Note

Semiquinones formed during alkaline, oxidative degradation of saccharides

Ivan Šimkovic,

Institute of Chemistry, Slovak Academy of Sciences, 842 38 Bratislava (Czechoslovakia)

Jozef Tiňo, Jan Placek, and Zdenek Maňásek

Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava (Czechoslovakia)

Anion radicals of the semiquinone type are formed during alkaline, oxidative degradation of saccharides and wood. Many factors influence the concentration and structure of these compounds, the most important being the presence of oxygen, the temperature, the concentration of alkali, and the solvent. Of the several semiquinone anion-radicals formed in 6M sodium or potassium hydroxide, the anion radical (1) of 1,2,4,5-tetrahydroxybenzene preponderates. In contrast, in 2M sodium hydroxide in aqueous 50% methanol, 1 is absent. The purpose of this work is the characterisation of the radicals not discussed previously[1,2].

Cellulose was prepared from beech chips by the sulphate method and bleached with ClO_2 (d.p. ~770), and holocellulose was prepared[3] from beech sawdust. E.s.r. measurements were carried out using a Varian E-4 X-band spectrometer at 1-mW microwave power and 5-μT modulation, when no deformation of the spectra was observed. All other procedures were as described previously[1,2].

Except for the component of structure 1, the other components of the e.s.r. spectra were analysed as in previous work[1] without ascribing the structures of the radicals. One of the spectra was a doublet of quartets (Table I) known[4] to be given by the semiquinone anion-radical (2) of 2,3,5,6-tetrahydroxymethylbenzene.

The other components of the spectra were two doublets with splitting constants[1] of 0.0825 and 0.1175 mT. On the basis of quantum chemical calculations using McLachlan's method[5], these two spectra were ascribed to semiquinone anion-radicals (3 and 4, respectively) of pentahydroxybenzene and 1,2,3-trihydroxy-dibenzo-[1,4]-dioxin (Table I). The formation of dioxin derivatives from benzoquinones is known[6].

In some alkaline, oxidative degradations of saccharides, an e.s.r. spectrum (Fig. 1A) consisting of two one-component spectra was observed, the first one characterised by hyperfine splitting (h.f.s.) of three non-equivalent protons: a_1 = 0.194, a_2 = 0.023, a_3 = 0.103 mT, and g = 2.0043. The second was the triplet
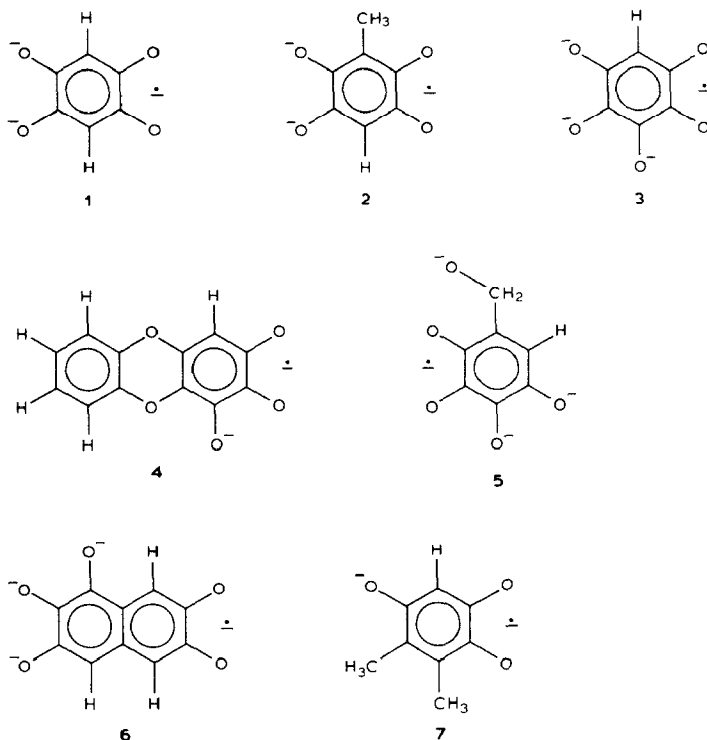
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TABLE I

EXPERIMENTAL AND THEORETICAL VALUES FOR THE HYPERFINE SPLITTING CONSTANTS OF STRUCTURES **1–7**

Structure	Position	a_i^{exp} (mT)	a_i^T (mT)
1[a]	3,6	0.080	0.117[b]
2[c]	1	0.124	—
	4	0.075	—
3	1	0.083	0.094[b]
4	4	0.118	0.125[d]
5	1	0.194 resp. 0.238[e]	0.194 resp. 0.238[e]
	1	0.023 resp. 0.015[e]	0.023 resp. 0.015[e]
	6	0.103 resp. 0.109[e]	−0.092 resp. −0.127[e]
6	4	0.028	0.012[d]
	5	0.048	0.043[d]
	8	0.106	0.093[d]
7[c]	3	0.057	—
	4	0.462	—
	6	0.057	—

[a] ^{13}C Hyperfine splitting constants were not studied in this work. [b] McLachlan's method ($h_O = 1.5$, $k_{C-O} = 1.6$, $Q = 2.7$, $\lambda = 1$). [c] The quantum chemical calculations were not done because the spectra are known[4.9]. [d] Same as [b], except $\lambda = 1.2$. [e] In the presence of $MgSO_4$.

spectrum[1]. When the degradation was performed in the presence of 0.25M magnesium sulphate, h.f.s. constants of the first spectrum changed to $a_1 = 0.238$, $a_2 = 0.015$, and $a_3 = 0.109$ mT (Fig. 1B); Mg^{2+} ions can form chelates with anion radicals[7]. The observed change in the spectrum could be due to a change in the conformation of the radical as a result of the redistribution of spin density. Using the results of McLachlan's method[5], it is proposed that the e.s.r. spectrum in Fig. 1 belongs to a semiquinone anion-radical (5) of 2,3,4,5-tetrahydroxyphenyl-methanol. The inductive effect of the CH_2O^- group was taken into account with the parameter $h_C \in (-0.1, -0.17)$. The splitting constants of the two β-protons were calculated from the equation[8] $a^\beta = B\ \zeta_C \cos^2\psi$. The theoretical values of the h.f.s. constants for structure 5 in the presence of pure hydroxide were calculated using the parameters $h_C = -0.13$ and $B = 3.7$ mT obtained for the conformation $\psi_1 = 10°$ and $\psi_2 = 70°$. The splitting constants for the changed conformation due to the presence of $MgSO_4$ were calculated with $h_C = -0.15$. Agreement between experimental and theoretical values of h.f.s. constants was obtained when a new conformation of 5 was assumed, namely, $\psi_1 = 16°$ and $\psi_2 = 76°$. This crude
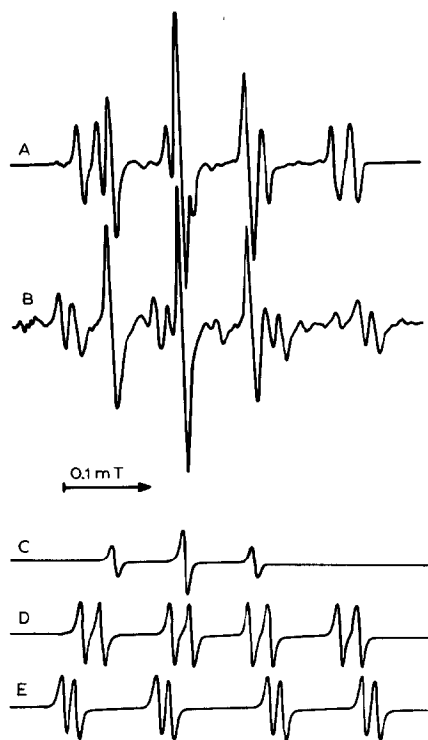

Fig. 1. The e.s.r. spectra of radicals formed on alkaline, oxidative degradation of A, M D-glucuronic acid in 6M potassium hydroxide at 100° for 2 min; B, 0.2M D-glucose in 6M potassium hydroxide at 100° for 8 min in the presence of 0.25M $MgSO_4$; C, simulated spectrum of structure 1; D, simulated spectrum of first conformation of radical 5; E, simulated spectrum of second conformation of structure 5.
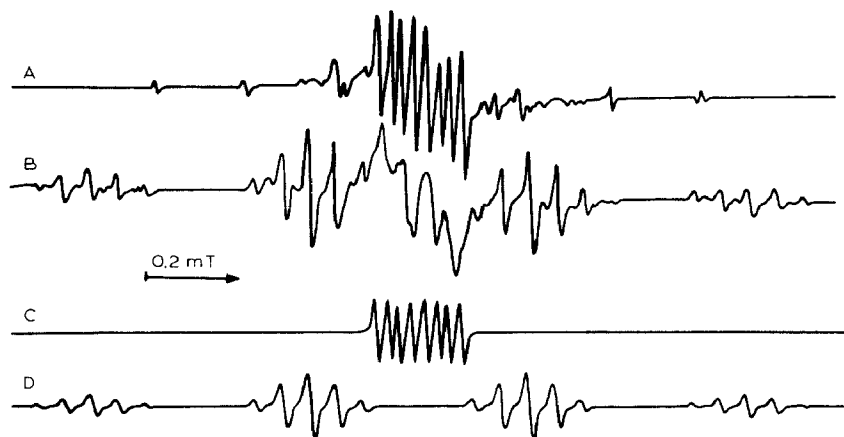
Fig. 2. The e.s.r. spectra of radicals formed on alkaline, oxidative degradation of *A*, cellulose (100 g) in 2M sodium hydroxide (300 mL) (the temperature was increased during 110 min from 100° to 167°); *B*, holocellulose (100 g) in 2M sodium hydroxide (300 mL) and conditions similar to those for *A*; *C*, simulated spectrum of structure **6**; *D*, simulated spectrum of radical **7**.

theoretical model, however, cannot describe properly all the effects (radical conformation, spin-density distribution) caused by the interaction of the radical with its environment. We sought to demonstrate that the spectra in Figs. 1A and 1B might belong to two different conformations of the radical **5**.

None of the previously mentioned radicals (**1–5**) was observed when the conditions of alkaline cooking of wood were used (167°, ~2M NaOH, steel autoclave)[2]. However, under these conditions, cellulose gave the spectrum shown in Fig. 2A. The dominating part of this spectrum was ascribed to the semiquinone anion-radical (**6**) of 1,2,3,6,7-pentahydroxynaphthalene. The values calculated using McLachlan's method are close to those obtained experimentally (Table I). When cellulose was degraded for 3 h using the same conditions, no e.s.r. signal was observed, probably because all the oxygen present in the autoclave was consumed.

In order to simulate the conditions of alkaline degradation of the polysaccharides during the delignification of wood, holocellulose was used as a substrate for the e.s.r. study. Under identical conditions (see legend to Fig. 2), the spectrum consisted of a quartet of quintets (Fig. 2B), which is known[9] to belong to the semiquinone anion-radical (**7**) of 1,2,5-trihydroxy-3,4-dimethylbenzene. However, there are lines in the middle of the spectrum which could not be interpreted.

The structure **6**, which was formed by the alkaline, oxidative degradation of cellulose, was not found during the degradation of holocellulose. The semiquinone anion-radical of 1,4-dihydroxy-2,3,5,6-tetramethylbenzene, which was formed during degradation of (4-*O*-methyl-D-glucurono)-D-xylan and wood[2], was also not observed.

Thus, when cellulose, xylan, holocellulose, and wood were used as substrates, different radical structures were found, reflecting the influence of cell-wall structure on the alkaline, oxidative degradation of wood.

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