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The Kinetics of Lignin Reactions during Chlorine Dioxide Bleaching. Part 1. Influence of pH and Temperature on the Reaction of 1-(3,4-Dimethoxyphenyl)ethanol with Chlorine Dioxide in Aqueous Solution

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Rate constants as well as the products formed from the reaction between chlorine dioxide and the non-phenolic lignin model compound 1-(3,4-dimethoxyphenyl)ethanol have been determined in the pH interval 3–8. Spectroscopic data for the substrate and some products are given. The pH of the reaction mixture has a large influence on both the rate constant and the product distribution. Under technical chlorine dioxide bleaching conditions (pH 3, 40 °C and an ionic strength of 0.3 mol kg^{-1}) the rate constant has been found to be 0.12(2) M^{-1} s^{-1}, which corresponds to a half-life of approximately 7 min in 0.01 M solution. The influence of temperature [$E_a = 29(7)$ kJ mol^{-1}] on the rate of reaction of this lignin model is small. At acidic pH (3–5) a large variety of both oxidized (quinones, lactones and ketones) and chlorinated products are formed. Above pH 8, one oxidation product, 3,4-dimethoxyacetophenone, predominates. No chlorinated products are found at a high pH. The mechanisms of formation of all these products are discussed.

Chlorine dioxide is an old, well known electron-transfer oxidant and is also nowadays one of the most widely used oxidising agents for the bleaching of fibers.[1–4] Technically, chlorine dioxide has been found to be very effective in the degradation of lignin and also in the brightening of chemical pulps. The use of chlorine dioxide in elemental chlorine free (ECF) bleaching is, however, being debated due to environmental concerns, and alternative total chlorine free (TCF) bleaching agents are now being introduced and developed, and are to some extent already being used in the pulp and paper industry.[5]

This trend from chlorine dioxide (and earlier chlorine) to other chemicals is due to the suspected formation of environmentally unwanted chloroorganics, 'adsorbable organic halogens' (AOX), and their discharge in the bleachplant effluents.[6,7] Efforts to modify the chlorine dioxide bleaching process by, e.g., the use of lower multiples (i.e., a lower charge of chlorine dioxide) or by changing the pH level have recently been made in order to lower the AOX levels without jeopardizing the bleaching efficiency.[8–10] However, very little is known about how lignin reactions are affected by these types of modification and how these effects are reflected in degradation, chlorination and brightening. In particular, the relationships between reactions that give rise to lignin dissolution (aromatic ring-opening reactions) and those that lead to brightening reactions (non-chromophoric products) are not fully known.

Mechanisms for how chlorine dioxide reacts with lignin and lignin models have been outlined in numerous works: product studies on phenolic lignin models have been conducted by several authors.[11–25] Kinetic studies have been carried out on phenolic lignin models.[26–29] Reactions between non-phenolic lignin and chlorine dioxide are not so well characterized. Only product studies on the reactions between chlorine dioxide and non-phenolic lignin models have been performed.[19,22,30–32] Isolated lignins have been characterized.[33,34] Data are still lacking as to how fast non-phenolic lignin models react with chlorine dioxide and to what extent the different products are formed. Since only ca. 10% phen-

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olic structures are left in lignin after oxygen prebleaching,[35] the reaction of lignin with chlorine dioxide during pulp bleaching will mainly, in our opinion, involve non-phenolic structures, cf., Ref. 36.

In this work, we have determined the rate constant and the products formed in the reaction with chlorine dioxide of a non-phenolic lignin model, 1-(3,4-dimethoxyphenyl)ethanol **1**. This model has never been examined before but is a good representative model for residual lignin, since it contains a hydroxy group in the α-position. The effects of pH, temperature and ionic strength and the presence of sodium chloride on the reaction rate of this model substrate and on the amounts of products formed have been determined.

Experimental

Materials. Commercial reagents, standards and starting materials were of *pro analysi* grade when available, otherwise the purest chemicals available were used.

1-(3-methoxy-4-trideuteriomethoxyphenyl)ethanol was prepared from 4-hydroxy-3-methoxyacetophenone by reaction with deuteriated iodomethane. The starting material was first extracted as an ion pair with tetrabutylammonium hydroxide into dichloromethane from aqueous solution. The dichloromethane solution was then dried over anhydrous sodium sulfate. Deuteriated iodomethane was added and the solution was refluxed for 30 min. The salt formed was removed by precipitation with diethyl ether. The yield was 92% and the purity was 97% as determined by gas chromatography. The product was then treated with sodium borohydride in aqueous solution for 4 h. Extraction with dichloromethane followed by drying over anhydrous sodium sulfate and evaporation of the solvent gave 1-(3-methoxy-4-trideuteriomethoxyphenyl)ethanol as a clear syrup. The yield was 93% and the purity was 98%

4-Chloroveratrole **10** was prepared from 4-chloroguaiacol by methylation with diazomethane in a diethyl ether–methanol solution. 4,5-Dichloroveratrole **11** was prepared in the same manner from 4,5-dichloroguaiacol. Chlorine dioxide was prepared by allowing sodium chlorite to react with hydrochloric acid. The chlorine dioxide produced was carried in a nitrogen stream into cold deionized water. The chlorine content was less than 1% and had no detectable effect on the chlorination reactions.[31] Stock solutions of chlorine dioxide were stored in the refrigerator in the dark.

Chlorine dioxide treatment. The kinetic experiments were performed in a 200 ml double bottomed glass reactor with a rubber-sealed plastic top. A water bath kept the temperature constant to within ±1 °C. The pH was kept constant by a PHM 63 digital pH meter, a TTT 60 titrator and an ABU 80 autoburette Radiometer Copenhagen. Water, salt solutions (sodium sulfate and sodium chloride), and chlorine dioxide were mixed for one min before a 0.1 M aqueous solution of the soluble lignin model was injected. Samples of the reaction mixture were taken with a syringe through a rubber septum. Sampling was done every tenth minute at the beginning of the reaction and every hour of the reaction towards the end. The reaction was monitored until all the chlorine dioxide or lignin model had been consumed, or for a reaction time of 5 h. Reaction mixtures for preparative separation and spectroscopic analysis were prepared in a glass bottle without keeping the pH and temperature constant. Experiments with isotope-labelled chlorine were performed in a glass vial. A solution of chlorine dioxide (10 mM) with the natural isotopic abundance was allowed to react with a 10 mM solution of 1-(3,4-dimethoxyphenyl)ethanol in a 0.25 M $Na^{35}Cl$ solution at pH 2–3.

Radiolysis. Solutions of 0.001 M 1-(3,4-dimethoxyphenyl)ethanol containing 0.05 M sodium bromide in a pH 5; 0.0001 M phosphate buffer or a pH 9; 0.0005 M borate buffer were degassed with dinitrogen oxide or with a mixture of 20% oxygen in dinitrogen oxide. The solutions were irradiated for 1 h with an AECL ^{60}Co-Gammaradiator producing a total of 3.1×10^{-4} M radical cations from the initially formed Br_2^--radicals.

Work-up procedure for the reaction mixtures. To determine the chlorine dioxide concentration, samples were titrated iodiometrically. The concentration of chlorine dioxide was taken as being the difference between the value found in the titration of a nitrogen-degassed sample and the value for a non-degassed sample. By this procedure, any interference by other oxidants present in the solution was avoided. Samples for liquid chromatography were immediately injected into the HPLC chromatograph using a syringe. For gas chromatography, 2 ml samples of the reaction mixture were quenched either by addition of 0.5 ml 0.4 M ascorbic acid or by nitrogen degassing. Quenching of the chlorine dioxide reaction with ascorbic acid gave a very distinct stop time but quinones were reduced and therefore could not be determined without derivatization. The quenched samples were extracted with 2 ml dichloromethane containing 0.6 mg l^{-1} Docosan as an internal standard. Thereafter, the samples were transferred to glass vials and injected into the gas chromatograph. Some samples were derivatized for gas chromatography mass spectroscopy analysis. Ethylation was done by allowing the sample to react with diethyl sulfate in 1,2-dimethoxyethane, ethanol, water and potassium hydroxide for ca. 24 h. Acetylation was performed overnight with acetic anhydride and pyridine (1:1) at room temperature.

Separation methods. For preparative separation, a low-pressure liquid chromatographic system was used as well as a semipreparative high-pressure liquid chromatographic system. Crude extracts of reaction mixtures were first prefractionated by straight phase chromatography

on the low-pressure system (a 10–30 cm long, 1.5 cm wide glass column dry packed with Silica Gel 60 was used in connection with a FLUID Metring Inc. lab pump). Complex fractions were then further separated by reversed-phase chromatography on a semi-preparative system (a Spectra Physics SP8700 solvent delivery system connected to a Kromasil reversed-phase column: 25 cm, 10 mm ID, 5 μm particles and an LKB 2140 diode array ultraviolet detector). For analytical samples, gas chromatography and high-pressure liquid chromatography were used.

Gas chromatographic analysis. The samples were injected (2 μl) and split 1:20 on a Hewlett Packard HP 5890A gas chromatograph equipped with a Hewlett Packard HP 7673A automatic sampler and a flame ionization detector. Separations were performed on a 30 m, 0.257 mm ID fused silica capillary column with 0.25 μm phenyl(methyl)polysilicone film (DB-17, 50% phenyl and 50% methyl). The injector temperature was 250 °C and the detector temperature was 280 °C. The temperature program started at 130 °C and increased by 4 °C min^{-1} to reach the final temperature of 270 °C. Peaks were integrated and amounts were determined from calibration curves of purified reaction products, commercially available or synthetically produced substances.

Liquid chromatographic analysis. The samples were injected (5 μl) on a Spectraphysics SP8700 solvent delivery system with a Rheodyne injector. The column was a 15 cm, 4.6 mm ID packed with 5 μm Kromasil C-18 particles. An Applied Biosystems 759A UV-absorbance detector was used at 280 nm. The gradient program started at 85% water, 4% acetonitrile and 10% methanol and the proportions were changed linearly to 10% water, 36% acetonitrile and 54% methanol in 15 min. After a further 2 min at the final conditions, the mobile phase was reset to the starting composition.

Mass spectrometry. Mass spectra were recorded on a Finnigan Mat TSQ 46-C mass spectrometer interfaced with a Hewlett Packard HP 5890 II gas chromatograph. The ion source temperature was 150 °C and the ionization energy was 70 eV. Samples were 1 μl and the split ratio was 1:20. The column was a SPB1 60 m, 0.32 mm ID with 025 μm crossed-linked methylpolysilicone film as the stationary phase. A typical temperature program ran from 100 to 270 °C by 4 °C min^{-1}.

Nuclear magnetic resonance spectroscopy. A Bruker AMX 300 MHz instrument was used to record proton and ^{13}C NMR spectra. Deuteriated chloroform was used as the solvent for the analysis. Chemical shifts are reported in δ downfield from tetramethylsilane.

Infrared spectroscopy. The samples were injected by a Science Glass Engineering (SGE) thermal desorption unit shisa-11 on a cold trap SGE-CTS-LN connected to a Hewlett Packard HP 5890 II gas chromatograph. The samples were then gasified by raising the temperature at a rate of 70 °C min^{-1} from 25 to 100 °C and thereafter at 10 °C min^{-1} to 300 °C. The column was a Restech RTX-5 30 m, 0.32 mm ID with 025μm phenyl(methyl)-polysilicone film (95% methyl and 5% phenyl) as the stationary phase. The flow was split at the detector side in a ratio of 1:9 using two non-coated columns of different lengths and widths. The infrared spectrometer was a Bruker IFS-85 FTIR with a 197 mm long and 1 mm wide light pipe. The scanning rate was 10 scans s^{-1} and the resolution was 8 cm^{-1}.

Ultraviolet spectroscopy. UV spectra were recorded on a Hitachi U-3200 spectrophotometer. Samples were dissolved in dichloromethane.

Mass, NMR, IR and UV spectroscopic data of compound **1**, *and of some identified oxidation products, compounds* **2–6.** **1**: MS: 183 (7), 182 (M^+, 65), 168 (8), 167 (83), 151 (4), 140 (8), 139 (100), 124 (29), 108 (16), 95 (8), 79 (13), 77 (20), 65 (14), 53 (11), 51 (13), 43 (45). ^1H NMR: δ 1.4 (d, 3 H, J=6.4 Hz), 2.0 (s, 1 H), 3.9 (s, 3 H), 3.9 (s, 3 H), 4.8 (q, 1 H, J=6.4 Hz), 6.8 (dd, 1 H, J_1=8.2 Hz, J_2=0.15 Hz), 6.9 (dd, 1 H, J_1=8.2 Hz, J_2=1.9 Hz), 7.0 (dd, 1 H. J_1=1.9, J_2=0.15). ^{13} C NMR: δ 25, 56, 56, 70, 109, 111, 117, 139, 148, 149. Ethyl derivative: MS: 211 (5), 210 (M^+, 39), 196 (11), 195 (100), 178 (3), 167 (24), 165 (49), 151 (7), 150 (8), 139 (59), 135 (8), 124 (14), 108 (6), 105 (6), 103 (6), 91 (9), 77 (14), 43 (17).

2: MS: 182 (M^+, 3), 181 (8), 167 (41), 153 (72), 149 (61), 140 (10), 139 (41), 137 (21), 125 (23), 121 (10), 111 (35), 107 (11), 97 (21), 95 (35), 93 (18), 69 (90), 55 (28), 53 (44), 43 (100). ^1H NMR: δ 1.4 (d, 3 H, J=6.5 Hz), 2.84 (d, 1 H, J=4.4 Hz), 3.84 (s, 3 H), 4.86 (dq, 1 H J_1=6.5, J_2=4.4), 5.92 (s, 1 H), 6.72 (s, 1 H). ^{13}C NMR: δ 22, 56, 64, 107, 128, 151, 158, 182, 187. ^{13}C H-Corr NMR: δ 22–1.4, 56–2.8, 64–3.8, 107–5.9, 128–6.7.

3: MS: 140 (7), 139 (6), 138 (M^+, 72), 125 (5), 123 (10), 111 (3), 110 (51), 109 (6), 108 (70), 97 (4), 96 (1), 95 (27), 82 (44), 80 (6), 79 (7), 69 (100), 55 (17), 54 (49), 53 (34), 52 (28), 51 (6), 50 (7), 41 (18). ^1H NMR: δ 3.9 (s, 3 H), 6.0 (s, 1 H), 6.7 (s, 2 H). ^{13}C NMR: δ 56, 108, 135, 137, 158, 182, 187. IR: 868 (w), 1003 (w), 1092 (m), 1173 (w), 1231 (s), 1296 (w), 1342 (w), 1593 (s), 1605 (w), 1670 (s), 1685 (s).

4: MS: 170 (3), 169 (1), 168 (M^+, 2), 155 (2), 153 (7), 141 (7), 140 (95), 125 (25), 109 (6), 97 (5), 82 (11), 69 (100), 59 (27), 53 (25). ^1H NMR: δ 4.0 (s, 6 H), 5.4 (s, 2 H). ^{13}C NMR: δ 56, 102, 163, 178. UV: 283, 406, 504. Acetate derivative: MS: 255 (1), 254 (M^+, 5), 213 (1), 212 (8), 171 (5), 170 (100), 169 (5), 156 (2), 155 (20), 141 (4), 126 (2), 111 (2), 109 (3), 69 (6), 53 (2), 43 (16).

5: MS: 181 (6), 180 (M^+, 52), 166 (11), 165 (100), 137 (11), 122 (7), 119 (4), 107 (5), 94 (5), 92 (4), 79

(11), 77 (12), 63 (4), 51 (7), 43 (11). ^{1}H NMR: δ 2.6 (s, 3 H), 3.9 (s, 3 H), 4.0 (s, 3 H), 6.9, (d, 1 H, J= 8.3 Hz), 7.5 (d, 1 H, J=1.6 Hz), 7.6 (dd, 1 H, J_1= 1.6 Hz, J_2=8.3 Hz). ^{13}C NMR: δ 26, 56, 56, 110, 110, 123, 130, 149, 153, 197. Deuteriated: MS: 184 (4), 183 (M^+, 50), 169 (8), 168 (100), 140 (8), 125 (2), 122 (2), 107 (6), 94 (3), 92 (3), 79 (19), 66 (4), 63 (4), 51 (18), 43 (31).

6: MS: 182 (M^+, 1), 168 (1), 167 (8), 151 (7), 150 (8), 140 (19), 139 (44), 138 (66), 123 (5), 122 (3), 112 (2), 111 (28), 109 (3), 108 (23), 95 (12), 80 (12), 79 (35), 59 (18), 53 (15), 52 (19), 51 (59), 50 (29), 43 (100). ^{1}H NMR: δ 1.6 (d, 3 H, J=6.7 Hz), 3.8 (s, 3 H), 5.2 (dq, 1 H, J_1=6.7 Hz, J_2=1.6 Hz), 5.9 (ddd, 1 H, J_1=1.6 Hz, J_2=1.1 Hz, J_3=1.8 Hz), 6.2 (dd, 1 H, J_1= 10.1 Hz, J_2=1.8 Hz), 8.3 (dd, 1 H, J_1=10.1 Hz, J_2= 1.1 Hz). ^{13}C NMR: δ 21, 51, 76, 118, 123, 137, 145, 162, 164. ^{13}C H-corr NMR: δ 21–1.6, 51–3.8, 76–5.2, 118–5.9, 123–6.2, 137–8.3. IR: 2997 (w), 2963 (w), 1759 (s), ca. 1740 (m), 1643 (w), 1254 (m), 1169 (s), 837 (w).

Mass, NMR and IR spectroscopic data of some identified chlorination products, compounds **7–11**. **7**: MS: 219 (3), 218 (28), 217 (9), 216 (M^+, 78), 204 (6), 203 (42), 202 (8), 201 (100), 185 (6), 175 (18), 174 (5), 173 (56), 160 (8), 158 (25), 139 (19), 138 (90), 123 (20), 100 (23), 77 (32), 65 (16), 63 (15), 51 (13), 43 (59). ^{1}H NMR: δ 1.4 (d, 3 H, J=6.3 Hz), 3.0 (s, 1 H), 3.8 (s, 3 H), 3.8 (s, 3 H), 5.2 (q, 1 H, J=6.3Hz), 6.8 (s, 1 H), 7.1 (s, 1 H). ^{13}C NMR: δ 24, 56, 56, 67, 109, 112, 122, 135, 148, 148. IR: 883 (w), 1030 (m), 1099 (w), 1157 (m), 1211 (m), 1261 (m), 1280 (m), 1385 (w), 1443 (w), 1501 (s), 1570 (w), 1605 (w), 2851 (w), 2950 (w), 2982 (w), 3009 (w), 3653 (w). Ethyl derivative: MS: 247 (1), 246 (13), 245 (1), 244 (M^+, 34), 232 (4), 231 (32), 230 (13), 229 (100), 204 (15), 203 (13), 201 (55), 199 (32), 189 (32), 184 (6), 175 (10), 173 (17), 164 (11), 158 (7), 149 (6), 138 (39), 121 (4), 105 (4), 91 (10), 77 (13), 43 (13). Acetate derivative: MS: 261 (3), 260 (24), 259 (9), 258 (M^+, 70), 243 (1), 224 (2), 223 (14), 218 (2), 216 (6), 204 (1), 203 (13), 202 (9), 201 (72), 200 (31) 199 (100), 198 (65), 185 (13), 184 (15), 183 (28), 181 (50), 164 (20), 155 (11), 138 (9), 91 (14), 77 (16), 65 (7), 63 (7), 51 (8), 3 (62).

8 (or **9**): MS: 219 (2), 218 (20), 217 (7), 216 (M^+, 65), 204 (3), 203 (30), 202 (9), 201 (96), 185 (4), 175 (17), 174 (4), 173 (51), 160 (6), 158 (21), 139 (16), 138 (100), 123 (11), 77 (15), 65 (8), 63 (4), 51 (10), 43 (56). Acetate derivative: MS: 261 (3), 260 (22), 259 (8), 258 (M^+, 68), 219 (2), 218 (31), 217 (11), 216 (92), 204 (1), 203 (9), 202 (6), 201 (49), 200 (16), 199 (72), 198 (24), 185 (22), 184 (15), 183 (40), 173 (9), 164 (18), 155 (13), 138 (8), 91 (16), 77 (19), 65 (7), 63 (6), 51 (9), 43 (100).

9 (or **8**): MS: 219 (1), 218 (13), 217 (3), 216 (M^+, 35), 204 (3), 203 (31), 202 (9), 201 (100), 185 (7), 175 (3), 174 (1), 173 (12), 160 (4), 158 (13), 139 (7), 138 (52), 123 (5), 100 (5), 77 (9), 65 (5), 63 (3), 51 (6), 43 (20). Acetate derivative: MS: 261 (3), 260 (24), 259 (9), 258 (M^+, 69), 243 (1), 224 (3), 223 (16), 218 (2), 216 (7), 204 (1), 203 (26), 201 (83), 200 (43), 199 (100), 198 (90), 186 (14), 185 (24), 184 (41), 183 (42), 181 (70), 164 (19), 155 (14), 138 (13), 91 (18), 77 (15), 65 (7), 63 (8), 51 (12), 43 (94).

10: MS: 175 (2), 174 (32), 173 (9), 172 (M^+, 100), 160 (1), 159 (18), 158 (5), 157 (58), 131 (7), 129 (22), 114 (6), 113 (7), 111 (14), 101 (4), 99 (10), 94 (21), 93 (31), 86 (5), 79 (20), 75 (7), 65 (25), 63 (14), 51 (17), 50 (8). IR: 876 (w), 1026 (m), 1126 (w), 1177 (w), 1231 (m), 1265 (m), 1400 (w), 1501 (s), 2847 (w), 2947 (w), 3009 (w).

11: MS: 210 (11), 209 (4), 208 (68), 206 (M^+, 100), 195 (6), 193 (32), 192 (6), 191 (50), 165 (8), 163 (13), 148 (3), 147 (6), 145 (7), 130 (14), 128 (27), 127 (16), 115 (4), 113 (14), 109 (4), 101 (4), 99 (16), 97 (7), 85 (6), 63 (5), 62 (4), 51 (6), 50 (21), 43 (36).

Kinetic methods. The rate constants of the reaction reported here between the lignin model **1** and chlorine dioxide were mainly determined by the common integration method, i.e., monitoring the concentrations of both the chlorine dioxide and the lignin model at different reaction times and calculation according to a second order rate law.[37] At low pH values, however, the reaction order and the rate constants were also determined by the initial rate method.[37] The data were fitted to the equation $\log r_0 = \alpha \log[A_0] + \beta \log[B_0] + \log k$, where r_0 is the initial rate, α is the order with respect to chlorine dioxide, $[A_0]$ is the initial concentration of chlorine dioxide, β is the order with respect to the lignin model, $[B_0]$ is the initial concentration of lignin model and k is the rate constant. In order to obtain a reliable estimate of the reaction order and rate constants by this method, the reaction should not proceed to more than 10% conversion of the starting material. The starting concentrations in our experiments were varied from 5 mM to 20 mM for the lignin model and from 10 mM to 20 mM for chlorine dioxide. To determine r_0, both the chlorine dioxide consumption and the lignin model disappearance were monitored during the first minute of the reaction.

By measuring the rate constant at different temperatures, the Arrhenius activation energy, E_a, was determined. The stoichiometry was determined by measuring the difference in starting materials consumed at different times and accepting the mean value as an estimate of the correct value.

Results

The reaction products. Many different products were formed when the lignin model **1** was treated with chlorine dioxide under acidic conditions. The detected and identified products result from different oxidation and chlorination reactions of the starting material. In Fig. 1, the different types of oxidation product identified are shown.

Five different chlorinated products (Fig. 2) were detected but most of them were present only in trace

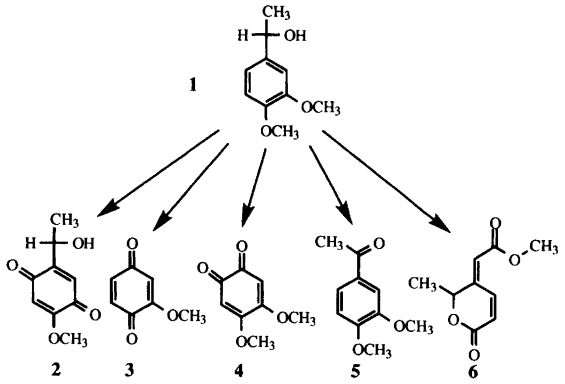

Fig. 1. Identified oxidation products: **2** and **3** *para*-quinones, **4** *ortho*-quinone, **5** 3,4-dimethoxyacetophenone and **6** lactone ester, formed during chlorine dioxide treatment of 1-(3,4-dimethoxyphenyl)ethanol **1**.

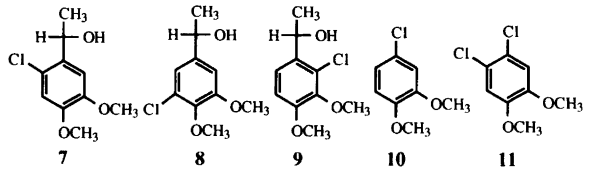

Fig. 2. Identified chlorinated products: **7–9** monochlorinated 1-(3,4-dimethoxyphenyl)ethanol, **10** monochloroveratrole and **11** dichloroveratrole, formed during chlorine dioxide treatment of 1-(3,4-dimethoxyphenyl)ethanol **1**.

amounts (**8**, **9** and **11**). The chlorinated products formed in measurable amounts were monochlorinated (**7** and **10**).

The reaction order and rate constants. It was not always possible to measure the initial reaction in the short times needed to keep within the 10% conversion limit required by the initial rate method (see the Experimental section). In some of the experiments, we had to use values of up to 30% conversion. However, the measured rate constant by this method at pH 3 is in good agreement with the rate that we have obtained with the integration method. At 39 °C and pH 3 we found a rate constant value of 0.12(2) M^{-1} s^{-1} (ionic strength 0.3 mol kg^{-1} in sodium sulfate solution). The overall order including the error limits (95% confidence interval) was found to be 1.7(7) and the individual orders 1.3(5) for chlorine dioxide and 0.4(6) for the lignin model at pH 3. Rate constants determined at 20 °C and other pH levels are given in Table 1.

The temperature dependence. The Arrhenius activation energy, E_a, was determined from the rate constants measured at pH 3 and pH 4 in the interval from 20–40 °C. The ionic strength was 0.3 mol kg^{-1} (sodium sulfate). At pH 3, E_a was found to be 29(7) kJ mol^{-1}, and at pH 4, $E_a = 26(16)$ kJ mol^{-1}. These values are in the same range as those for diffusion-controlled processes. It is important to notice that these values refer to the sum of all reactions occurring in the mixture. The yields of the different products had the same ratios to each other at the different temperatures except in one case; the formation of 3,4-dimethoxyacetophenone **5** showed a larger temperature dependence than the other products. This indicates that this product probably has a different mechanism of formation than do the other products.

Effect of the ionic strength on the reaction. The ionic strength (in a sulfate buffer) was varied from 0.3 to 0.9 mol kg^{-1} at pH 3 and the effects on the product ratio and rate constant were measured. It was found that the rate constant was not affected by the ionic strength, according to the obtained values: $6.0(6) \times 10^{-2}$ M^{-1} s^{-1} at an ionic strength of 0.3 mol kg^{-1} and $6.2(7) \times 10^{-2}$ M^{-1} s^{-1} at 0.9 mol kg^{-1} (temperature 20 °C). The ratios between the products at the different ionic strengths were also the same. The ionic strength, therefore, has no significant effect on either the rate constant or the ratios between the products in the studied interval.

Effects of pH on the reaction. The pH has been found to have a large effect on both the reaction rate and the product distribution. The overall reaction rate (with respect to both chlorine dioxide and the lignin model) decreases when the constant pH value was changed in the interval 3–6 (Table 1).

However, the fit to a second-order rate law is gradually lost as the pH is increased and at pH 8 the experimental data deviate from a second-order rate plot (Fig. 3). To obtain an approximate rate constant, we used data to

Table 1. Second-order rate constants (k) and stoichiometry for the reaction at different constant pHs and in different ionic strength buffer solutions (approximate k at pH 8, see the text). Error estimations are given as 95% confidence interval (CI) for the rate constant. Errors in the stoichiometry are less than 5%, expressed as 95% confidence interval. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1}.

	In 0.1 M sodium sulfate solution		In 0.3 M sodium chloride solution	
pH	$k/10^{-2}$ M^{-1} s^{-1}	Stoichiometry (ClO_2 : lignin model)	$k/10^{-2}$ M^{-1} s^{-1}	Stoichiometry (ClO_2 : lignin model)
3	6.0 (6)	1.35:1	35 (30)	1.19:1
4	2.3 (3)	1.61:1	18 (30)	1.15:1
5	0.41 (9)	2.83:1	0.93 (2)	1.72:1
6	0.19 (6)	5.23:1	0.48 (1)	2.70:1
8	[0.34 (9)]	6.26:1	[0.18 (5)]	8.46:1

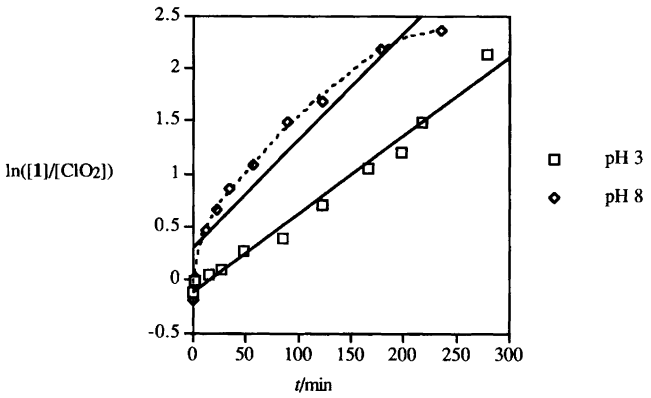

Fig. 3. Fit of kinetic data to a second-order rate plot (solid lines) at two constant pH levels. Observe the deviation of the data (broken line) from runs at pH 8 compared with the data from runs at pH 3. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate).

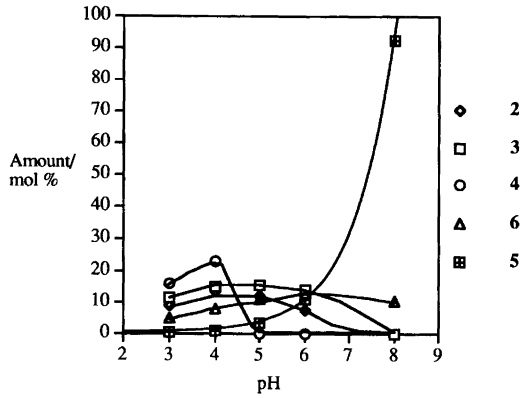

Fig. 5. Effect of pH on the formation of *para*-benzoquinone (**2**), *para*-benzoquinone (**3**), *ortho*-benzoquinone (**4**), 3,4-dimethoxyacetophenone (**5**) and lactone (**6**) at 15% extent of reaction as a mole percentage of consumed starting material. The value at pH 8 for **5** has been adjusted to a theoretical yield of 82.2% by substracting the minimum lactone amount from the maximum total yield of 100%. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate).

calculate a second-order rate constant, which is given in Table 1.

The stoichiometry of the reaction is affected when the reaction pH is changed. When the pH is raised from 3 to 8, the consumption of chlorine dioxide increases (Table 1). A consequence of this different stoichiometry is depicted in Fig. 4: when the same mole ratio of ClO_2 to the lignin model is used, the extent of degradation of the lignin model is shown to decrease markedly as the pH is increased.

The product formation also depends on the pH during the reaction, as shown in Figs. 5 and 6. When the pH is raised from 3 to 5, *para*-quinones are formed in a slightly higher yield (see Fig. 5). When the pH is raised above 4, *ortho*-quinone formation is rapidly reduced compared with the formation of *para*-quinones. The formation of 3,4-dimethoxyacetophenone **5** is, however, markedly increased when the pH is raised over the whole interval studied, and it is almost the only product at pH 8. On the other hand, the formation of chlorinated products

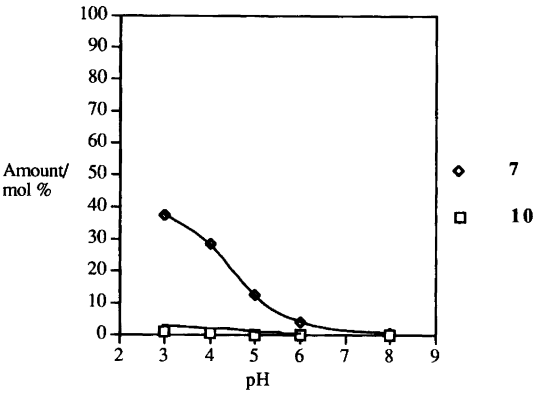

Fig. 6. Effect of pH on the formation of monochlorinated **1** (**7**) and chloroveratrole (**10**) at 15% extent of reaction as a mole percentage of consumed starting material. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate).

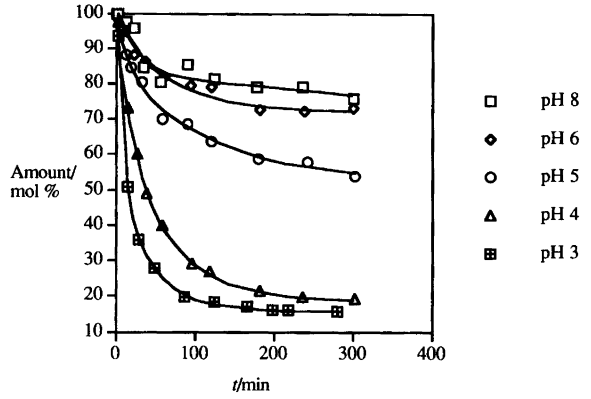

Fig. 4. The degradation of the lignin model **1** at different constant pH values. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate).

decreases constantly at pH values above 3, as is shown in Fig. 6. The mass balance of all the products found at different pH values is depicted in Fig. 7. It is obvious here that at high and low pH values most of the products are found and identified but that at intermediate pH levels (5–6) only about half of the products are found. This lack of identified products may be due to the formation of unstable quinones[38] and/or acids remaining in the aqueous phase, which were not extracted and identified.

Effects of the chloride solutions. When the ionic strength buffer was changed from sodium sulfate to sodium chloride solution, several differences in rate, stoichiometry and product pattern were observed. First, the rate constant of the reaction increased by a factor of as

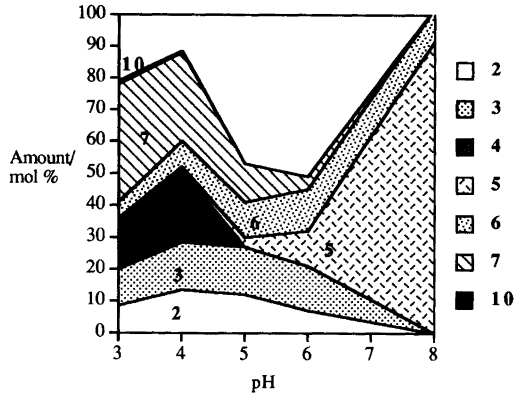

Fig. 7. The mass balance at different pHs given at 15% extent of reaction as a mole percentage of consumed starting material. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate).

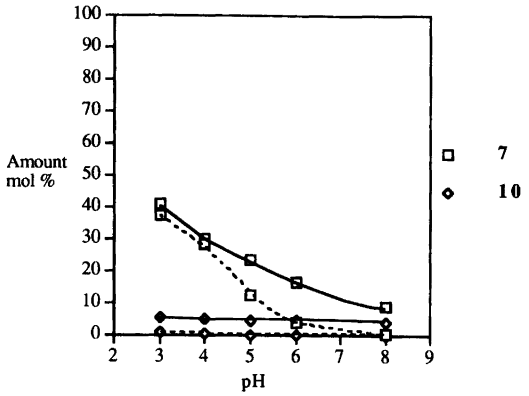

Fig. 9. Effect on formation of chloroveratrole (**10**) and monochlorinated **1** (**7**) of the pH and different ionic strength solutions. Solid lines correspond to chloride solution and broken lines to sulfate solution. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate or 0.3 M sodium chloride).

much as 5 at pH levels 3 and 4 (Table 1). The stoichiometry decreased at all pH levels except at pH 8, where instead a higher chlorine dioxide consumption was observed. Secondly, some of the products were affected by this change, as is evident in Figs. 8 and 9. Fig. 8 shows that the sudden drop in formation of the *ortho*-quinone at pH 5 in the sulfate solution is shifted to pH 8 in the presence of chloride. Also, at high pH, the 3,4-dimethoxyacetophenone **5** is formed in only half the yield (ca. 45%) of that formed in the sulfate solution. Furthermore, in the presence of chloride more chloroorganics are formed: the yield of the chlorinated compound **7** increases especially at higher pH (6–8) (Fig. 9). The effect of chloride and its significance for the chlorine dioxide bleaching process will be described more thoroughly in a forthcoming publication.[39]

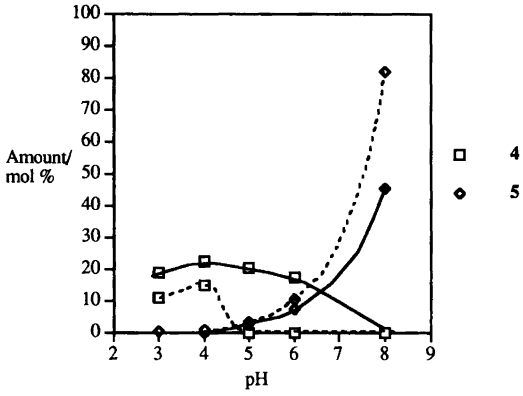

Fig. 8. Effect on formation of *ortho*-benzoquinone (**4**) and 3,4-dimethoxyacetophenone (**5**) of the pH in different solutions: solid lines correspond to chloride solution and the reference broken lines correspond to sulfate solution. Conditions: 20 °C, 12 mM chlorine dioxide, 10 mM lignin model and ionic strength 0.3 mol kg^{-1} (0.1 M sodium sulfate or 0.3 M sodium chloride).

Discussion

Mechanisms for the formation of products. The initial reaction when chlorine dioxide reacts with the aromatic lignin model substrate has been suggested in the literature to be the following. Chlorine dioxide is first reduced to chlorite by abstraction of electron from an aromatic nucleus.[1–4,16,26] In the case of non-phenolic lignin structures a radical cation is formed.[19,20] The radical cation reacts with a new molecule of chlorine dioxide and has been suggested to form a labile chlorite ester (e.g., Fig. 10).[16,19] The radical cation can be pictured as being a hybrid of six resonance structures. This rationalizes the formation of the different isomers of the chlorite ester. All the different products, described below, thus have a unique chlorite ester precursor.

The chlorite ester shown in Fig. 10 undergoes addition of water and decomposes to a muconic dimethyl ester. Cyclization and concomitant methanol elimination give the identified product **6** from **1**. This mechanism, proposed earlier[19] for the formation of an analogous product from the reaction of 4-methylveratrole is in

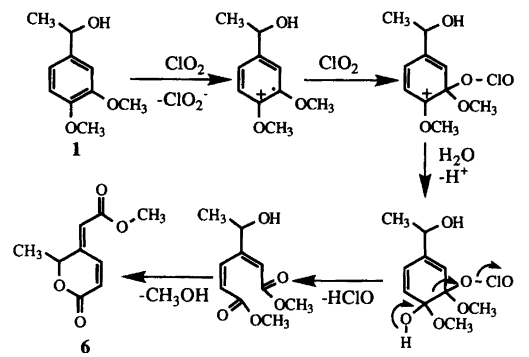

Fig. 10. Possible mechanism for the formation of the isolated lactone **6** from 1-(3,4-dimethoxyphenyl)ethanol **1**.

agreement with our studies of compound **1**, 1-(3,4-dimethoxyphenyl)ethanol.

Quinones are known to be unstable in alkali and may polymerize to high molecular weight products.[38] This may be one explanation of why there is no detectable formation of these products at intermediate to high pH values. Another explanation, and this is certainly effective at pH > 8, is that the reactions leading to benzoquinones are acid-catalysed. An indication for the latter is that the mass balance is nearly complete at pH 8 and benzoquinones are not found at all. The possible mechanisms for the formation of the *para*-benzoquinone **3** and *para*-benzoquinone **2** are outlined in Figs. 11 and 12, respectively.

The difference between sulfate and chloride solution with regard to the formation of the *ortho*-benzoquinone **4** (Fig. 8) is interesting. In Fig. 13, a possible mechanism is shown. According to this mechanism, the formation of the *ortho*-benzoquinone requires twice as much chlorine dioxide (4 mol) as does the formation of *para*-quinones. In the sulfate solution, less chlorine dioxide is available owing to the higher stoichiometry (Table 1). Thus, there is probably not enough chlorine dioxide available for reaction to the *ortho*-benzoquinone. Another possibility is that chlorite formed in the oxidation reactions may consume any *ortho*-benzoquinones formed. The amount of chlorite present is lower in the

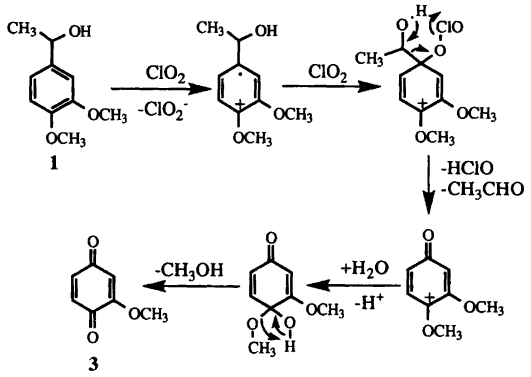

Fig. 11. Possible mechanism for the formation of *para*-benzoquinone **3** from 1-(3,4-dimethoxyphenyl)ethanol **1**.

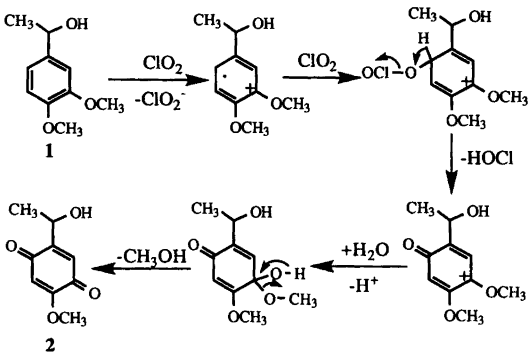

Fig. 12. Possible mechanism for the formation of *para*-benzoquinone **2** from 1-(3,4-dimethoxyphenyl)ethanol **1**.

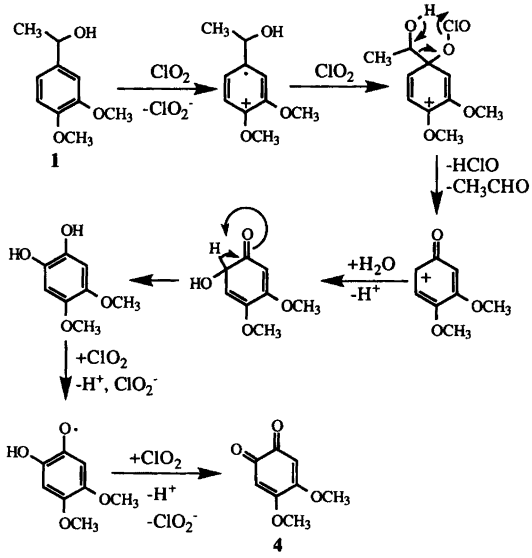

Fig. 13. Possible mechanism requiring 4 mol of chlorine dioxide for the formation of *ortho*-benzoquinone **4** from 1-(3,4-dimethoxyphenyl)ethanol **1**.

chloride buffer owing to the catalytic effect of chloride on the disproportionation of chlorite.[40] Thus, less chlorite will be present in the chloride solution and more *ortho*-benzoquinones will be found.

The formation of 3,4-dimethoxyacetophenone **5** increases rapidly at high pH (Fig. 5), which indicates that the formation of the ketone is base-catalysed. In fact the amount of the product **5** formed is proportional to the hydroxide concentration. The mechanism for the formation of the 3,4-dimethoxyacetophenone may be formulated as in Fig. 14. The conversion from the initially formed radical cation into the oxygen-centred radical is hard to rationalise, but at least it is clear that the reaction does not proceed via a benzylic radical. This was confirmed in a separate experiment. The generation of the radical cation by radiolytic oxidation with $Br_2^{\bullet -}$ at pH 5 and 9 in both the presence and absence of oxygen gave rise to only one mole of 3,4-dimethoxyacetophenone for every two moles of $Br_2^{\bullet -}$. If a benzylic radical had been

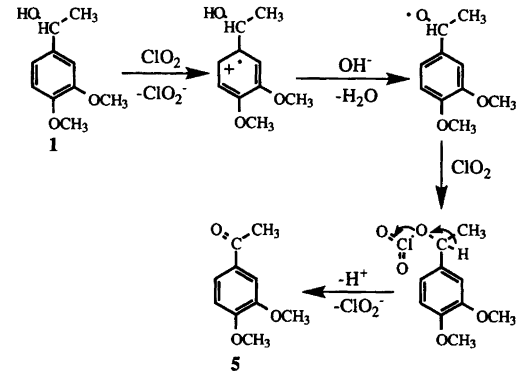

Fig. 14. Suggested hydroxide-ion-catalysed mechanism for the formation of 3,4-dimethoxyacetophenone **5** from 1-(3,4-dimethoxyphenyl)ethanol **1**.

formed, two moles of 3,4-dimethoxyacetophenone for every two moles of $Br_2^{\bullet -}$ would have been formed in the presence of oxygen.

The next step of the mechanism may be addition of chlorine dioxide to the oxygen-centered radical which gives a chlorate ester. The chlorate ester may decompose via chlorite and proton release to the product 3,4-dimethoxyacetophenone. In the chloride solution, nucleophilic attack on the aromatic nucleus by chloride ion may compete with attack by water (hydroxide ion). This may explain the lower formation of this product in chloride solution then in sulfate solution (Fig. 8). One referee has suggested an alternative mechanism as shown in Fig. 15.

From the experiment described here below, using isotopically labelled chloride it was found that chlorine dioxide is not able to chlorinate by itself but instead chlorinates via the by-products hypochlorous acid (HOCl) and/or chlorine (Cl_2). This was determined by allowing 10 mM chlorine dioxide with the natural isotopic relationship $^{37}Cl/^{35}Cl$ (24.5:75.5%) to react with 10 mM of the lignin model in the presence of 250 mM $Na^{35}Cl$ at pH 3. If chlorine dioxide chlorinated by itself, the natural isotopic ratio whould have been retained in the chlorinated products. However, the chlorinated products formed contained only 1.6% of ^{37}Cl and 98.4% ^{35}Cl. This strongly supports the idea that chlorine (or hypochlorous acid) is (are) the chlorinating species involved. This has also been indicated in earlier experiments using the chlorine scavenger sulfaminic acid.[22] Another conclusion from the above experiment is that the equilibrium reaction between hypochlorous acid and chlorine, reaction (1), is faster than the chlorination reaction. Otherwise, a higher content of ^{37}Cl would have been found in the ^{37}Cl chlorinated products.

$$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O \quad (1)$$

Kinetic aspects of the reactions involved. The kinetic data deviate significantly from a second order rate law at high pH values (Fig. 3). To explain this deviation, the kinetics and mechanisms for the reaction of the initially formed radical cation must be considered. The formation of the radical cation by reaction (2) can also proceed backwards, i.e., an equilibrium is established[41] if the amount of chlorite is large enough. This was tested by adding 6 mM chlorite to a reaction solution of 10 mM chlorine dioxide and 10 mM lignin model at pH 3. During the first 10 min, only 20% of the lignin model reacted compared with 50% when chlorite was absent. However, this retardation of the reaction did not significantly affect the final product ratio. This result supports the contention that reaction (2) may be considered to be an equilibrium.

$$ClO_2 + Ar \rightleftharpoons ClO_2^- + Ar^{\bullet -} \quad (2)$$

At low pH, the reverse reaction has no influence on the overall rate, as the amount of chlorite is low owing to consumption in different ways. One is decomposition via its conjugate acid ($HClO_2$) to chlorine dioxide and chlorate by, e.g., reaction (3).[40] Chlorite can also be consumed by reaction with hypochlorous acid to give additional chlorine dioxide and chlorate by reactions (4) and (5).[42]

$$4HClO_2 \rightarrow 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O \quad (3)$$

$$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + OH^- + Cl^- \quad (4)$$

$$HOCl + ClO_2^- + H_2O \rightarrow ClO_3^- + 2H^+ + Cl^- + OH^- \quad (5)$$

However, *at high pH*, all these reactions become much slower[40,43] and the amount of chlorite therefore remains high at high pH values. Furthermore, some additional chlorite may be formed by the relatively slow alkaline disproportionation reaction (6) of chlorine dioxide.[1] (This decomposition reaction probably explains part of the increased stoichiometry of ClO_2 with increasing pH.)

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \quad (6)$$

Therefore, at high pH levels in the beginning of the reaction when no chlorite is present, reaction (2) followed by (7) or (8) leads, via further reactions, to the rapid formation of the products. Later in the reaction, when the amount of chlorite has increased, the back reaction (2) competes with reactions (7) and (8) and the overall rate is decreased, which affects the second-order rate law.

$$ClO_2 + Ar^{\bullet +} \rightarrow Ar^+ - ClO_2 \quad (7)$$

$$OH^- + Ar^{\bullet +} \rightarrow Ar^{\bullet} + H_2O \quad (8)$$

It is also possible that reaction (8) with the subsequent reactions obeys a quite different rate law than reaction (7). This would also explain the deviations from a second order rate law at high pH.

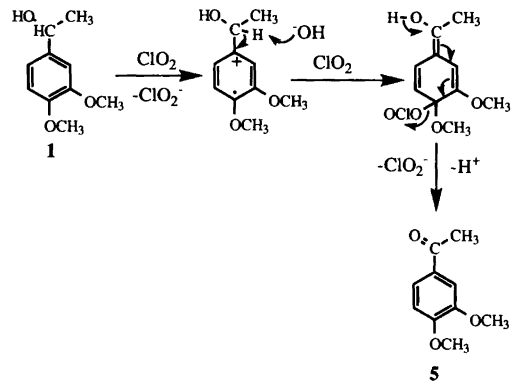

Fig. 15. Another mechanism suggested by one referee for the formation of **5** from **1**.

Conclusions

These kinetic studies show that a non-phenolic lignin model can react with chlorine dioxide on about the timescale of the first (D1)-stage of pulp bleaching (30–60 min). In particular the pH, but also the presence

of sodium chloride, influences the rate constant and the product distribution. At high pH, less chlorination (38% at pH 3 and only <1% at pH 8) and more oxidation (>41% at pH 3 and as much as >99% at pH 8) of lignin occurs during chlorine dioxide treatment. The temperature dependence of the reactions is low. It has been confirmed that the chlorination reaction does not occur via a direct reaction between the chlorine dioxide molecule and lignin. The chlorination reaction is due to released hypochlorous acid or chlorine. Furthermore, a base-catalysed mechanism for the side-chain oxidation in the α-position to a carbonyl group has been suggested.

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