and amounts to glucose in water at 150°C. The ability of the $NaHSO_3$ in IPA system to provide hydrogen atoms to reduce the radical intermediates appears to be greater than glucose. This conclusion stems from the higher levels of the first radical intermediate reduction product (3) and lower levels of the slower formed reduction products, 7 and 8, in the $NaHSO_3$/IPA case.

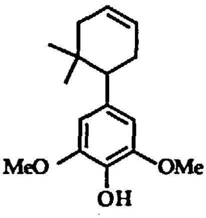
Second, it is obvious from the results in the table that IPA plays a major role in promoting electron transfer reactions in the $NaHSO_3$ case. The small amount of electron transfer reactions observed with $NaHSO_3$ and Na_2SO_3 in water can be attributed to NaOH-induced reactions. This result confirms our earlier findings that sodium sulfite in 1 M NaOH has very little ability to electron transfer.[3]

Isopropyl alcohol appears to have some ability to promote electron transfer reaction on its own. Both **5a** and **9** were observed during heating ETD in IPA at 150°C; however, no reduction products are formed at 135°C. The electron transfer reactions may be a result of a process like that shown in eq. 1; however, we have no direct proof for the reactions shown, nor of the fate of the postulated cation radical.

Based on the observed GC/MS molecular weight (m/e 262) and fragmentation pattern, we suspect that the major (fast eluting) unknown produced in the IPA reactions is **10** or an isomer. Two slower eluting unknowns (classified as "others" in the table) have mass spectra suggesting structures **11** and **12** as likely candidates. It is also probable that the α-sulfonate **13** is a product but goes undetected because of its poor GC volatility.



(1)



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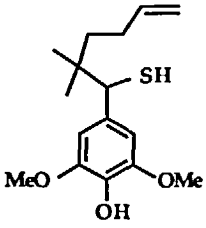

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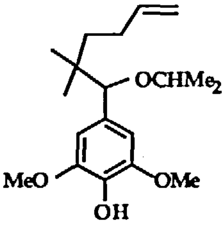

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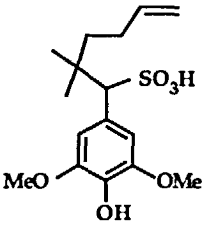

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Third, the rates of disappearance of the starting material are rather slow; ETD is generally still present in substantial amounts after 18 hr at 135°C in all the cases examined. The reagents and conditions listed in the table are not nearly as good in transferring electrons as anthrahydroquinone, which completely consumes ETD in 2 hr at 135°C in 1 M NaOH and leads to high yields of reduction products 3 and 5.

A follow-up experiment was performed to examine the time versus ETD amount with alcohol bisulfite treatment done at 160°C with a 2.7/1 $NaHSO_3$/ETD ratio. This temperature and ratio were used to match that employed by Sakai and co-workers in their studies.[7] The ratio used previously (Table 1) was 8.5/1. Disappearance of ETD was followed by GC, using syringyl alcohol as an internal standard (Fig. 1).

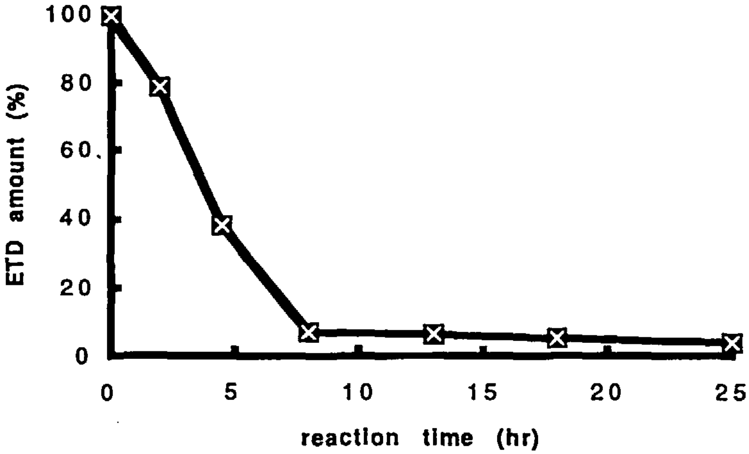

Figure 1. Time decrease of ETD during alcohol bisulfite cooking at 160°C

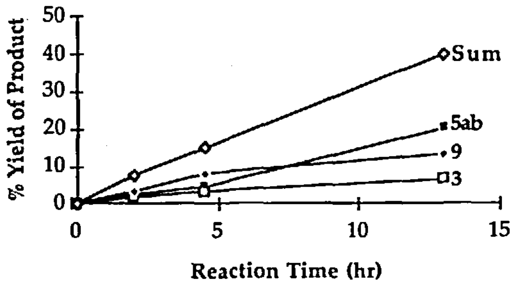

Figure 2. Product yields with ETD and $NaHSO_3$ in 50% IPA at 160°C

About 93% of ETD was lost within the first 8 hr, after which the amount leveled to about 4%. The lack of complete reaction may have been due to the low level of $NaHSO_3$ used. The yields of products **5a**, **5b**, **3** and **9** from 2 - 13 hr were also determined (Fig. 2). The product distribution was somewhat different than the previous $NaHSO_3$/50% isopropyl alcohol treatment (Table 1); there was less relative amount of **5a/b** products. This may be due to the lower level of $NaHSO_3$ employed and/or changes in the relative rates of hydrogen atom abstraction and donation with a higher temperature. The progressive development of products suggests that once formed the products are relatively stable.

The total yield of products was about 40%. Considering the small amount of starting material remaining, we estimate that about 50% of the ETD was converted to products not detectable under the selected GC conditions. This trend was also observed when comparing GC intensities of the alcohol bisulfite treatments with the other treatments listed in Table 1. [It is not, however, apparent from the presentation of the data in Table 1, since the various GC areas were normalized.] The material unaccounted for may reflect the formation of involatile compounds, such as α-sulfonate (13).

CONCLUSIONS

The products observed upon heating compound 1 with $NaHSO_3$ in 50% isopropyl alcohol provide evidence that electron transfer reactions have occurred. It is obvious that the electron transfer reactions are being aided by the solvent since $NaHSO_3$ in aq. NaOH showed very few products typical of an electron transfer system, while 50% isopropyl alcohol at 150°C, in the absence of $NaHSO_3$, provided some of the typical products. The electron transfer ability of the 50% isopropyl alcohol/$NaHSO_3$ system increases with increasing temperature, but is less than that of aqueous anthrahydroquinone at similar temperatures.

EXPERIMENTAL

Materials

Oxygen-free water was prepared by boiling distilled water for 30 min, bubbling nitrogen in the water as it cooled, and sealing the container until needed. Oxygen-free 1 M NaOH solution was prepared in a similar manner, using O_2-free water for dilution to the right molarity. Commercial $NaHSO_3$ (J. T. Baker Chemical Co.), Na_2SO_3 (Mallinckrodt, Inc.), glucose (Matheson Coleman and Bell Manufacturing Chemists), NaOH (Mallinckrodt, Inc.), and isopropyl alcohol (Aldrich Chemical Company, Inc.) were used without specific purifications.

Reactions of ETD

All reactions of ETD were conducted in a nitrogen atmosphere with oxygen-free water in 4 mL stainless steel pressure vessels (bombs). Typically, each bomb contained 20 mg (70 µM) of ETD and 3.5 mL of solvent. The additives used for comparative study were as follows: glucose (113 mg, 13 mol. equiv. at 150°C and 63.1 mg, 5 mol. equiv. at 135°C[3]), Na_2SO_3 (45.1 mg, 4.5 mol. equiv. at 150°C and 43.6 mg, 4.9 mol. equiv. at 135°C), $NaHSO_3$ (62.8 mg, 8.5 mol. equiv. at 150°C and 66.0 mg, 8.6 mol. equiv. at 135°C), and 50% isopropyl alcohol.

The sealed bombs were rotated for selected time periods in a hot oil bath and then cooled quickly. The contents of bombs were neutralized with diluted HCl, if necessary, and extracted with chloroform. The $CHCl_3$ solution was washed with water, dried (Na_2SO_4 overnight), and concentrated *in vacuo* below 40°C before analysis by GC.

The reactions for estimating ETD and products as a function of time were carried out similarly; 20 mg (190 µM) of $NaHSO_3$ and 2 mL of 50% isopropyl alcohol were employed. The work-up was as described above except for the addition of known amounts of syringyl alcohol as an internal standard prior to the chloroform extraction.

Analysis

The ETD reaction mixtures were analyzed by gas chromatography (Hewlett-Packard HP 5890 GC) using a HP-17 packed column, helium carrier gas (flow rate 22.5 mL/min), and a temperature program of 150°C (2 min), 150 to 275°C at 5°C/min, and then held at 275°C. The injection port and the flame ionization detector (FID) were kept at 250°C and 275°C, respectively. For quantitative work, a known amount of syringyl alcohol was added as an internal standard prior to analysis. The GC response factor determined for syringyl alcohol to ETD was also applied to estimate the yields of the products (Fig. 2); authentic product component samples were not available. Identification of the GC signals was carried out by comparison with the published mass spectral fragmentation data,[3] *except for the following tentative assignments:*

Compound **10** (six-membered ring side chain):
EI mass spectrum: *m/e* 262 (80%, M^+), 180 (100%, $ArCH=CH_2$), 167 (97%, $ArCH_2^+$).
Isobutane CI mass spectrum: *m/e* 263 (100%, $M + H^+$).
Compound **11** (α-sulfide):
EI mass spectrum: *m/e* 296 (100%, M^+), 199 (98%, $ArCHSH^+$).
Compound **12** (α-isopropoxy):
EI mass spectrum: *m/e* 322 (8%, M^+), 280 (6%, $M^+ - CH_2=CHCH_3$), 167 (100%, $ArCH_2^+$).

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