

The Significance of α -Sulfone and α -Sulfonate Groups for the Cleavage of β -Aryl Ether Structures in Lignin

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The kinetics of the alkaline cleavage of the β -aryl ether linkage in lignin containing a sulfonate or a sulfone group in the α -position has been studied by the use of model compounds. In the presence of either of these groups the β -ether cleavage reaction is a first order reaction with respect to the cleavage product. The rate constants and their temperature dependence were determined in each case and compared with data for cleavage in normal structures (α -hydroxyl groups). It was found that the activation energy with a sulfone group is 121 kJ/mol; the rate of cleavage is comparably very fast even at 0 °C. In the presence of an α -sulfonate group, the activation energy is somewhat lower, 97 kJ/mol. The reaction rate is much slower than in the presence of a sulfone group but is still faster than cleavage in normal structures. At 110 °C it is about the same as the rate of cleavage in normal structures at 170 °C.

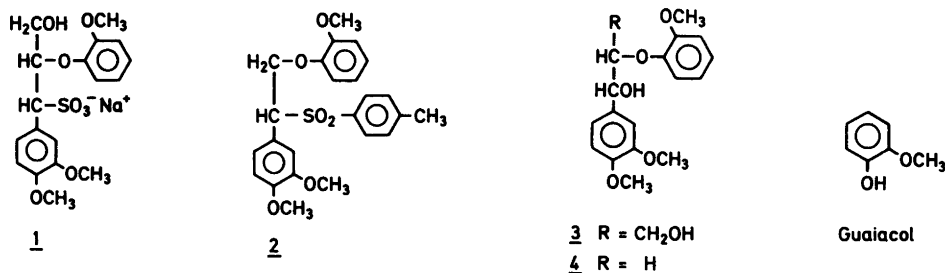
These results support a β -elimination mechanism induced by the electron-withdrawing power of the sulfone and sulfonate groups as has been previously proposed. It is suggested that the un-ionized nature of the sulfone substituent generates a strong inductive effect whereas the ionized nature of the sulfonate groups gives a weaker effect.

In recent papers, the significance of aryl ether cleavage for the kraft delignification of wood is discussed.^{1,2} It was concluded that the cleavage of the non-phenolic β -aryl ether linkages in lignin may be of major importance for the rate of lignin dissolution during the bulk phase of kraft or soda pulping. In our view, efforts to promote delignification should, therefore, be concentrated on the search for methods to increase the rate of

cleavage of this type of linkage in lignin. One possible method is to modify the lignin structure in the α -position of aryl propane units by substituting the ordinarily present benzyl alcohol group with another group which promotes cleavage of β -aryl ether bonds. It has previously been demonstrated that the presence of an α -carbonyl group increases the rate of β -aryl ether cleavage considerably, especially in non-phenolic lignin models.^{3,4} In the presence of hydrogen sulfide ions, this cleavage proceeds at ambient temperature.

The present work shows similar results for the alkaline β -ether cleavage in non-phenolic models containing an α -sulfonate or an α -sulfone group. It has previously been reported^{5,6,10-13} that such groups in the α -position of lignin models facilitate the cleavage of the β -aryl ether linkage and it was therefore of interest to extend these qualitative studies in order to acquire quantitative (kinetic) information. The results given here are compared with earlier kinetic data for the cleavage of the original β -aryl ether linkage models containing the α -hydroxyl group 3 and 4 in order to evaluate the effect of the sulfonate and of the sulfone on the rate of the β -aryl ether cleavage. The rate of this cleavage in the presence of these groups was studied using two slightly different non-phenolic β -aryl ethers: 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propanol-1-sulfonate 1 and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethyl-*p*-tolyl sulfone 2.

Compound 2 lacks the terminal hydroxymethyl group assumed to be originally present in the side-chains of lignin. This simplified model was chosen because of its facile preparation according to a synthesis reported previously.⁶



Aqueous solutions of sodium hydroxide were used as solvents. The aqueous solutions were mixed with methylcellosolve or dioxane to ensure complete solubility of the compounds, the mixtures being carefully made up in the presence of alkali to avoid phase separation (see Experimental).

RESULTS

The kinetic data from the alkaline treatment of compounds *1* and *2* are summarized in Table 1 together with reference data for compounds *3* and *4*.

Figs. 1, 3 and 4 illustrate the course of the ether cleavage reactions at different temperatures and different alkali concentrations.

Cleavage of the β -aryl ether α -sulfonate. Alkaline treatment of the sulfonate *1* affords guaiacol as main product. Fig. 1 shows the liberation of guaiacol at different temperatures as a function of time. A high temperature (above 100 °C) is required if the guaiacol is to be formed in a reasonable time. A logarithmic plot of the yield of guaiacol versus time gave straight lines which confirmed that the ether cleavage reaction follows a pseudo first-order behaviour as was expected. The rate constants are given in Table 1 and it is evident that the rate constant for the sulfonate compound *1* at 119 °C is higher than those for the reference compounds *3* and *4* obtained at 170 °C.

The reference compounds *3* and *4* were run in a mixture of organic solvent and water (see Table

Table 1. Alkaline cleavage of the β -aryl ether linkage in compounds *1*, *2*, *3*, *4*. Reaction conditions and rate data. Concentration of substrate: *1*: 3.3×10^{-3} mol l⁻¹, *2*: 0.9×10^{-3} mol l⁻¹. Solvent: H₂O, except: see ^b and ^c.

Compound	Conditions		Observed rate constants for guaiacol formation		Final yield of guaiacol (mol % of theor.)
	Temp. ^a °C	[HO ⁻] mol l ⁻¹	10 ³ k ₁ (min ⁻¹)	10 ³ k ₂ (min ⁻¹ mol ⁻¹ l)	
<i>1</i>	100	0.53	9.4	17.7	93
	119.0	0.51	41.0	80.4	98
	140.0	0.55	199.0	362	100
<i>2</i> ^b	0	0.001	—	30 · 10 ³	60
	10	0.001	—	190 · 10 ³	80
	22	0.001	—	1500 · 10 ³	70
3-diacetate ^c (threoform)	172.0	0.30	13.3	44	95
<i>4</i> ^c	170	0.51	23	45	100

^a Total error was $\leq \pm 1.6$ °C except in treatment at 0–50 °C where the error was $\leq \pm 0.5$ °C. ^b 60 % dioxane in H₂O, allowance for the solvent effect on rates: see text. ^c Data from literature. Compound *4* was run in 30 % methyl cellosolve⁴ and compound *3* in 40 % methyl cellosolve³ in H₂O.

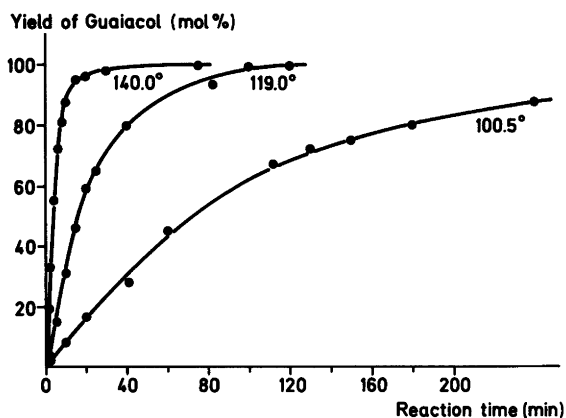


Fig. 1. Formation of guaiacol from cleavage of the β -aryl ether α -sulfonate **1** in 0.5 mol/l sodium hydroxide at different temperatures. Solvent: water.

1). This will in principle give rise to slightly higher rate constants due to increased activity of HO^- ions. The rate constants of the reference compounds in "pure" water would be somewhat lower.*

The fact that the β -aryl ether cleavage in the sulfonate compound **1** proceeds much faster than it does in ordinary β -aryl ether compounds **3** and **4** is further illustrated in Fig. 2 which shows the temperature dependence of the observed (at 0.5 mol/l HO^-) rate constants. The temperature dependence of each compound is of the same order of magnitude as is shown by the similarity of the slopes of the curves. The Arrhenius activation energy of the alkaline ether cleavage reaction in the sulfonated compound **1** is about 97.1 kJ/mol (23.2 kcal/mol) and in the reference compound **4** (or **3**) about 123 kJ/mol (29.6 kcal/mol).¹

*Cleavage of the β -aryl ether α -(*p*-tolyl) sulfone.* Alkaline treatment of the sulfone **2** had to be performed at very low temperatures due to the great ease of ether cleavage. The formation of guaiacol was found to take place readily at 0 °C and increased with increasing alkali concentration as is depicted in Fig. 3. Since it was difficult

to achieve full solubility of the sulfone in the reaction mixture at this temperature, it was necessary to run the reaction with 60 % dioxane in the NaOH water mixture.* Due to difficulties in following the very fast increase of guaiacol at the higher alkaline levels (and temperature), the calculated rate constants given in Table 1 are

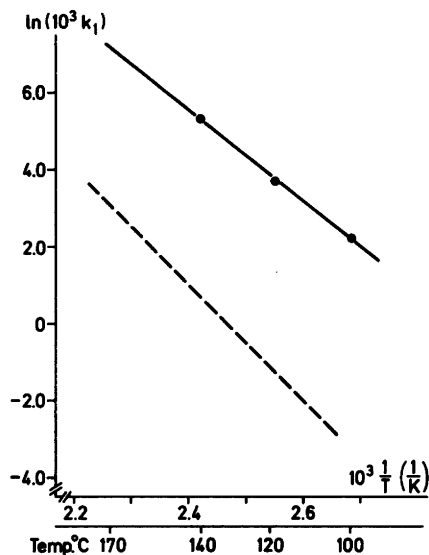


Fig. 2. Arrhenius diagram. Temperature dependence of the observed rate constants (k_1) in 0.5 mol/l sodium hydroxide for the cleavage of the β -aryl ether α -sulfonate **1** (●) and the normal β -aryl ether **4** (**3**) (—) as reference.

* The presence of the organic solvent (as mentioned above) will increase the base strength of HO^- -ions and thus raise the rate of cleavage. However, this rate increase is not estimated to be more than one power of ten. This corresponds roughly to only about a 10–20 °C change in temperature and is thus of negligible significance for these rate comparisons.

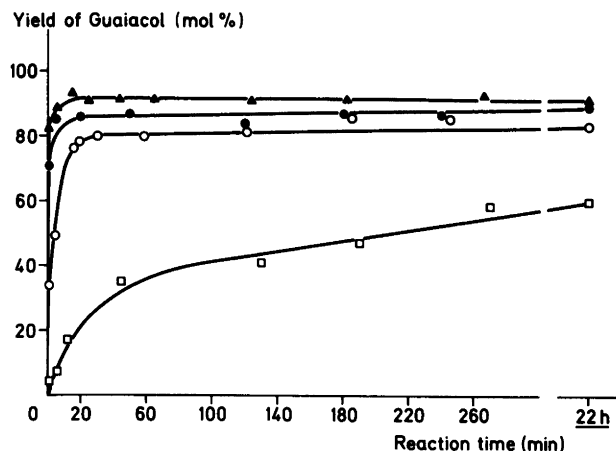


Fig. 3. Formation of guaiacol from cleavage of the β -aryl ether α -sulfone 2 in 0.5 (\blacktriangle), 0.1 (\bullet), 0.01 (\circ), 0.001 (\square) mol/l sodium hydroxide at 0 °C. Solvent: dioxane/water 3:2.

evaluated from a second-order rate expression using data from runs in 0.001 mol/l sodium hydroxide. Linear plots could be obtained showing the reaction to be of first order with respect to both substrate and alkali (*i.e.* overall second order). In 0.001 mol/l sodium hydroxide, the guaiacol yield reaches a maximum of only about 60–80 %, even after a very long reaction time, 22 h (Figs. 3 and 4). (It could not be decided whether this was real or due to experimental error in determination of the yield, caused by the unusual conditions *e.g.* solvent effects during the

extraction.)

As can further be seen in Fig. 4, the rate is dependent on the temperature. The Arrhenius activation energy is 121 kJ/mol (28.8 kcal/mol) (Fig. 5) which is about the same as for the reference compound 4 (or 3).

Thus, a comparison of the rate constants in Table 1 shows that the cleavage of sulfone 2 is much faster than that of the reference compound 4 (or 3) even if the solvent effect is considered (see footnote p. 005). Furthermore, a comparison by inserting equal rates in the respective

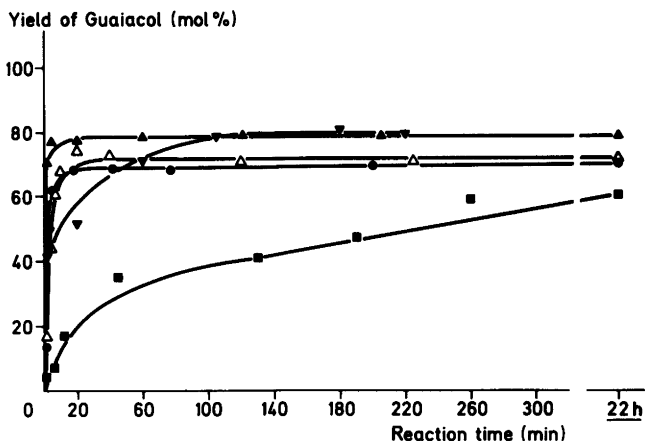


Fig. 4. Formation of guaiacol from cleavage of the β -aryl ether α -sulfone 2 in 0.001 mol/l sodium hydroxide at 0 °C (\blacksquare), 10 °C (\blacktriangledown), 22 °C (\bullet), 50 °C (\triangle), and in 0.01 mol/l sodium hydroxide at 50 °C (\blacktriangle). Solvent: dioxane/water 3:2.

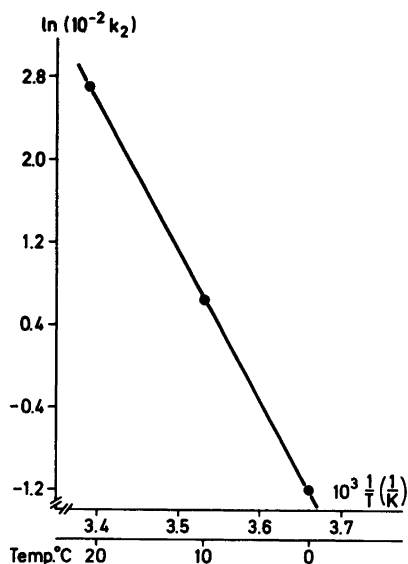
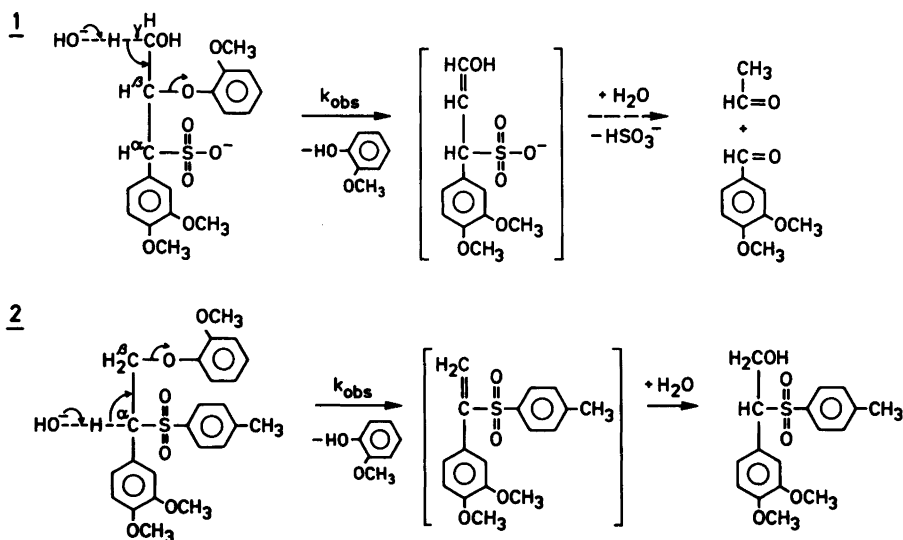


Fig. 5. Arrhenius diagram. Temperature dependence of the observed rate constants (k_2) for the cleavage of the β -aryl ether α -sulfone 2.

Arrhenius equations shows a temperature difference of about 200 °C for the same rate of cleavage.



Scheme 1. The β -elimination mechanisms for the alkaline cleavage of the β -aryl ether linkage with electron-withdrawing α -substituents. Corresponding alkene intermediates are formed by hydrogen elimination in the γ - and α -positions. Formation of the main final products according to literature: cf. further Refs. 10–13 for compound 1 and Refs. 5–6 for compound 2.

DISCUSSION

The great influence of the substituents, the α -sulfonate and the α -sulfone groups, on the alkaline cleavage of the β -aryl ether linkage can be rationalized as an inductive, electron-withdrawing effect on the neighbouring α -carbon-hydrogen bond thus making this hydrogen more acidic. This effect is strongest from the sulfone substituent (because of its un-ionized nature, see below) and brings about a β -elimination of the aryloxy residue with simultaneous formation of an alkene-product of intermediate. The β -elimination mechanism has been studied in the literature and suggested to be the dominating mechanism.^{5,7-9} From an alkaline treatment of a non-phenolic glycol- β -aryl ether- α -sulfonic acid the corresponding styrene- α -sulfonic acid (i.e. lacking the α -hydrogen) has been isolated.⁵ Similarly, from the glycol- β -aryl ether- α -sulfone 2 the corresponding β -hydroxy- α -sulfone was isolated by alkaline treatment⁶ (Scheme 1, compound 2). (The β -hydroxy group is likely to be formed by the addition of water to the intermediate styrene α -sulfone.) It could be argued that the β -hydroxy reaction product could also be formed by a direct substitution (e.g. an $\text{S}_{\text{N}}2$ -reaction, by hydroxide-ions attacking the β -carbon atom) instead of an E2 or E1cB-reaction. However, this

alternative is ruled out by the extensive studies by Stirling and coworkers⁷⁻⁹ of the elimination of phenoxide from similar α -substituted ethyl phenyl ethers. In these studies, it was proved that sulfone substituents (among others) activate β -elimination of phenol by a reversible E1cB-mechanism. This was shown by trapping the alkene intermediate with piperidine to give the piperodino adduct.⁷ The kinetic data for the formation of phenol (*i.e.* guaiacol) presented here are of the same order of magnitude as the earlier kinetic data although a stronger base was used to induce the β -elimination.⁹

Altogether, it may therefore be concluded that the presence of the α -sulfone group in the glycol- β -aryl ether structure (*i.e.* like 4) activates the β -elimination reaction easily expelling the phenoxy substituent.

Concerning the effect of the α -sulfonate in glycerol- β -aryl ether structures, two alternative ways of β -elimination have been discussed in the literature,¹⁰⁻¹³ elimination of the α -hydrogen (Saytzeff elimination) or the γ -hydrogen (Hofmann elimination). Product analysis and labelling experiments (of carbon side-chain by ¹⁴C) showed that the dominating β -elimination reaction occurs by abstraction of the γ -hydrogen. *i.e.* Hofmann elimination.¹¹ (See Scheme 1, compound 1.) This suggested therefore that the expected increase in the acidity of the α -hydrogen is less than the increase in the acidity of the γ -hydrogen due to the presence of the α -sulfonate. Thus the lower acidity of the α -hydrogen might partly be due to delocalization of the free electron pair in the ionized sulfonate group towards the α -carbon-hydrogen bond. In addition, the ionized nature of this substituent may exert a shielding effect towards hydroxide ions attacking the α -hydrogen so that these therefore more easily attack the γ -hydrogen.¹³ If the latter is the major cause, then the sulfonate group still exerts an inductive electron-withdrawing effect on the γ -hydrogen in spite of the long distance (over two carbon atoms). However, as is also discussed in Ref. 13, steric relationships seem to favour γ -hydrogen elimination in the presence of the sulfonate and this may also contribute to the increase in the reaction rate.

By the use of an un-ionized electron-withdrawing substituent such as the sulfone, electron delocalization and/or charge shielding effect are avoided. This type of substituent would then

exert an uncomplicated, stronger electron-withdrawing effect on the nearest carbon-hydrogen bond, *i.e.* the α -hydrogen. Thus, although only the α -hydrogen elimination was studied here with a model containing the sulfone substituent, its ease of elimination supports the mechanism suggested above. Accordingly, in general, electron-withdrawing effects are much stronger from an un-ionized substituent than from an ionized substituent. This explanation accounts for the fact that a much higher temperature is needed to cleave the β -aryl ether linkage by use of sulfonate substituents than by use of sulfone as is shown by the kinetic data in this work.

CONCLUSIONS

Electron-withdrawing substituents such as sulfonate or sulfone groups in the α -position of non-phenolic β -aryl ether structures activate the alkaline fission of the β -aryl ether linkage. In normal β -aryl ether structures (*i.e.* with α -OH) a temperature of about 170 °C is required for the cleavage to occur at a reasonable rate. With the activating sulfonate group in the α -position, the temperature required to attain the same rate is around 110 °C and with the sulfone in the same position the corresponding temperature is less than 0 °C. Earlier work indicates that the sulfone substituent activates the β -elimination reaction (E1cB) from the α -position whereas the sulfonate tends rather to activate a β -elimination from the γ -position in such structures.

The kinetic data obtained suggest that sulfone groups introduced into the α -position of aryl propane units in lignin would exert a very great effect on the rate of the β -aryl ether cleavage during alkaline pulping.

Thus, in order to promote alkaline delignification, sulfone groups seem to be the most interesting substituents to try to introduce into lignin in wood prior to pulping.

EXPERIMENTAL

Materials. Compound 1 [1-(3,4-dimethoxyphenyl)-2-(methoxy-phenoxy)-propanol-1-barium sulfonate] was prepared according to earlier description¹⁴ by heating the compound 3¹⁵ (2 g) with 80 ml sulfite solution (total SO₂-content 6,2 %, pH 1,5) in a rotating autoclave at 135 °C for 7 h. The work-up procedure in Ref. 14 was in

principle followed: After cooling and extraction with CH_2Cl_2 , the residue was passed through a column of Dowex 50W-X8 resin (H^+ -form). BaCO_3 was added to pH 6 and the mixture was allowed to stand overnight and was finally filtered and evaporated twice. After drying in a desiccator, the barium salt of the sulfonic acid was precipitated by adding ether to a solution in methanol. The mixture was allowed to stand for four days and the solvent was then filtered off and the crystals of the salt collected. Yield 65 % m.p. 178–180 °C.

Methyl ester of compound 1: The acetate of the sulfonic acid methyl ester [1-(3,4-dimethoxy-phenyl)-3-(2-methoxy-phenoxy)-3-acetoxy-propane-1-sulfonic acid methyl ester] was prepared according to the procedure in Ref. 14. The mass spectra pattern and the ^1H NMR spectra were identical with those described in Ref. 14.

Compound 2 [1-(3,4-dimethoxy-phenyl)-2-(2-methoxy-phenoxy)-ethyl-*p*-tolyl sulfone] was prepared from 4¹⁵ as described in Ref. 6: Yield 75 % crystalline; m.p. 79–82 °C. (Found C 65.05 H 5.99 O 21.59 S 7.32. $\text{C}_{24}\text{H}_{26}\text{O}_6$ requires: C 65.16 H 5.88 O 21.72 S 7.25.) ^{13}C NMR: δ 151.3–112.4 (16 signals, aromatic) 70.7 (α -C) 68.4 (β -C) 56.2 (OCH_3) 21.5 (CH_3). α -C and β -C was assigned by “off-resonance”-decoupled spectra. ($(\text{CD}_3)_2\text{CO}$ -solvent with TMS as reference.) ^1H NMR (80 MHz): δ 2.38 (s, 3H, ar- CH_3); 3.67, 3.71, 3.83 (3xs, 3x3H, 3x- OCH_3); 4.90–4.52 (m, 3H, 1H_α 2 H_β); 7.52–6.71 (m, 11H, ar-H). MS: (40 eV) *m/e* (rel.int %): 442 (M, 0.25), 287 (M-155,127), 259 (0.22), 164 (M-155-123,578.8), 156 (0.13) 150 (6.6), 149 (100), 123 (23.3).

Cooking liquors. Compound 1: NaOH (*p.a.*) was dissolved in 225 ml of distilled water to the desired concentration. Compound 2: NaOH was dissolved in a mixture (20.0 ml) of 40 % distilled water and 60 % dioxane to the desired concentration. 60 % dioxane was necessary when conducting the experiments at 0 °C in order to achieve full solubility of the sulfone 2. At a temperature below 0 °C, precipitation occurred (in presence of 0.01 mol/l NaOH). Phase separation occurred at all temperatures if NaOH concentration exceeds 0.5 mol/l.^{16,17}

Solutions of substrate. Compound 1: The model compound (350 mg) was dissolved in H_2O (20 ml) to give an ultimate substrate concentration during the cook of 3.3 mmol/l. Compound 2: 10 mg were dissolved in 5 ml dioxane to give an ultimate substrate concentration during the run of 0.9 mmol/l.

Cooking apparatus and procedure. Compound 1: The same apparatus and procedure were used as described in Ref. 4. Compound 2: 20.0 ml of

the alkaline solution was equilibrated at the desired temperature. The run was started by carefully (to avoid precipitation, especially at low temperatures) adding 5.0 ml of the substrate solution to the alkaline solution under vigorous stirring.

Work-up procedure. The same procedure was used for compounds 1 and 2 after the alkaline treatments (cookings) of the model compounds. After a fast cooling of the sample to room-temperature (in the case of cooking) a 3.0 ml aliquot was immediately withdrawn and transferred to a separation funnel diluted with water (5 ml containing 1 mol/l Na_2SO_4), neutralized with 10 % phosphoric acid and extracted with dichloromethane (2.0 ml) containing *p*-cresol as internal standard. The extraction was repeated twice with fresh CH_2Cl_2 (1 ml).

The guaiacol formed from the model compounds was determined directly (GLC) in aliquots from the dried (Na_2SO_4) CH_2Cl_2 -extracts. (No other products were identified or isolated in this work.)

GLC-analysis. The analyses of guaiacol and *p*-cresol were performed on a 5 % Castorwax column (steel; 2 m, 3 mm diam) at a temperature of 150 °C (inj. temp. 200 °C; det. temp. 200 °C) isothermally, cf. Ref. 3). The GLC-apparatus was F17 or F270 equipped with a flame ionization detector. The areas of the peaks were measured by means of a computing integrator (Minigrator, Spectra Physics) and converted into mg per aliquot using a calibration curve. The amounts of guaiacol are expressed in the figures as mol % of theoretical yield. The starting materials (1 and 2) could not be found in the chromatograms (on SE-30 column) probably due to thermal decomposition in the GLC-injector port. It was not therefore certain whether or not any starting material remained after reaction.

Kinetic method. The reactions were in general studied under pseudo first-order conditions using at least a tenfold excess of sodium hydroxide over substrate. Integration of the rate equation gives the expression¹⁸ $\ln(a/a-x) = k_1 t$ where a refers to the maximal and x to the actual concentration of guaiacol. Plots of $\ln(a/a-x)$ versus time were linear and the pseudo first-order rate constants (k_1) were calculated from the slopes of the lines. When studying compound 2 under very low $[\text{HO}^-]$ (0.001 mol/l), the starting $[\text{OH}^-]$ was almost equal to the initial [substrate] and therefore a mathematically equivalent second-order rate expression of one reactant was used.¹⁸ Integration of this rate equation gives the expression¹⁸ $1/(a-x) = kt + 1/a$. Plots of $1/(a-x)$ versus time were linear with some scattering. From the estimated slopes of the lines, the

second-order rate constants (k_2) were calculated. They are given in Table 1. The Arrhenius activation energies (E_a) for the reactions were calculated from the integrated expression¹⁸ $\ln k = -E_a/RT + A$. Plots of $\ln k$ versus the inversed absolute temperature $1/T$ are given in Figs. 2 and 5.

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