ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2092–2097. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © N.R. Popova, A.L. Beloglazova, K.G. Bogolitsyn, T.V. Tortseva, K.M. Verkholomova, S.A. Pokryshkin, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 11, pp. 1794–1799.

Oxidation of Model Lignin Compounds with Peracetic Acid under Homogeneous Catalysis with Polyoxometalates

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Received June 30, 2014

Abstract—Oxidation of lignin model compounds with peracetic acid using polyoxometalate manganese-containing sodium vanadomolybdophosphate $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$ as a catalyst has been studied. The effect of pH, concentration and nature of the oxidized compound, concentration of the catalyst and peracetic acid, and temperature on kinetics of oxidation and the products composition has been investigated.

Keywords: homogeneous catalysis, polyoxometalate, oxidation, aromatic compounds

DOI: 10.1134/S1070363214110085

Recently, more and more studies have been devoted to development of environmentally friendly, energy- and resource-saving processes of deep refining of renewable herbal sources to prepare a wide range of products with predefined properties [1, 2]. In this regard, using “green” oxidants (molecular oxygen, ozone, and peroxides) is promising. The oxidation processes can be intensified by metal complexes, in particular, polyoxometalates.

Lignin, a polyfunctional aromatic polymer, is among major components of plants and a promising source for preparation of valuable chemical products.

Depending on the conditions, different functional groups of lignin can be reactive. Their accessibility for the reagents can be changed due to conformational and steric features of lignin macromolecules. Therefore, mechanism of lignin reactions is usually investigated using model compounds containing the same reactive functional groups as these of lignin. In particular, the following aromatic compounds were used in this study:

– ferulic acid, vanillin, and vanillyl alcohol, representing the guaiacylpropane units of coniferous lignin;

– sinapic acid, representing the syringylpropane units of hardwood lignin;

– coumaric and cinnamic acids, representing the *p*-oxyphenylpropane units of lignin of annual plants.

Earlier, we have studied oxidation of the lignin-mimicking aromatic compounds with molecular oxygen in alkaline [3] or acidic [4] medium under the conditions of homogeneous catalysis.

To establish principal regularities of catalytic oxidation of aromatic compounds with peracetic acid (PAA), kinetics of the oxidation and the products composition was studied, including effects of the solution pH, the nature and concentration of the substrate, concentrations of the catalyst and oxidant, and temperature. Heteropolyanion (HPA), a manganese-containing sodium vanadomolybdophosphate of gross formula $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$ was used as a catalyst.

Preliminary studies of oxidation of ferulic acid with PAA in the presence of HPA revealed a notable decrease of the substrate concentration with time (no changes occurred in the absence of the catalyst). The initial rate of oxidation of ferulic acid decreased with increasing pH (Fig. 1).

The observed fact can be caused by the following reasons:

– decrease of the catalyst concentration due to its destructive dissociation enhanced at higher pH [5]:

$$[PMo_7V^V_5O_{40}]^{8-} \rightleftarrows [PMo_7V^V_4O_{37}]^{7-} + VO_3^-; \qquad (1)$$

– decrease of PAA concentration due to its decomposition at higher pH:

$$H_2O + CH_3COOOH \rightleftarrows H_2O_2 + CH_3COOH; \qquad (2)$$

– decrease of concentration of the active form of the oxidized compound (carbocation) formed by protonation of the substrate (in acidic aqueous medium lignin and its model compounds are bases) [6]. The substrates basicity is due to the presence of lone-electron pairs at oxygen atoms of α- and γ-alcoholic, α- and β-ethereal, and α- and γ-carbonyl groups of the propane chain, as well as of π-electrons of the C=C bonds.

The lignin models used in this study (vanillyl alcohol and vanillin; ferulic, cinnamic, coumaric, and sinapic acids) are capable of formation of the benzyl-type carbocations due to the presence of α-alcoholic, carbonyl group at the α-C atom and the C=C bond in the aliphatic chain. Hence, decrease of pH favored formation of electrophilic carbocations that reacted with HPA $[PMo_6V_5O_{39}Mn(OH)]^{-11}$ to form activated complex, thus accelerating the substrates oxidation. Chromato-mass spectrometry analysis of products of ferulic acid oxidation confirmed the mentioned kinetic results and demonstrated decrease of vanillin (the major oxidation product) yield with increasing pH (Table 1).

Investigation of the effect of concentrations of ferulic acid and of the catalyst (Fig. 2) showed that initial rate of the reaction increased linearly with concentration of the both components, indicating the first order with respect to both the substrate and the catalyst.

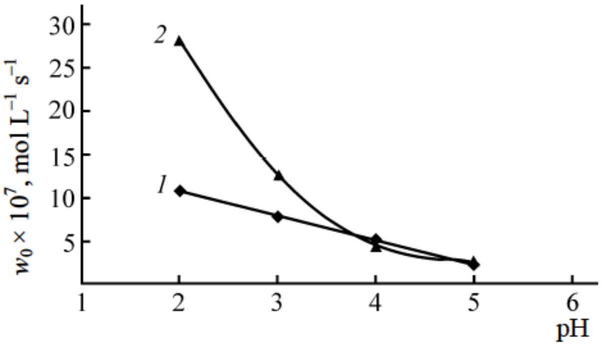

Fig. 1. Initial rate of catalytic oxidation of ferulic acid with PAA as function of pH: $c_{fa} = 10^{-3}$ mol/L, $c_{PAA} = 4.0 \times 10^{-3}$ mol/L, $c_{cat} = 10^{-4}$ mol/L; T, °C: (*1*) 25 and (*2*) 50.

On the other hand, nature of the oxidized compound had a substantial impact on the initial rate of the reaction (Table 2); the effect was caused by redistribution of the electron density of the aromatic ring (e.g., OH, OCH_3 groups).

Reactivity of the unsaturated aromatic acids decreased in the following series: sinapic acid > ferulic acid > coumaric acid > cinnamic acid.

Major products of oxidation of the unsaturated aromatic acids were the corresponding aldehydes (OH to CHO oxidation), whereas oxidation of vanillyl alcohol yielded vanillin and 2-methoxy-1,4-benzoquinone (Table 3), the latter being the product of vanillin oxidation.

Degree of conversion of the unsaturated aromatic acids under the oxidative conditions (Table 4) was in line with the results of kinetic studies (Table 2): the highest reactivity was revealed in the case of sinapic acid.

Investigation of the effect of the oxidant concentration on catalytic oxidation of ferulic acid

Table 1. Effect of pH on the relative content (%) of the products of catalytic oxidation of ferulic acid: $c_{fa} = 10^{-3}$ mol/L, $c_{PAA} = 1.6 \times 10^{-3}$ mol/L, $c_{cat} = 10^{-4}$ mol/L, $T = 25$°C

Product	pH = 2			pH = 3		pH = 4		
	sampling time, min							
	10	30	60	10	30	10	30	60
4-Hydroxy-3-methoxycinnamic (ferulic) acid	81.8	73.1	72.6	91.6	78.7	89.0	85.5	80.2
4-Hydroxy-3-methoxybenz-aldehyde (vanillin)	3.9	4.5	6.8	0.6	3.2	0.5	0.6	0.8
1-(3-Methoxy-4-hydroxy-cyclohexyl)-ethanediol-1,2	2.5	2.0	3.5	1.6	3.7	–	–	–
2-(3-Methoxy-4-hydroxy-cyclohexyl)ethanol	4.6	7.5	7.0	–	–	–	–	–

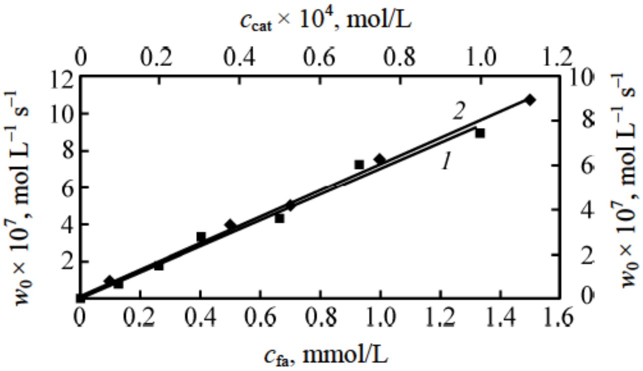

Fig. 2. Initial rate of the catalytic oxidation of ferulic acid as function of (*1*) the substrate and (*2*) the catalyst concentration: pH = 3, $c_{PAA} = 1.6 \times 10^{-3}$ mol/L, $c_{cat} = 10^{-4}$ mol/L (*1*), $c_{fa} = 10^{-3}$ mol/L (*2*), $T = 50$°C.

demonstrated (Fig. 3) that the highest reaction rate was observed at 4×10^{-3} mol/L of the oxidant, corresponding to the $[CH_3COOOH]$: [HPA] ratio of 40 : 1. Further increase of PAA concentration had no substantial effect on the reaction kinetics. The high reaction rate was assigned to formation of catalytically more active intermediates, peroxocomplexes of sodium vanadamolybdophosphate $[HPA(O_2)_n]$. Indeed, according to the reference data, reaction of peroxo compounds (i.e. hydrogen peroxide) with molybdates, tungstates [7–9], vanadates [10], and polyoxometalate ions [11] yields peroxocomplexes acting as reactive intermediates in epoxidation of olefins as well as oxidation of alcohols, glycols, and phenols [11]; the complexes contain 1 to 24 peroxo groups [7]. The complexes were often detected by spectroscopy [7, 12] and sometimes could even be isolated [13].

In order to explain the insignificant effect of PAA concentration above 4 mmol/L on the initial rate of the reaction (Fig. 3), we analyzed kinetics of ferulic acid concentration change in the course of its oxidation at varied concentration of PAA (Fig. 4). The results revealed that the initial induction period became proportionally longer with increasing concentration of the oxidant.

Table 2. Initial rate of catalytic oxidation of lignin model compounds with PAA: pH = 2, $c_{substrate} = 10^{-3}$ mol/L, $c_{PAA} = 8.3 \times 10^{-3}$ mol/L, $c_{cat} = 10^{-4}$ mol/L, $T = 50$°C

Oxidized compound	$w_0 \times 10^7$, mol L^{-1} s^{-1}
Cinnamic acid	No reaction
Coumaric acid	0.9±0.1
Ferulic acid	34.3±0.6
Sinapic acid	79.4±0.9
Vanillin	4.0±0.3
Vanillyl alcohol	5.7±0.3

It was natural to assume that a competing reaction of PAA decomposition under the action of the *in situ* formed peroxocomplex occurred:

$$2CH_3COOH \xrightarrow{HPA(O_2)_n} 2CH_3COOH + O_2. \qquad (3)$$

Similar phenomenon was observed in study of allyl alcohol oxidation with hydrogen peroxide in the presence of phosphorustungsten heteropolyacid (HPA) [2]. At high ratios $[H_2O_2]/[HPA]$, the product yield decreased due to retardation of the target reaction (competing with decomposition of hydrogen peroxide by the peroxocomplex).

To determine thermodynamic parameters of the catalytic oxidation of ferulic acid with peroxide compounds, temperature dependence of the reaction rate was studied, and the following activation parameters were obtained: $E_a^{\neq} = 20.8$ kJ/mol, $\Delta H^{\neq} = 18.2$ kJ/mol, and $\Delta S^{\neq} = -247$ J mol^{-1} K^{-1}. Relatively low activation energy (≤40 kJ/mol) was apparently due to participation of ionic and radical species in the studied processes. Large negative entropy of activation indicated formation of an activated complex (hence, decreasing number of the particles in the solution) [2–5].

Analysis of the obtained results and the reference data resulted in the following schematic mechanism of the catalytic oxidation.

$$A + H^+ \rightarrow AH^+, \qquad (4)$$

$$HPA^{-m} + 2nCH_3COOOH \rightarrow HPA(O_2)_n^{-q} + 2nCH_3COOH, \qquad (5)$$

$$AH^+ + HPA(O_2)_n^{-q} \rightarrow [AH^+ \cdot HPA(O_2)_n^{-q}], \qquad (6)$$

$$[AH^+ \cdot HPA(O_2)_n^{-q}] \rightarrow B + HPA(O_2)_{n-1}^{-q}, \qquad (7)$$

$$HPA(O_2)_{n-1}^{-q} + 2CH_3COOOH \rightarrow HPA(O_2)_n^{-q} + 2CH_3COOH. \qquad (8)$$

At the first stage, the oxidized compound A was activated via protonation with formation of the carbocation AH^+ [Eq. (4)], and the peroxocomplex of the manganese-containing vanadomolybdophosphate $[HPA(O_2)_n^{-q}]$ was formed via reaction of polyoxometalate (HP^{-m}) with PAA [Eq. (5)].

Table 3. Major products of catalytic oxidation of aromatic compounds with PAA: pH = 2, $c_{\mathrm{substrate}} = 10^{-3}$ mol/L, $c_{\mathrm{PAA}} = 8.3 \times 10^{-3}$ mol/L, $c_{\mathrm{cat}} = 10^{-4}$ mol/L, $T = 50$°C

Oxidized compound	Product (content after 1 h from the beginning of the reaction)
Coumaric acid	4-Hydroxybenzaldehyde (13%)
Ferulic acid	Vanillin (29%)
Sinapic acid	3,5-Dimethoxy-4-hydroxybenzaldehyde (17%)
Vanillyl alcohol	Vanillin (8%); 2-Methoxy-1,4-benzoquinone (25%)
Vanillin[a]	2-Methoxy-1,4-benzoquinone (63%)

[a] $c_{\mathrm{PAA}} = 0.1$ mol/L.

On the second stage, an intermediate was formed in reaction of the carbocation and the peroxocomplex [Eq. (6)]. The peroxocomplex could be regenerated via addition of PAA [Eq. (8)].

In the excess of PAA, it was decomposed via reaction with peroxocomplex of the manganese-containing sodium vanadomolybdophosphate [Eq. (3)].

To conclude, the results confirmed parallel realization of both the activation mechanism based on the formation of an intermediate between the oxidized compound and the catalyst [Eq. (6)] and the cyclic mechanism of catalysis based on regeneration of the reduced catalyst form under the action of PAA.

EXPERIMENTAL

Manganese-containing sodium vanadomolybdophosphate $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$ was used as a liquid-phase catalyst; it was prepared using a procedure adopted from [14, 15]. To do so, a flask was charged with 350 mL of water, 45.5 g of V_2O_5 (0.25 mol), and 100.8 g of MoO_3 (0.7 mol) upon stirring, and 37.1 g of dry Na_2CO_3 (0.35 mol) and 13.8 g of $NaH_2PO_4{\cdot}H_2O$ (0.1 mol) were added portionwise. The mixture was heated with a reflux condenser during 3 h and then cooled to room temperature; 19.79 g (0.1 mol) of $MnCl_2$ and 50 mL of 5M H_2SO_4 were then added, and the mixture was incubated during 12 h.

Solid $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$ was isolated using a method reported elsewhere [16]. To do so, 40 mL of the solution of manganese-containing sodium vanadomolybdophosphate was placed in a separating funnel, 10 mL of diethyl ether was added, the mixture was vigorously stirred, and 22 mL of conc. HCl was gradually added till formation of heavy oily liquid ("etherate") ceased. The lower ethereal layer was separated off and washed in a separating funnel with

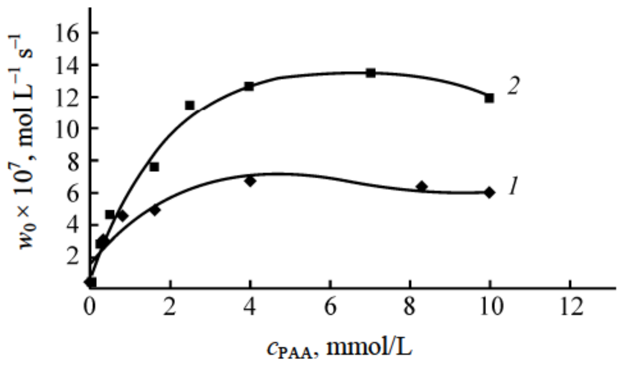

Fig. 3. Initial rate of catalytic oxidation of ferulic acid as function of PAA concentration: pH = 3, $c_{\mathrm{fa}} = 10^{-3}$ mol/L, $c_{\mathrm{cat}} = 10^{-4}$ mol/L, *T*, °C: (*1*) 25 and (*2*) 50.

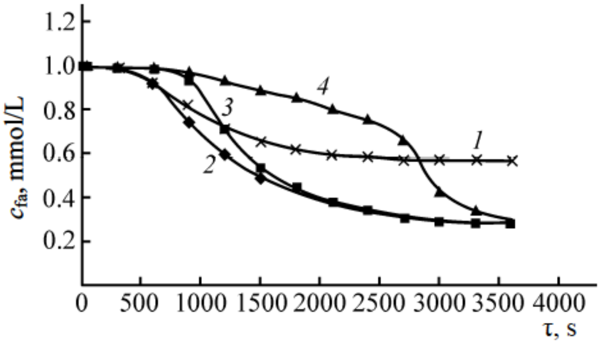

Fig. 4. Kinetics of ferulic acid concentration change in the course of its catalytic oxidation with PAA: pH = 3, $c_{\mathrm{fa}} = 10^{-3}$ mol/L, $c_{\mathrm{cat}} = 10^{-4}$ mol/L, $T = 25$°C; (*1*) $c_{\mathrm{PAA}} = 1.6 \times 10^{-3}$ mol/L; (*2*) $c_{\mathrm{PAA}} = 8.3 \times 10^{-3}$ mol/L; (*3*) $c_{\mathrm{PAA}} = 1.6 \times 10^{-2}$ mol/L; (*4*) $c_{\mathrm{PAA}} = 8.3 \times 10^{-2}$ mol/L.

Table 4. Conversion of aromatic compounds (%) in the course of catalytic oxidation

Oxidized compound	Sampling time, min	
	10	60
Sinapic acid	100	100
Ferulic acid	51	77
Coumaric acid	47	72

Table 5. Characteristic wavelengths (λ) and molar absorptivity (ε) of the oxidized compounds at pH = 2

Oxidized compound	λ, nm [ε, L mol^{-1} cm^{-1}]
Cinnamic acid	277 [21400]
Coumaric acid	307 [20700]
Ferulic acid	320 [16800]
Sinapic acid	319 [17800]
Vanillin	228 [14600]
Vanillyl alcohol	197 [42400]

40 mL of water, 22 mL of conc. HCl, and several mL of diethyl ether. The "etherate" was separated off, and water was added to it in small portions until complete decomposition of "etherate" (at that point effervescence ceased).

The content of phosphorus in manganese-containing sodium vanadomolybdophosphate was determined by spectrophotometry using a Specord-200 instrument. The content of molybdenum and vanadium was determined with X-ray fluorescent analysis using a Spectroscan-Max instrument at K_α = 709 and K_α = 2503 nm. The P : Mo : V ratio was found to be of 1 : 6 : 5, in agreement with the $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$ formula.

Concentration of PAA (Acros) in solution was determined as described elsewhere [17].

Kinetics of oxidation was studied by means of spectrophotometry with a Specord 200 PC (Analytic Jena) instrument by monitoring the optical density of the reaction mixtures at wavelength of the characteristic absorption band of the oxidized compound (Table 5).

Constant pH was maintained adding proper buffer solutions, and was measured with a pH-meter-ionomer Expert-001. The solutions were kept at constant temperature in a UT-3 thermostat (±0.1°). The primary kinetic parameter determined was the initial reaction rate; it was calculated using Curve Expert 1.3 software by differentiating the $c_{substrate} = f(\tau)$ equation and calculation of the rate at $\tau = 0$.

Products of the catalytic oxidation were identified using gas chromatography with mass-spectrometry detector QP-2010 Plus (Shimadzu). To do so, the formed products were extracted with 10 mL of chloroform from 10 mL samples. The organic layer was dried with sodium sulfate, and chloroform was removed on a vacuum evaporator. To avoid decomposition of the reagents and the products, they were silylated prior to the analysis. To do so, 100 μL of *N,O*-bis(trimethylsilyl)trifluoroacetamide was added, and chromato-mass analysis was performed after 1 h.

X-ray fluorescence and chromato-mass spectrometry analyses were performed at the Center for collective use of equipment "Arctic" of the Northern (Arctic) Federal University (agreement no. 14.594.21.0004.

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