RKCL2686

ON THE MECHANISM OF VANILLIN FORMATION IN THE CATALYTIC OXIDATION OF LIGNIN WITH OXYGEN

V.E.Tarabanko, N.A. Fomova, B.N.Kuznetsov,
N.M. Ivanchenko and A.V.Kudryashev

Institute of Chemistry of Natural Organic Materials
Siberian Division of the Russian Academy of Sciences
Akademgorodok, Krasnoyarsk 660036, Russia

The influence of catalyst ($CuSO_4$ solution), pH and temperature on the vanillin formation and oxygen consumption in oxidation of lignin in alkaline media have been studied. It was shown that the main role of catalyst in the lignin oxidation is to change the selectivity of hydroperoxide fragmentation rather than to accelerate oxidation.

Vanillin is well known to be produced by oxidation of different lignins in alkaline media [1,2]. The first hypothesis for the mechanism of this process was put forward by Hibbert [3,4]. It includes the cleavage of carbon-carbon bonds by alkali-promoted retrograde aldol reaction:

$$Ar-CH-C-C \xrightarrow{OH^-} Ar-CHO + > CH-CHO \qquad (1)$$

(I)   (II)
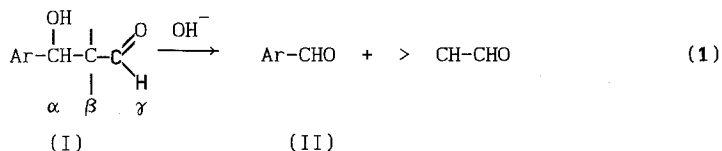
where Ar is the 3-methoxy-4-phenoxy anion. Hibbert's scheme (1) is in a good agreement with known data on alkaline hydrolysis of lignins in the absence of oxidants [3-5]. However, in the presence of oxygen the formation of a carbonyl group in γ-position of the arylpropene units of lignin (I) seems to be less likely in comparison with α- or β-ones.

Another viewpoint of the vanillin formation mechanism was put forward later [6]:
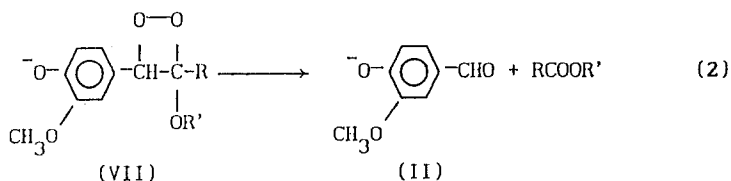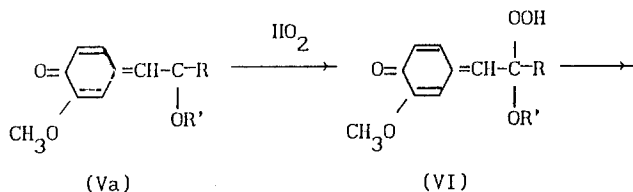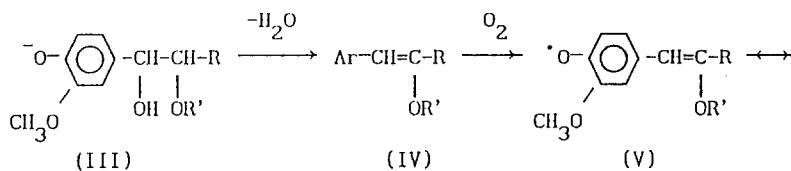
According to scheme (2) the reaction begins with dehydration of the lignin structural unit III, followed by abstraction of an electron from IV by oxygen, giving the radical V. The latter combines with a $HO_2^{\cdot}$ radical to yield hydroperoxide VI. The hydroperoxide intermediate of quinone methide type (VI) then undergoes intramolecular rearrangement to give a dioxetane (VII). Its cleavage leads to the vanillate ion (II). Scheme 2

has been developed on the basis of Gierer's works [7,8] on the mechanism of oxygen bleaching of cellulose in alkaline media. In this case the formation and fragmentation of dioxetane (VII) were discussed in detail [7-9]. Contrary to bleaching processes lignin oxidation into vanillin occurs at higher temperature (160 - 180°C). Such a temperature increase may change the mechanism of lignin oxidation.

The use of cupric and other catalysts is well known to increase the yield of vanillin approximately two times [5,10]. Schemes 1 and 2 are not yet sufficient to account for the catalytic effect noted.

The main purpose of this paper is to suggest a new mechanism of vanillin formation in the alkaline oxygen oxidation of lignins. For this aim, the influence of catalyst, hydrogen ion concentration and temperature on vanillin formation and oxygen consumption in the process have been studied.

This study was made using commercial softwood lignosulfonates (Syas paper-mill, Leningrad region, Russia), namely fermented sodium-base spent sulfite liquor concentrated to a solid content of 42.6 wt.%. Solid composition included 18.3 wt.% of ash, 5.26% of H, 40.5% of C, and 6.05% of S. The content of lignosulfonates was taken to be equal to 65 wt.% of solids [11].

The process was carried out in a 0.1 L stainless steel shaken autoclave at 110 - 160°C and an O_2 partial pressure of 0.2 MPa. 60 mL of mixture consisting of 120 - 180 g/L solids of spent liquor, 120 g/L NaOH, and $CuSO_4$ solution was charged into the reactor, which was then fed with oxygen from a calibrated buffer; oxygen consumption during the process was measured. Samples of about 4 g were taken out through a special valve during the experiments. The samples were acidified with sulfuric acid and extracted with chloroform. Vanillin concentration was determined by GLC.

Figures 1-4 show the influence of the nature and concentration of catalyst, pH and temperature on the curves of vanillin formation and oxygen consumption. The main data of the figures are summarized in Table 1.
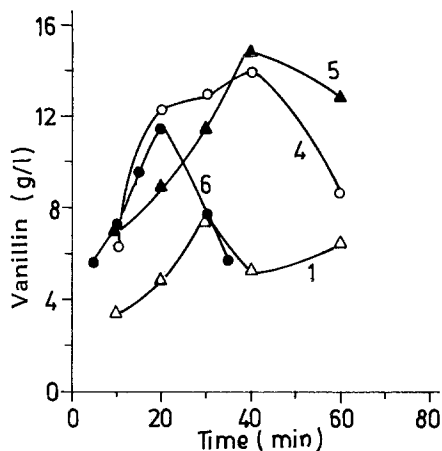

Fig. 1. Influence of catalyst concentration on vanillin
formation (160°C). Curve numbers in Figs 1-4
correspond to the numbers of experiments
in Table 1

Plots of vanillin accumulation have two maxima as was shown earlier [10]. Without catalyst or at 110°C the second maximum was not achieved. It should be emphasized that the catalyst effect on the vanillin yield and oxygen consumption is described by opposite dependences. Catalyst increases the maximum concentration of vanillin two times at 160°C (Fig. 1). The rate of oxygen consumption, on the contrary, shows little dependence on the catalyst concentration (Table 1). In a similar manner, decreasing the pH from 11 to 10 stops vanillin formation almost completely and does not influence oxygen consumption (Table 1, Fig.2). Finally, at 110°C catalysts increase the rate of oxygen consumption up to five times and the vanillin yield is almost independent of them (Figs 3 and 4).
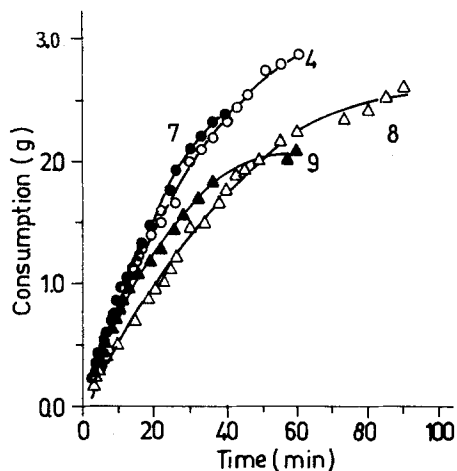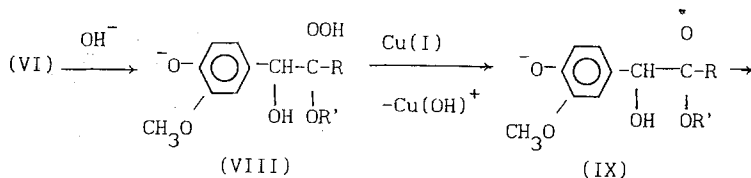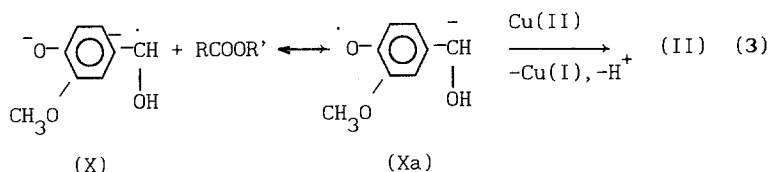
164

Fig.2. Influence of the nature of alkali on oxygen consumption ($160^{\circ}C$)

By this means the observed influence of catalyst and pH media on the rate of substrate oxidation is not connected with the selectivity of vanillin formation. Hence the increase of vanillin yield is determined by interaction of the catalyst with some intermediates of the process. We also assume that protonation of such intermediates leads to a termination of vanillin formation below pH 10.3 - 10.5.

We assume the results obtained and the literature data could be explained on the basis of the well known mechanism of catalytic autoxidation of organic compounds [12,13]. We suppose that the scheme of vanillin formation is similar to mechanism **2** [6] up to hydroperoxide (VI) formation. According to our viewpoint (scheme (**3**)) the compound VI is turned into an α-hydroxy-β-hydroperoxyarylpropene unit (VIII). The latter is reduced with Cu(I) giving the oxyradical IX with subsequent fragmentation to the anion radical X. Oxidation of X gives vanillate anion II.

$$O^{-} \text{—} \langle O \rangle \text{—} \overset{\cdot}{C}H + RCOOR' \longleftrightarrow \overset{\cdot}{O} \text{—} \langle O \rangle \text{—} \overset{-}{C}H \xrightarrow[-Cu(I), -H^{+}]{Cu(II)} \quad (II) \quad (3)$$

(X)   (Xa)

Cu(I), Co(II), Fe(II) are well known to reduce hydroperoxides into oxyradicals [12,14]. The mechanism of C-C bond cleavage in polymer autoxidation through oxyradical fragmentation has long been known [13,15]. Emanuel [13] showed that oxidative destruction of polymers could proceed through oxyradical fragmentation with the formation of the most stable alkyl radical. In our scheme the benzylic anion radical X is
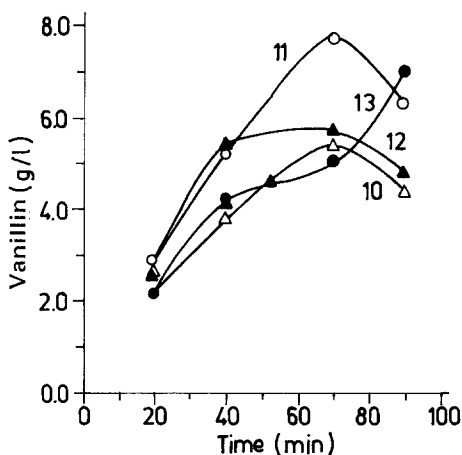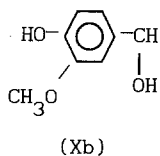

Fig. 3. Influence of the nature of catalyst on vanillin formation (110°C)

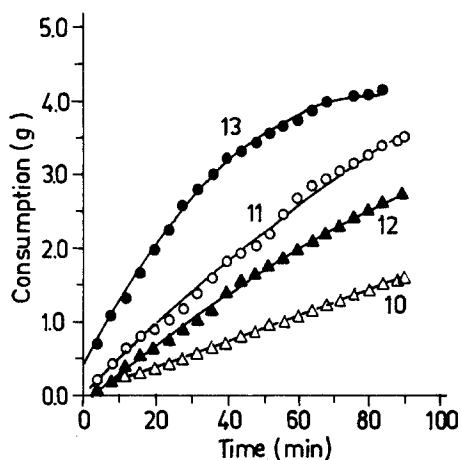stabilized by the mesomeric form (Xa). Such stabilization is impossible in the protonated form of the radical (Xb):

(Xb)

Fig.4. The influence of catalyst nature on the dynamic
of oxygen consumption $(110^{\circ}C)$.

Hence, protonation of alkoxy radical IX could reduce the
selectivity of vanillin formation. This is the possible
explanation of the influence of pH on the selectivity of
vanillin formation. Further oxidation of the anion radical (X)
into vanillate ion (II) can be performed by oxygen and/or
Cu(II) [12].

Within the framework of scheme **3** the influence of catalyst
on the selectivity of vanillin formation could be explained by
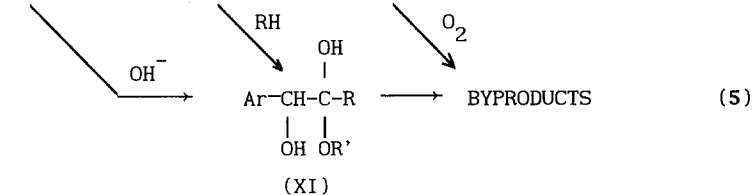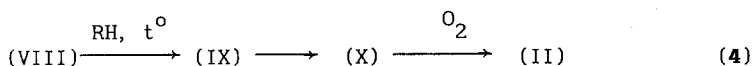the competition of different decay paths of hydroperoxide
(VIII)

Table 1

Influence of catalyst concentration and pH (measured at 20°) on the parameters of maximum vanillin concentration. Partial pressure of O_2 0.2 MPa, concentration of spent liquor 180 g/L except for No.8 and 9 (120 g/L); temperature $160^\circ C$, except for No. 10-13 (110°))

No.	Cata- lyst (g/L) Cu(OH)$_2$	Base (g/L)	Ini- tial pH	W_{O_2} (g/min) ini- tial	Parameters of maximum of vanillin concentration		
					[V] (g/L)	t_{max} (min)	Final pH	O_2 con- sump- tion(g)
1	-	NaOH,120	>13	0.094	6.5	>60	9.7	2.8
2	3.24	NaOH,120	>13	0.110	8.7	>60	10.4	2.8
3	6.51	NaOH,120	>13	0.136	11.3	40	9.8	3.0
4	9.75	NaOH,120	>13	0.080	13.9	40	9.9	2.4
5	16.3	NaOH,120	>13	0.103	14.7	40	10.9	2.5
6	26.0	NaOH,120	>13	0.137	11.4	20	10.6	1.9
7	9.75	NaOH, 80	>13	0.115	10.7	20	11.0	1.3
8	9.75	NaOH, 40+ K$_2$CO$_3$,300	10.8	0.056	3.3	25	10.5	1.2
9	9.75	K$_2$CO$_3$,300	10.3	0.071	0.9	20	10.0	1.5
10	-	NaOH,120	>13	0.018	5.4	70	-	1.25
11	9.80	NaOH,120	>13	0.050	7.7	70	9.9	3.00
12	12.5[a]	NaOH,120	>13	0.042	5.7	70	9.5	2.25
13	9.8+ 12.5[b]	NaOH,120	>13	0.092	7.0	>90	10.0	4.10

a) Catalyst - AgOH;
b) Catalyst - 9.8 g/L Cu(OH)$_2$+12.5 g/L AgOH

Pathway **3** in the presence of catalyst leads to a fast and selective fragmentation of the hydroperoxide giving aldehyde II. In the absence of catalyst, the cleavage of hydroperoxide VIII to radical IX proceeds slowly (Pathway **4**) and competes with its hydrolysis to byproducts (**5**). The low selectivity of vanillin formation at $110^{\circ}C$ could be accounted for by the known increase of the role of oxyradical (IX) reduction into alcohol XI due to decreasing temperature [12]. The known relationship between activation energies of fragmentation and reduction (chain propagation) of oxyradicals could explain the low yields of vanillin during bleachig processes [8,9].

In conclusion, we suppose that the main role of catalyst in lignin oxidation is to change the selectivity of hydroperoxide (VIII) fragmentation rather than to accelerate oxidation. It is well known that lignins can be oxidized selectively into vanillin not only with oxygen but also nitrobenzene, cupric oxide, etc. [5]. These processes may be assumed to involve some common intermediates, one ofwhich could be the anion radical X in scheme **3**.

REFERENCES

1. Encyclopedia of Chemical Technology, 2nd Ed., ed. H. Mark, vol.21, p.180. Interscience Publ., New-York, London 1972.
2. M.I. Tchudakov: Industrial Uses of Lignin, p. 42. *Lesnaya Promishlen.*, Moscow, 1983.
3. I.K. Bucklund, G.H. Tomlison, H. Hibbert: *J. Am. Chem. Soc.*, **59**, 597 (1937).
4. A. Bell, W.L. Hawkins, G.F. Write, H. Hibbert: *J. Am. Chem. Soc.*, **59**, 598 (1937).
5. K. Kurschner: *Zh. Prikl. Khim.* **28**, 950 (1955).
6. S. Dardelet, P. Froment, N. Lacoste, A. Robert: *Revue A.T.I.P.*, **39**, 267 (1985).

7. J. Gierer: *Svensk. papperstidn.*, **80**, 510 (1977).
8. J. Gierer: *Holzforschung,* **36,** 55 (1982).
9. J. Gierer, N.-O. Nilvebrant: *Holzforschung,* **40,** 107 (1986).
10. V.E. Tarabanko, N.V.Koropatchinskaya, A.V. Kudryashev, B.N. Kuznetsov: *Izv. Russ. Akad. Nauk, ser. khim.,* 1995, No 2, in press.
11. L.G. Primatcheva, T.N. Bugaeva: *Izv. VUZ, Lesn. Zhurn.* (USSR), **4,** 92 (1985).
12. E.T. Denisov, N.I. Mitskevitch, V.E. Agabekov: Mechanism of liquid-phase oxidation of oxygen-containing compounds, Nauka, Minsk, 1975.
13. N.M. Emanuel, A.L. Butchatchenko: *Chemical Physics of Aging and Stabilization of Polymers,* p.83. Nauka, Moscow 1982.
14. Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds. V.1. Oxygen compounds. Ed. by J.F. Stoddart. Vol. 2. p.465. Pergamon Press, Oxford, New-York, Moscow 1982.
15. N. Grassie: *Chemistry of High Polymer Degradation Processes.* Butterworths, London 1956.