



# Comparative studies on oxidation of lignin model compounds with hydrogen peroxide using Mn(IV)-Me<sub>3</sub>TACN and Mn(IV)-Me<sub>4</sub>DTNE as catalyst

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## Abstract

Comparative studies are conducted on the kinetics and reaction mechanism for the oxidation of lignin model compounds, 1-(3,4-dimethoxyphenyl)ethanol (**1**), 1-(3,4-dimethoxyphenyl)-1-propene (**2**) and *E*-1,2-diphenylethene (**3**) with hydrogen peroxide at reaction temperatures below 80 °C using [LMn(IV)(μ-O)<sub>3</sub>Mn(IV)L](PF<sub>6</sub>)<sub>2</sub> (**C-1**) and [L'Mn(IV)(μ-O)<sub>3</sub>Mn(IV)]-(ClO<sub>4</sub>)<sub>2</sub> (**C-2**) as catalyst. The disappearance rate of **1** and **2** in the first phase of **C-1**-catalyzed oxidation increases up to the temperature range of 50–60 °C then decreases with increasing reaction temperature. The cause for the slow down of the disappearance rate is not known. Based on the kinetic data and reaction products identified, **C-1** is found to be more effective as catalyst in the oxidation of **1** and **2** than **C-2**, but less effective in the oxidation of **3**. In the **C-1**- and **C-2**-catalyzed oxidation, **1** is oxidized to the corresponding α-carbonyl derivative **4**, while **2** readily undergoes epoxidation of the conjugated double bond to produce the corresponding epoxides **5** and **6**. The anti-Markovnikov nucleophilic addition of hydroxide and hydroperoxide anions on **5** and **6** then produced α,β-diol **7** and benzaldehyde derivative **8**, which are non-catalytic reactions and rate determining steps. The compound **3** also undergoes epoxidation of conjugated aliphatic double bond producing the corresponding epoxide **9**. However, none of the corresponding α,β-diol and benzaldehyde derivative is detected in the reaction mixture. In addition, **2** is more susceptible to exoxidation than **3**. On the basis of the kinetics and reaction mechanism of the reactions, the catalytic cycles of the **C-1**- and **C-2**-catalyzed oxidation of **1–3** are postulated.

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## 1. Introduction

In previous papers, we showed [1–3] that non-phenolic lignin model compounds, such as those with

*Abbreviations:* Me<sub>4</sub>DTNE, 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane; Me<sub>3</sub>TACN, 1,4,7-trimethyl-1,4,7-triazacyclononane

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α-hydroxyl and double bonds conjugated to aromatic moieties, readily undergo oxidation by hydrogen peroxide under the catalytic influence of the binucleus manganese complex [L'Mn(IV)(μ-O)<sub>3</sub>Mn(IV)](ClO<sub>4</sub>)<sub>2</sub> (**C-2**), [Mn(IV)-Me<sub>4</sub>DTNE], where L' is 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (Me<sub>4</sub>-DTNE), at relatively low temperatures (30–80 °C). The catalyst **C-2** was prepared in situ by oxidation of the precatalyst [L'Mn(IV)(μ-O)<sub>2</sub>(μ-OAc)Mn(IV)]-(ClO<sub>4</sub>)<sub>2</sub> (**C-3**) with hydrogen peroxide in aqueous

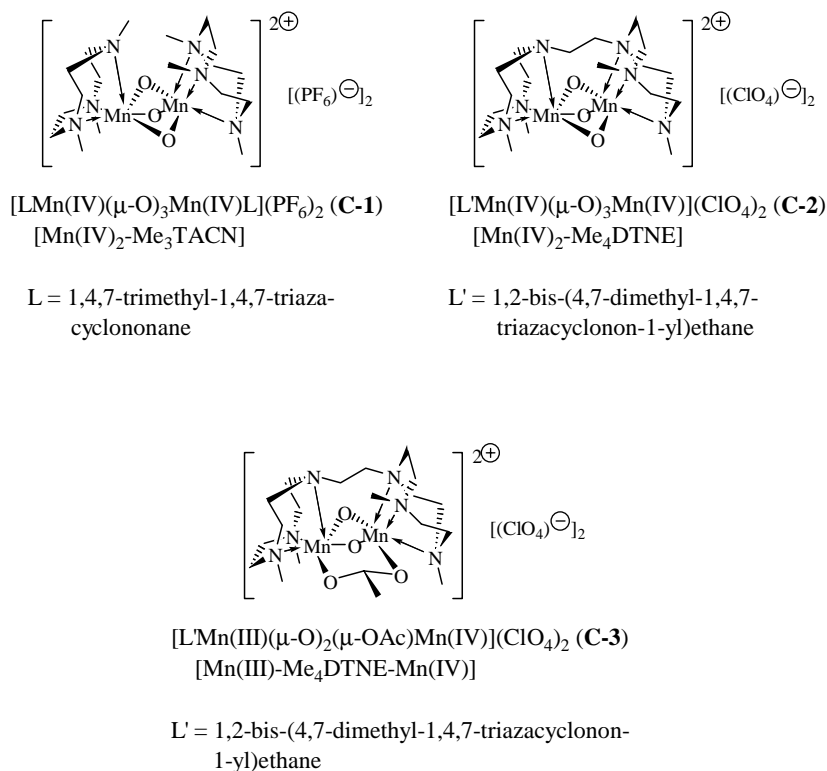


Fig. 1. Structure of binucleus Mn(IV) complexes.

solution. Otherwise, these compounds would not be oxidized by hydrogen peroxide. Kinetics studies on delignification of pine Soda-AQ Kraft pulp with hydrogen peroxide using **C-2** prepared in situ from **C-3** as catalyst showed that selectivity and reactivity of hydrogen peroxide as an oxidant is improved by catalytic effect of **C-2**. In general, hydrogen peroxide becomes effective as a delignifying agent only at temperatures above 100 °C in delignification of pulps in the absence of a catalyst [4,5]. In addition, it is not cost-effective to carry out the hydrogen peroxide bleaching of pulps at temperature higher than 120 °C, because of high decomposition rate of hydrogen peroxide [6–8].

Very recently, Odermatt et al. [9] postulated that a similar binucleus manganese complex, [L<sub>1</sub>Mn(IV)-(μ-O)<sub>3</sub>Mn(IV)L<sub>1</sub>](PF<sub>6</sub>)<sub>2</sub> (**C-1**), [Mn(IV)-Me<sub>3</sub>TACN], where L<sub>1</sub> is 1,4,7-trimethyl-1,4,7-triazacyclononane (Me<sub>3</sub>TACN), is less effective as catalyst than **C-2**

prepared in situ from **C-3** for the bleaching of pulps with hydrogen peroxide on the basis of experimental data (see Fig. 1 for structures). In addition, the catalyst **C-2** is now available, and catalyst charge is recently optimized to 10 ppm instead of 60 ppm on pulp in recent investigations [9–11]. In view of these developments, comparative kinetic studies on the oxidation of lignin model compounds with hydrogen peroxide using the catalysts **C-1** and **C-2** were undertaken. The objective of present investigation is to evaluate the efficiency of **C-1** and **C-2** as catalyst in the delignification of pulps as well as the underlying reaction mechanisms. As lignin model compounds, 1-(3,4-dimethoxy-phenyl)ethanol (**1**), 1-(3,4-dimethoxyphenyl)-1-propene (**2**) and *E*-1,2-diphenylethene (**3**) (see Fig. 2 for structures) were used to represent α-hydroxyl group, double bond conjugated with aromatic moieties and stilbene-type structures in lignins.

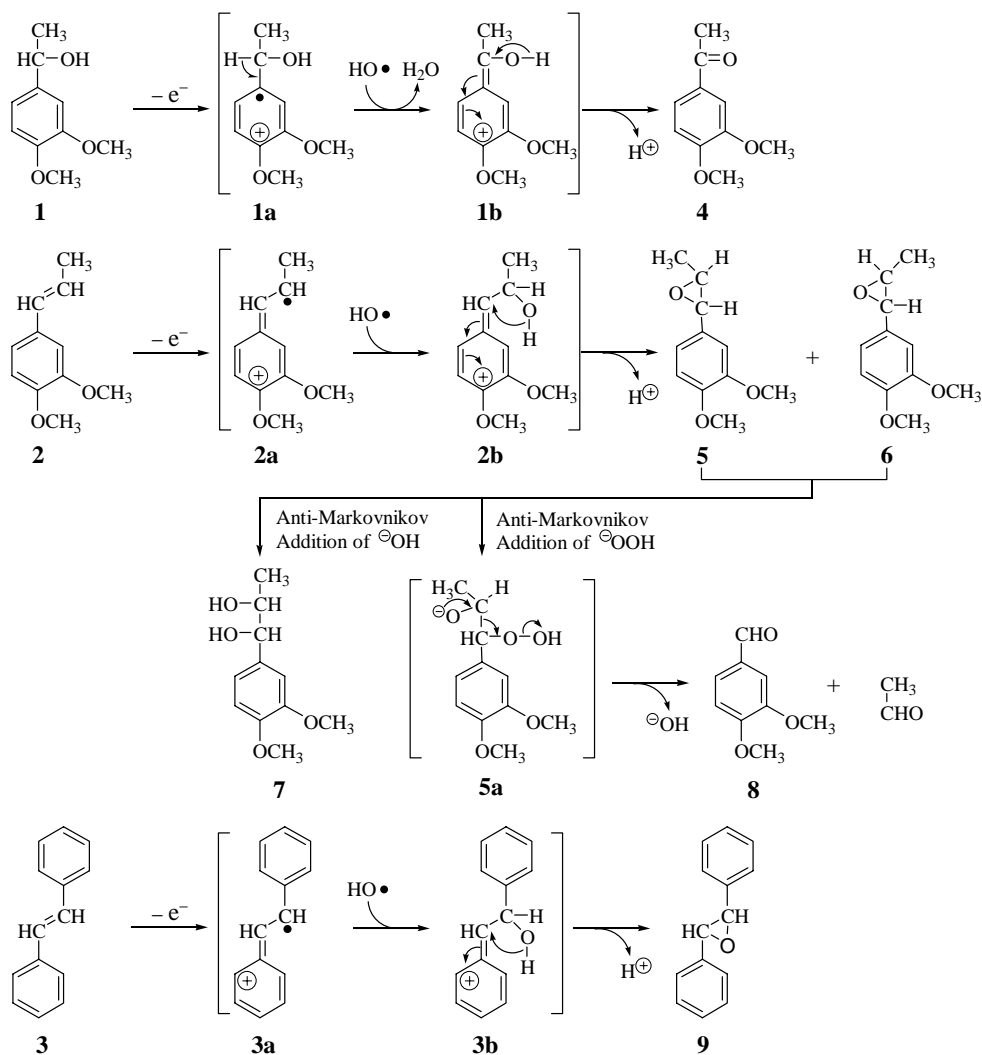


Fig. 2. Reaction mechanisms for lignin model compounds, 1-(3,4-dimethoxyphenyl)ethanol (**1**), 1-(3,4-dimethoxyphenyl)-1-propene (**2**) and *E*-diphenylethene (**3**), in the C-1- and C-2-catalyzed oxidation with hydrogen peroxide.

## 2. Experimental

### 2.1. Lignin model compounds and chemicals

3,4-Dimethoxyacetophenone, 1-(3,4-dimethoxyphenyl)-1-propene, and *E*-1,2-diphenylethene, were purchased from Aldrich. 1-(3,4-Dimethoxyphenyl)ethanol was synthesized by reduction of 3,4-dimethoxyacetophenone with  $\text{NaBH}_4$  [2]. Aqueous solution of  $\text{H}_2\text{O}_2$  (30%) was purchased from Fisher Scientific Corp. and

diluted to appropriate concentration for experiment. The catalysts,  $[\text{LMn(IV)}(\mu\text{-O})_3\text{Mn(IV)L}](\text{PF}_6)_2$  (**C-1**), and  $[\text{L}'\text{Mn(IV)}(\mu\text{-O})_3\text{Mn(IV)}](\text{ClO}_4)_2$  (**C-2**) were donated by Degussa AG, Hanau, Germany.

### 2.2. General procedure for non-catalyzed oxidation

$(\text{CH}_3)_2\text{CO}$  was refluxed with finely powdered  $\text{K}_4\text{MnO}_4$ , then was distilled before use. Water was doubly distilled. A solution of 0.05 mmole substrate

in 5 ml  $(\text{CH}_3)_2\text{CO}$  was placed in a 25 ml two necked round bottomed flask equipped with reflux condenser. To this solution were added 0.57 g of 30% aqueous solution of  $\text{H}_2\text{O}_2$  (approximately 5 mmole) and 0.007 mmole 2,3,4,5-tetramethylbenzene as the internal standard.  $(\text{CH}_3)_2\text{CO}$  was then added to the resulting solution until the total volume is 10 ml. The resulting solution was heated on a water bath with a thermostat at  $60^\circ\text{C}$  for 2 h. Samples of the reaction mixture were taken at certain time intervals by pipette followed by extraction with  $\text{CH}_2\text{Cl}_2$ , then analyzed by GC and GC–MS. At the end of reaction, the residual  $\text{H}_2\text{O}_2$  was quantitatively determined according to the procedure of Mielisch et al. [12].

### 2.3. General procedure for the C-1- and C-2-catalyzed oxidation

$(\text{CH}_3)_2\text{CO}$  was refluxed with finely powered  $\text{K}_4\text{MnO}_4$ , then was distilled before use. Water was doubly distilled. A solution of 0.05 mmole substrate in 5 ml  $(\text{CH}_3)_2\text{CO}$  was placed in a 25 ml two necked round bottomed flask equipped with reflux condenser. To this solution were added 0.57 g of 30% aqueous solution of  $\text{H}_2\text{O}_2$  (approximately 5 mmole) and 0.007 mmole 2,3,4,5-tetramethylbenzene as the internal standard.  $(\text{CH}_3)_2\text{CO}$  was then added to the resulting solution until the total volume is 10 ml. The resulting solution was placed on a water bath with a thermostat. The reaction was initiated by addition of 0.4 mg (0.0005 mmole) C-1 or C-2. When C-1 was used as catalyst, the reaction was carried out at 50, 60 and  $80^\circ\text{C}$  for 2 h except for compound **1**, the reaction of which was carried out at 25, 40, 50, 60 and  $80^\circ\text{C}$  for 2 h. Samples of the reaction mixture were taken at certain time intervals by pipette, followed by extraction with  $\text{CH}_2\text{Cl}_2$ , then analyzed by GC and GC–MS. When C-2 was used as catalyst, the reaction was carried out at 60 and  $80^\circ\text{C}$  for 2 h. At the end of reaction, the residual  $\text{H}_2\text{O}_2$  was quantitatively determined according to the procedure of Mielisch et al. [12].

### 2.4. General condition of gas chromatography and GC–MS

All GC analysis of reaction mixtures were carried out with HP 6890 Gas Chromatograph equipped with a HP-1 column (methyl siloxane;  $30\text{ m} \times 320\text{ mm} \times$

$0.25\ \mu\text{m}$ ) using helium as the carrier gas (2 ml/min). Samples were injected into the GC by a HP automatic injector using 2,3,4,5-trimethylbenzene as internal standard. Injector and detector temperatures were 200 and  $240^\circ\text{C}$ , respectively. The initial oven temperature was  $80^\circ\text{C}$  and was held for 1 min, then raised at a rate of  $20^\circ\text{C}/\text{min}$  to  $200^\circ\text{C}$  and held for another 1 min. The oven temperature was again raised at the rate of  $20^\circ\text{C}/\text{min}$  to  $280^\circ\text{C}$  and held for 1 min. The relative error for the quantitative determination of the constituents of reaction mixtures is  $\pm 3\%$ .

GC–MS analysis was carried out with HP GCD Plus gas chromatography instrument equipped with a J&W DB-5 column (phenyl methyl;  $30\text{ m} \times 320\text{ mm} \times 0.25\ \mu\text{m}$ ) using helium as the carrier gas (2 ml/min). Samples were injected manually into the injection port at  $200^\circ\text{C}$ . Signals were detected by an EID at  $280^\circ\text{C}$ . The initial oven temperature was  $70^\circ\text{C}$  and was held for 2 min, then raised at a rate of  $20^\circ\text{C}/\text{min}$  to  $200^\circ\text{C}$  and held for another 1 min. The oven temperature was again raised at the rate of  $20^\circ\text{C}/\text{min}$  to  $300^\circ\text{C}$  and held for 1 min. The electron energy used was 70 eV.

### 2.5. Compounds identified by GC–MS analysis

#### 2.5.1. Internal standard

2,3,4,5-Trimethylbenzene: GC retention time, 3.48 min; EI/MS,  $m/z$  (relative intensity), 134 ( $M^+$ , 47.6), 119 (100), 91 (15.0).

#### 2.5.2. Compounds identified in the oxidation mixture of 1-(3,4-dimethoxyphenyl)ethanol (**1**)

1-(3,4-Dimethoxyphenyl)ethylene (**10**): GC retention time, 6.3 min; EI/MS,  $m/z$  (relative intensity), 164 ( $M^+$ , 100), 149 (28.0), 121 (10.8), 103 (20.4), 91 (29.0), 77 (23.7).

1-(3,4-Dimethoxyphenyl)ethanol (**1**): GC retention time, 7.3 min; EI/MS,  $m/z$  (relative intensity), 182 ( $M^+$ , 55.4), 167 (82.6), 139 (100), 124 (25.0), 108 (20.1), 91 (22.3), 77 (32.6).

Acetoveratrone (**4**): GC retention time, 7.6 min; EI/MS,  $m/z$  (relative intensity), 180 ( $M^+$ , 44.1), 165 (100), 137 (6.5), 122 (7.5), 107 (4.8), 79 (11.3).

#### 2.5.3. Compounds identified in the oxidation mixture of 1-(3,4-dimethoxyphenyl)-1-propene (**2**)

3,4-Dimethoxybenzaldehyde (**8**): GC retention time, 6.9 min; EI/MS,  $m/z$  (relative intensity), 166

( $M^+$ , 100), 165 (62.4), 151 (9.7), 137 (3.4), 95 (20.4), 77 (23.7).

1-(3,4-Dimethoxyphenyl)-1-propene (**2**): GC retention time, 7.1 min; EI/MS,  $m/z$  (relative intensity), 178 ( $M^+$ , 100), 163 (29.0), 147 (9.7), 115 (11.8), 107 (36.6), 91 (30), 77 (15.0).

*E*-1-(3,4-Dimethoxyphenyl)propane-1,2-epoxide (**5**): GC retention time, 7.6 min; EI/MS,  $m/z$  (relative intensity), 194 ( $M^+$ , 14.0), 151 (100), 135 (3.2), 107 (10.6).

1-(3,4-Dimethoxyphenyl)propane-1,2-diol (**7**): GC retention time, 9.0 min; EI/MS,  $m/z$  (relative intensity) 212 ( $M^+$ , 5.4), 178 (2.2), 167 (100), 151 (6.4), 139 (61.3), 124 (20.4), 108 (15.6).

*Z*-1-(3,4-Dimethoxyphenyl)-1-epoxypropane (**6**): GC retention time, 8.4 min; EI/MS,  $m/z$  (relative intensity) 194 ( $M^+$ , 14.8), 166 (26.0), 165 (19.4), 151 (100), 135 (5.4).

#### 2.5.4. Compounds identified in the oxidation mixture of *E*-1,2-diphenylethene (**3**)

*E*-1,2-Diphenylethene (**3**): GC retention time, 8.4 min; EI/MS,  $m/z$  (relative intensity) 180 ( $M^+$ , 98.4), 179 (100), 178 (64), 165 (47.3), 152 (110.8), 89 (34.4), 76 (21.5).

*E*-1,2-Diphenyletheneoxide (**9**): GC retention time, 8.2 min; EI/MS,  $m/z$  (relative intensity) 196 ( $M^+$ , 3.3), 167 (100).

#### 2.6. General condition of thermogravimetric analysis

The thermal gravimetric analysis of the catalyst **C-1** was performed in TGA-Q500 TA Instrument. The initial oven temperature was 25 °C, the temperature was raised at rate of 5 °C/min to 100 °C and then the temperature was raised again at rate of 10 °C/min to 200 °C and held for 10 min.

### 3. Results and discussion

Lignin model compounds are frequently used to simplify the investigation of the reactivity of corresponding lignin substructures because of the difficulty associated with the characterization of structural changes of residual lignins in pulps in bleaching processes. In this study, 1-(3,4-dimethoxyphenyl)ethanol

(**1**), 1-(3,4-dimethoxyphenyl)-1-propene (**2**) and *E*-1,2-diphenylethene (**3**) were chosen to represent the non-phenolic  $\alpha$ -hydroxyl, conjugated C=C double bond and stilbene functionalities in the residual lignins (see Fig. 2 for structures). As expected, hydrogen peroxide was found incapable of oxidizing **1**, **2**, or **3** when applied alone. However, these substrates readily undergo oxidation by hydrogen peroxide in a significant extent under the catalytic influence of Mn(IV)-Me<sub>3</sub>TACN (**C-1**) and Mn(IV)-Me<sub>4</sub>DTNE (**C-2**).

#### 3.1. Kinetics of the **C-1**- and **C-2**-catalyzed oxidation of lignin model compounds with hydrogen peroxide

In the oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**), 1-(3,4-dimethoxyphenyl)-1-propene (**2**) and *E*-1,2-diphenylethene (**3**) with hydrogen peroxide in the presence of either **C-1** or **C-2**, the compounds were found to readily undergo oxidation. Figs. 3, 7 and 9 show the decrease in the concentration of substrate versus reaction time of **1**, **2** and **3**, respectively. Fig. 5 shows the increase in the concentration of acetoveratrone (**4**) versus reaction time, which is produced, in both the **C-1**- and **C-2**-catalyzed oxidation of **1**. The disappearance rate constants for the compounds were then calculated (in case of **4**, the formation rate constant) from the experimental data showed in Figs. 3, 5, 7 and 9. The results are given in Figs. 4, 6, 8 and 10 as well as in Tables 1–4. The reactions investigated are all consisting of two phases. The concentrations of substrates decreased exponentially in the first phase then leveled off in the

Table 1  
Effect of reaction temperature on the pseudo-first-order reaction rate constant in the first phase of the **C-1**- and **C-2**-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide [catalyst/substrate mole ratio (C/S ratio) = 0.01]

Reaction temperature (°C)	$\kappa$ ( $\times 10^{-4}$ s <sup>-1</sup> )		
	<b>C-1</b> catalyzed	<b>C-2</b> catalyzed	Uncatalyzed
25	7.3	–	–
40	11.3	–	–
50	14.5	–	0.05
60	9.9	4.0	0.05
80	8.5	5.5	–

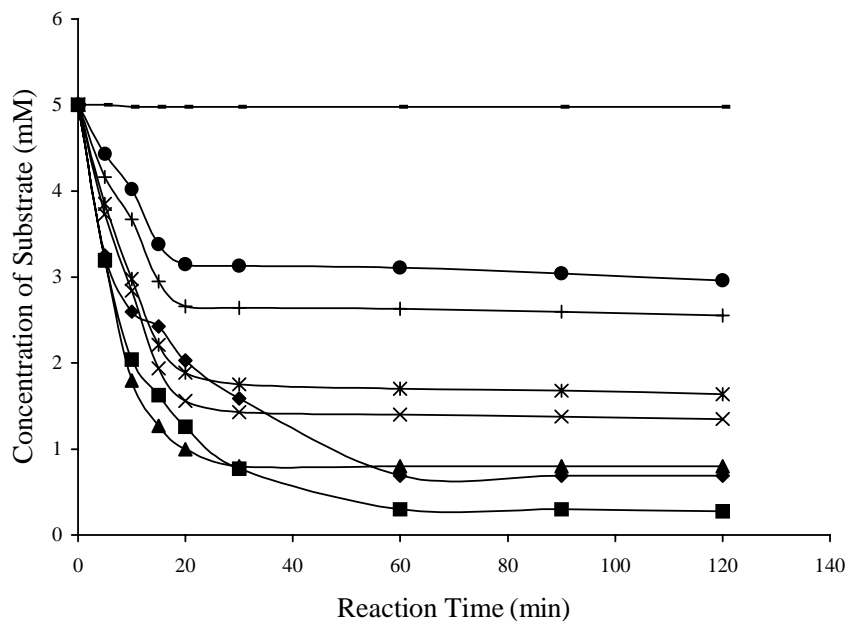


Fig. 3. Effect of reaction temperature on the disappearance rate of substrate in the C-1- and C-2-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide: (◆) C-1 at 25 °C; (■) C-1 at 40 °C; (▲) C-1 at 50 °C; (×) C-1 at 60 °C; (✱) C-1 at 80 °C; (●) C-2 at 60 °C; (+) C-2 at 80 °C; (—) uncatalyzed at 60 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

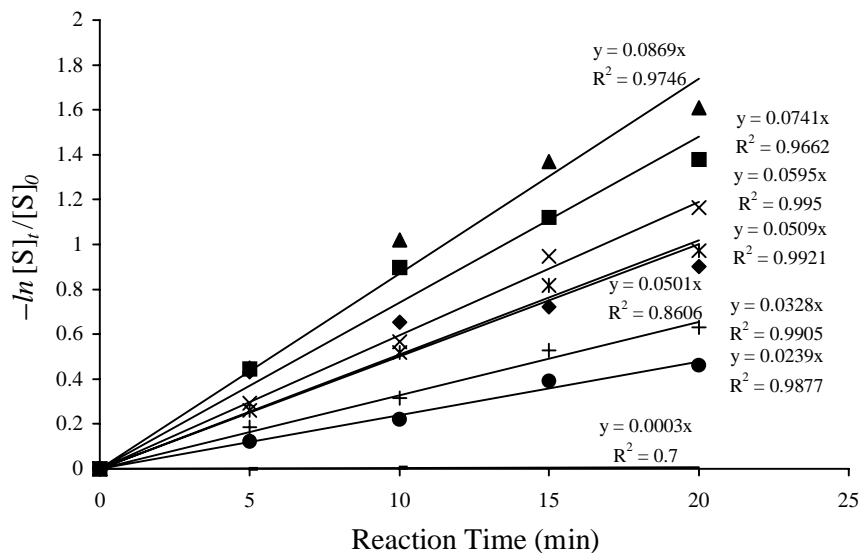


Fig. 4. The pseudo-first-order nature of the first phase in the C-1- and C-2-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide: (◆) C-1 at 25 °C; (■) C-1 at 40 °C; (▲) C-1 at 50 °C; (×) C-1 at 60 °C; (✱) C-1 at 80 °C; (●) C-2 at 60 °C; (+) C-2 at 80 °C; (—) uncatalyzed at 60 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

Table 2

Effect of reaction temperature on the pseudo-first-order rate constant for the formation of 3-4-dimethoxyacetophenone (**4**) in the first phase of the **C-1**- and **C-2**-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide [catalyst/substrate mole ratio (C/S ratio) = 0.01]

Reaction temperature (°C)	$\kappa$ ( $\times 10^{-4}$ s $^{-1}$ )		
	<b>C-1</b> catalyzed	<b>C-2</b> catalyzed	Uncatalyzed
25	3.7	–	–
40	7.4	–	–
50	14.3	–	0
60	7.0	2.0	0
80	6.1	2.7	–

Table 3

Effect of reaction temperature on the pseudo-first-order reaction rate constant in the first phase of the **C-1**- and **C-2**-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)-1-propene (**2**) with hydrogen peroxide [catalyst/substrate mole ratio (C/S ratio) = 0.01]

Reaction temperature (°C)	$\kappa$ ( $\times 10^{-4}$ s $^{-1}$ )		
	<b>C-1</b> catalyzed	<b>C-2</b> catalyzed	Uncatalyzed
50	25.2	–	0
60	32.4	5.3	0
80	23.1	7.2	–

second phase. In general, the first phase is the range of 20–40 min, the length of which depends on the nature of the substrate and reaction temperature. In all cases, the first phase of the reactions is pseudo-first-order with respect to substrate as evidenced by liner relationship between  $-\ln[s]_t/[S]_0$  and reaction time  $t$ . This is attributable to the fact that hydrogen peroxide was used in great excess (100 mole eq.). The residual hydrogen peroxide recovered at the end of reaction is, in general, in the range of 90–95 mole% of the starting concentration, which is determined

Table 4

Effect of reaction temperature on the pseudo-first-order reaction rates constant in the first phase of the **C-1**- and **C-2**-catalyzed oxidation of *E*-1,2-diphenylethene (**3**) with hydrogen peroxide [catalyst/substrate mole ratio (C/S ratio) = 0.01]

Reaction temperature (°C)	$\kappa$ ( $\times 10^{-4}$ s $^{-1}$ )		
	<b>C-1</b> catalyzed	<b>C-2</b> catalyzed	Uncatalyzed
50	0	–	0
60	0.67	2.1	0
80	0.67	2.7	–

according to the procedure of Mielisch et al. [12].

### 3.1.1. The **C-1**- and **C-2**-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**)

In the **C-1**-catalyzed oxidation of **1** at reaction temperatures 25 and 40 °C, the concentration of substrate decreased exponentially until reaction time of 40 min, then leveled off (Fig. 3). However, at reaction temperatures 50, 60 and 80 °C, the concentration of **1** decreased exponentially until reaction time of 20 min, then leveled off. In the **C-2**-catalyzed oxidation of **1** at 60 and 80 °C, the concentration of **1** also decreased exponentially until reaction time of 20 min, then leveled off. The disappearance rate constant of **1** in the first phase of **C-1**-catalyzed oxidation increases up to 50 °C then decreases with increasing reaction temperature (Table 1). In contrast, in the **C-2**-catalyzed oxidation of **1** in the temperature range of 60–80 °C, the increase in the reaction temperature results in increase in the disappearance rate constant. The cause is not known for the slow down of the disappearance rate constant at reaction temperature higher than 50 °C in the **C-1**-catalyzed oxidation of **1**. The thermogravimetric analysis of the catalyst **C-1** showed that there was no weight loss up to temperature 200 °C.

Comparing the efficiency of **C-1** and **C-2** as catalyst in the oxidation of **1** at the same reaction temperature in the temperature range of 60–80 °C, it can be observed that **C-1** is more effective than **C-2**. At the first phase, the rate constant for the disappearance of **2** is much faster in the **C-1**-catalyzed oxidation than that in the **C-2**-catalyzed oxidation,  $9.9 \times 10^{-4}$  s $^{-1}$  versus  $4.0 \times 10^{-4}$  s $^{-1}$  at 60 °C and  $8.5 \times 10^{-4}$  s $^{-1}$  versus  $5.5 \times 10^{-4}$  s $^{-1}$  at 80 °C, respectively (Fig. 4, Table 1). The pseudo-first-order nature of the reaction was established by the liner relationship between  $-\ln[s]_t/[S]_0$  and reaction time  $t$  (Fig. 4).

In the **C-1**-catalyzed oxidation of **1**, the formation of **4** increased correspondingly until reaction time of 60 min at 25 and 40 °C then leveled off (Fig. 5). At the temperature range of 50–80 °C, the formation of **4** increased until reaction time of 20 min, then leveled off. The formation rate constant of **4** in the first phase of the oxidation increased with increasing reaction temperature up to 50 °C, then decreased with increasing reaction temperature (Table 2). In contrast, in the **C-2**-catalyzed oxidation of **1**, the formation of

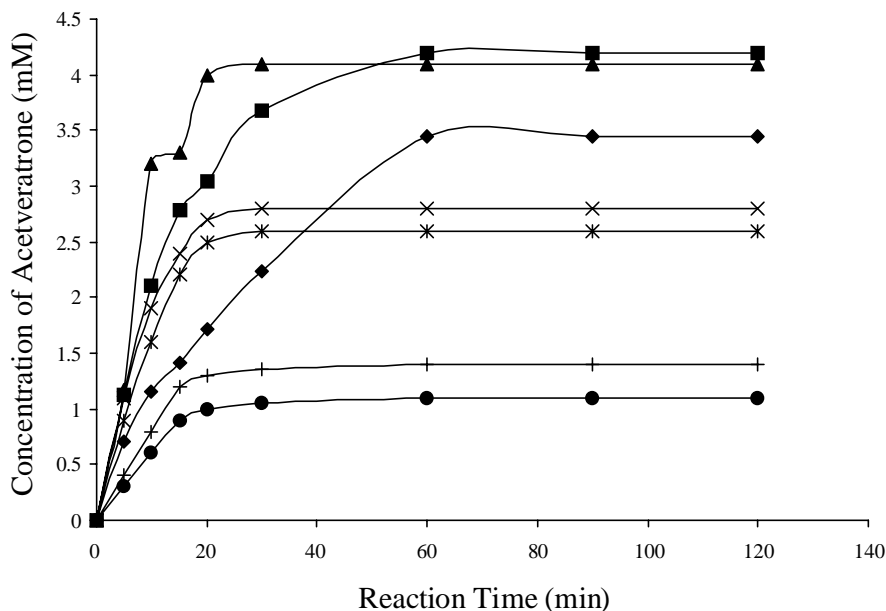


Fig. 5. Effect of reaction temperature on the formation rate of acetoveratrone (**4**) in the **C-1**- and **C-2**-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide: (◆) **C-1** at 25 °C; (■) **C-1** at 40 °C; (▲) **C-1** at 50 °C; (×) **C-1** at 60 °C; (✱) **C-1** at 80 °C; (●) **C-2** at 60 °C; (+) **C-2** at 80 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

**4** increased until reaction time of 20 min at 60 and 80 °C then leveled off (Fig. 5). The formation rate constant of **4** in the first phase of the oxidation increased when the reaction temperature increased from 60 to 80 °C (Table 2). The formation rate of **4** from **1** is also pseudo-first-order with respect to the product (Fig. 6). Moreover, at the reaction time of 60 min, the yield of **4** per the substrate consumed in the **C-1**-catalyzed oxidation of **1** is approximately 80, 89, 98, 76, and 77 mole% at 25, 40, 50, 60 and 80 °C, respectively (Figs. 3 and 5). Under the same reaction condition, the yield of **4** per the substrate consumed in the **C-2**-catalyzed oxidation of **1** is only 54 and 55 mole% at 60 and 80 °C, respectively. Thus, the substrate consumed is not quantitatively converted into **4** except in the **C-1**-catalyzed oxidation of **1** at 50 °C. Since no other aromatic products are detected in the reaction mixture, this implies that aromatic ring cleavages could have been occurred in addition to the oxidation of  $\alpha$ -hydroxyl group to the corresponding  $\alpha$ -carbonyl group in the **C-1**- and **C-2**-catalyzed oxidation of **1** with hydrogen peroxide. Further investigations are required to elucidate the nature of aromatic ring cleavage reactions.

### 3.1.2. The **C-1**- and **C-2**-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)-1-propene (**2**)

In the **C-1** and **C-2**-catalyzed oxidation of **2** with hydrogen peroxide, the concentration of substrate decreased until reaction time of 20 min at 50, 60 and 80 °C then leveled off (Fig. 7). The disappearance rate constant of **2** in the first phase of **C-1**-catalyzed oxidation increases with increasing reaction temperature up to 60 °C then decreases (Table 3). However, when reaction temperature is increased from 50 to 80 °C, the disappearance rate constant of **2** at 60 °C is faster than those at 50 and 80 °C, while that at 80 °C is slower than those at 50 and 60 °C in the **C-1**-catalyzed oxidation. In contrast, the disappearance rate constant of **2** at 60 °C is slower than that at 80 °C in the **C-2**-catalyzed oxidation. At the same reaction temperature, the rate constant for the disappearance of **2** is much faster in the **C-1**-catalyzed oxidation than that in the **C-2**-catalyzed oxidation,  $32.4 \times 10^{-4} \text{ s}^{-1}$  versus  $5.3 \times 10^{-4} \text{ s}^{-1}$  at 60 °C and  $23.1 \times 10^{-4} \text{ s}^{-1}$  versus  $7.1 \times 10^{-4} \text{ s}^{-1}$  at 80 °C (Fig. 8). Thus, it is evident that **C-1** is also more effective than **C-2** as catalyst in the oxidation of **2** with hydrogen peroxide.



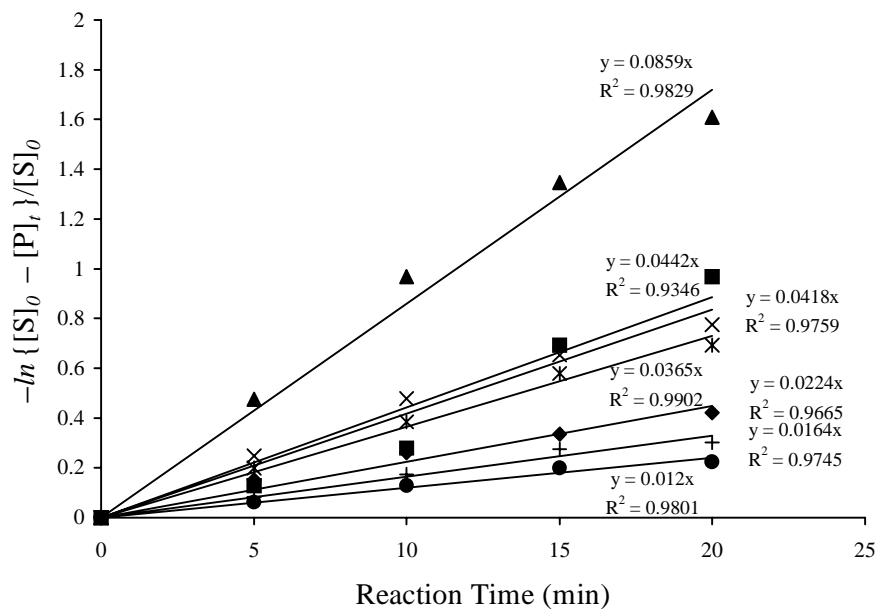


Fig. 6. The pseudo-first-order nature of the first phase in the formation of acetoveratrone (**4**) in the C-1- and C-2-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide: (◆) C-1 at 25 °C; (■) C-1 at 40 °C; (▲) C-1 at 50 °C; (×) C-1 at 60 °C; (✱) C-1 at 80 °C; (●) C-2 at 60 °C; (+) C-2 at 80 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

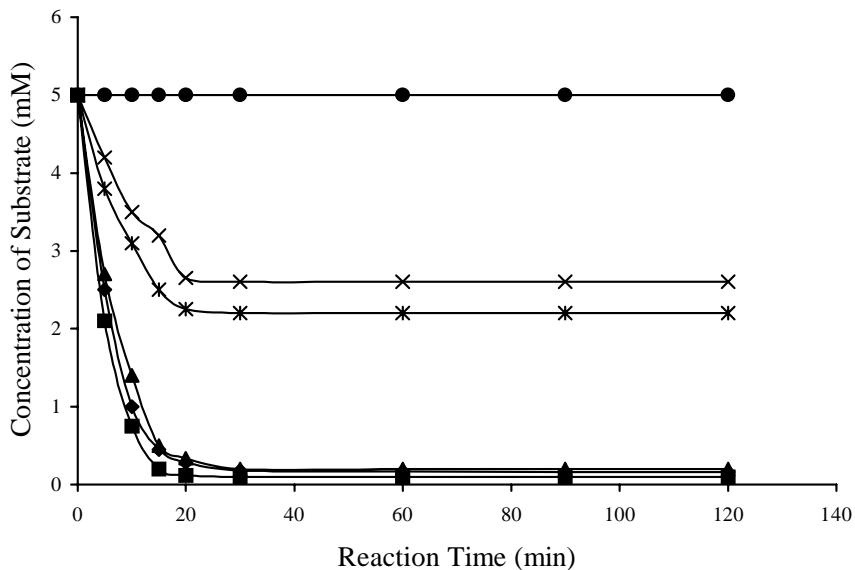


Fig. 7. Effect of reaction temperature on the disappearance rate of substrate in the C-1- and C-2-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)-1-propene (**2**) with hydrogen peroxide: (◆) C-1 at 50 °C; (■) C-1 at 60 °C; (▲) C-1 at 80 °C; (×) C-2 at 60 °C; (✱) C-2 at 80 °C; (●) uncatalyzed at 60 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

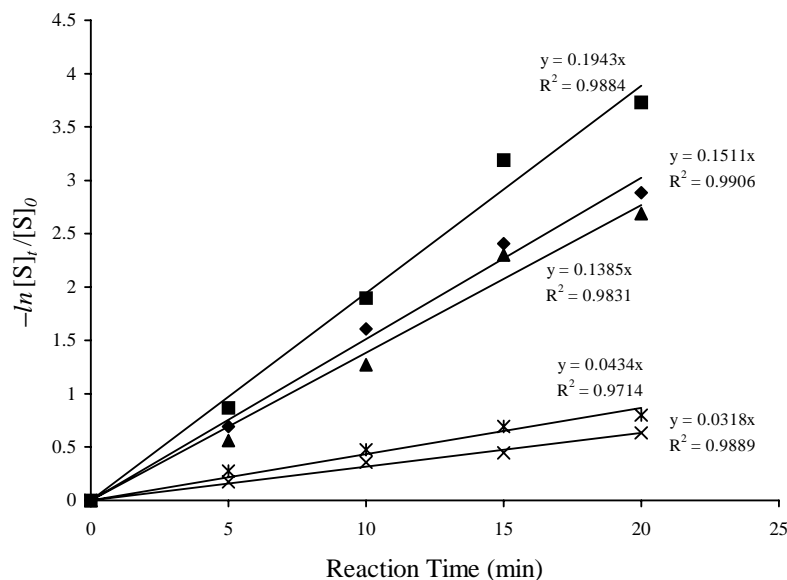


Fig. 8. The pseudo-first-order nature of the first phase in the C-1- and C-2-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)-1-propene (**2**) with hydrogen peroxide: (◆) C-1 at 50 °C; (■) C-1 at 60 °C; (▲) C-1 at 80 °C; (×) C-2 at 60 °C; (✱) C-2 at 80 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

The rate constants for the disappearance of **2** in the C-1-catalyzed oxidation are much larger than the corresponding values for the disappearance of **1** and **3**. In addition, at the reaction time of 30 min, the yields of **5**, **6**, **7** and **8** are approximately 0.6, 0.8, 44 and 35 mole% per the substrate consumed in the C-1-catalyzed oxidation of **2** at 60 °C, respectively, with the total yield of oxidation products approximately 81 mole% per the substrate consumed. Under the same reaction condition, the yields of **5**, **6**, **7** and **8** are approximately 0.6, 0.8, 37 and 25 mole% per the substrate consumed in the C-2-catalyzed oxidation of **2**, respectively, with the total yield of oxidation products approximately 63 mole% per the substrate consumed. Moreover, in both cases, the total yield of **5** and **6** is approximately 75 mole% per the substrate consumed at the reaction time of 2 min and the yield of **7** and **8** each approximately 1 mole%. These results show that C-1 and C-2 are very effective catalysts for the epoxidation of double bonds conjugated to aromatic rings and that **5** and **6** are the intermediates in the formation of **7** and **8**. It is conceivable that in the consecutive reactions,  $2 \rightarrow 5 + 6 \rightarrow 7 + 8$ , the rate determining steps are the nucleophilic attacks on **5** and **6** by hydroxide ion and hydroperoxide ion that produce **7** and **8**, respec-

tively (see Fig. 2). Here again, the results imply that aromatic ring cleavages could have been occurred in addition to the epoxidation of conjugated double in **2**, since no other aromatic products are detected in the reaction mixtures.

### 3.1.3. The C-1- and C-2-catalyzed oxidation of E-1,2-diphenylethene (**3**)

In contrast to compounds **1** and **2**, the C-1-catalyzed oxidation of **3** with hydrogen peroxide is slower than the corresponding C-2-catalyzed oxidation (Fig. 9). In the C-1-catalyzed oxidation, the substrate does not undergo oxidation up to 50 °C. In addition, the rate constant for the disappearance of **3** in the C-1-catalyzed oxidation is almost the same at 60 and 80 °C, and much slower than the corresponding values in the C-2-catalyzed oxidation,  $0.67 \times 10^{-4} \text{ s}^{-1}$  versus  $2.1 \times 10^{-4} \text{ s}^{-1}$  at 60 °C and  $0.67 \times 10^{-4} \text{ s}^{-1}$  versus  $2.7 \times 10^{-4} \text{ s}^{-1}$  at 80 °C (Fig. 10, Table 4). Thus, in contrast to the oxidation of **2**, C-1 is less effective than C-2 as catalyst in the oxidation of **3** with hydrogen peroxide. Moreover, the rate constant for the disappearance of **3** at 60 and 80 °C in the C-1-catalyzed oxidation is less than one-thirtieth of the corresponding values in the oxidation of **2**, and in the C-2-catalyzed

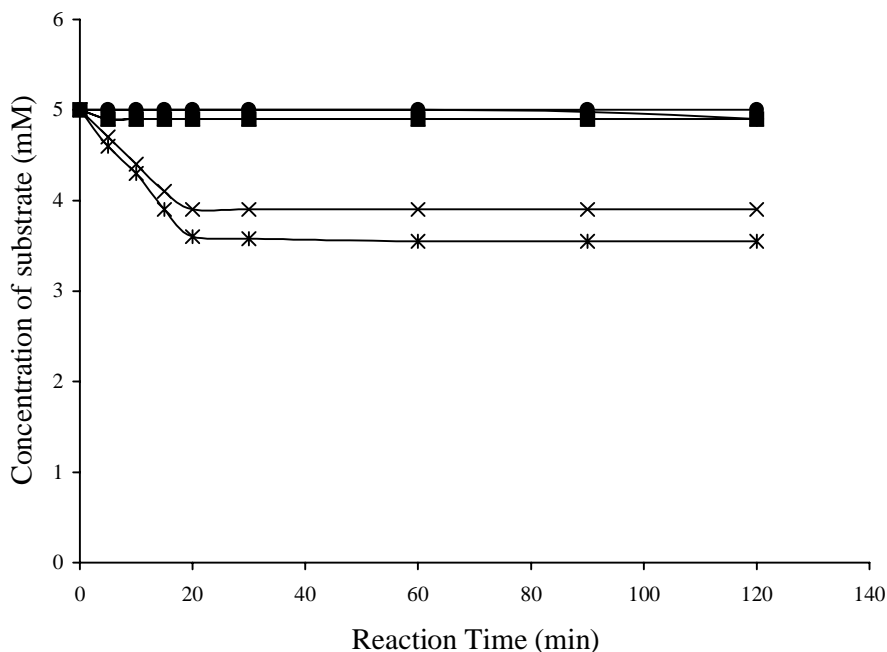


Fig. 9. Effect of reaction temperature on the disappearance rate of substrate in the C-1- and C-2-catalyzed oxidation of *E*-diphenylethene (**3**) with hydrogen peroxide: (◆) C-1 at 50°C; (■) C-1 at 60°C; (▲) C-1 at 80°C; (×) C-2 at 60°C; (✱) C-2 at 80°C; (●) uncatalyzed at 60°C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

oxidation less than two-fifth (Tables 3 and 4). These results indicate that the conjugated double bond in the stilbene-type structures are less susceptible to the C-1- and C-2-catalyzed oxidation, i.e. epoxidation, with hydrogen peroxide than the conjugated double bond in the cinnamyl-type structures.

### 3.2. Reaction mechanisms of the C-1- and C-2-catalyzed oxidation of lignin model compounds with hydrogen peroxide

#### 3.2.1. Oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**)

In the reaction mixture of the C-1- and C-2-catalyzed oxidation of **1** with hydrogen peroxide, the corresponding  $\alpha$ -carbonyl derivative, acetoveratrone (**4**) (Fig. 2), and 1-(3,4-dimethoxyphenyl)-ethylene (**10**) were identified. The compound **10** is a dehydration product of **1** produced in the capillary column in the GC and GC-MS analyses. The reaction mechanism is the same for both oxidations.

The oxidation of **1** in the C-1-catalyzed oxidation is initiated by nucleophilic attack of hydroperoxide

anion ( $\text{HOO}^-$ ) on one of the Mn(IV) nuclei with concomitant cleavage of the one of the three  $\mu$ -O bonds (Fig. 11). This gives the catalyst intermediate C-1a with one Mn(IV) nuclear being bonded to  $-\text{OOH}$  group, and the other Mn(IV) nucleus to  $-\text{OH}$  group. The Mn(IV) nucleus of Mn(IV)-OOH group then abstract a single electron from the aromatic ring of **1** to produce a corresponding aryl cation radical **1a** and the catalyst intermediate C-1b with concomitant transferring of the electron to the  $3d_{(x^2-y^2)}$  orbital in the  $e_g(\sigma^*)$  set of Mn (IV) nucleus [13,14], which is now the highest occupied molecular orbital (HOMO) and the oxidation state of the Mn nuclear is reduced to Mn(III). The resulting Mn(III)-OOH group of C-1b then undergoes homolytic cleavage of the  $-\text{O}-\text{OH}$  bond with concomitant transferring of an electron from the  $e_g(\sigma^*)$  orbital to the resulting Mn(III)-O $\cdot$  radical, producing Mn(IV)-O $^-$  group in the catalyst intermediate and hydroxyl radical (HO $\cdot$ ). The latter then abstracts a hydrogen atom from the C- $\alpha$  to give an  $\alpha$ -hydroxyquinonemethide cation ion intermediate **1b** that immediately undergo rearrangement to produce the corresponding  $\alpha$ -carbonyl compound

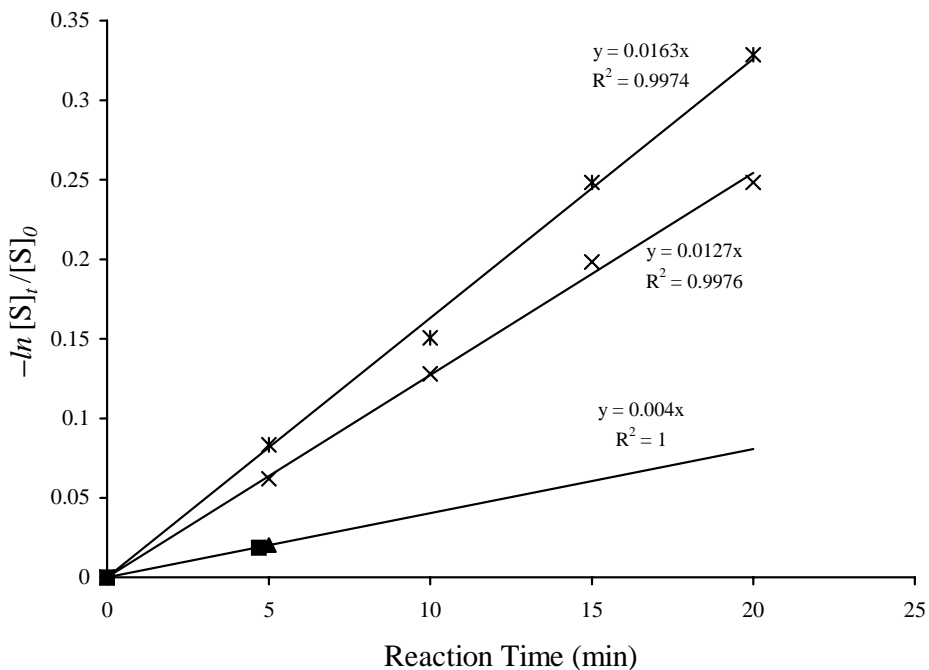


Fig. 10. The pseudo-first-order nature of the first phase in the C-1- and C-2-catalyzed oxidation of *E*-diphenylethene (**3**) with hydrogen peroxide: (■) C-1 at 60 °C; (▲) C-1 at 80 °C; (×) C-2 at 60 °C; (✱) C-2 at 80 °C [catalyst/substrate mole ratio (C/S ratio) = 0.01].

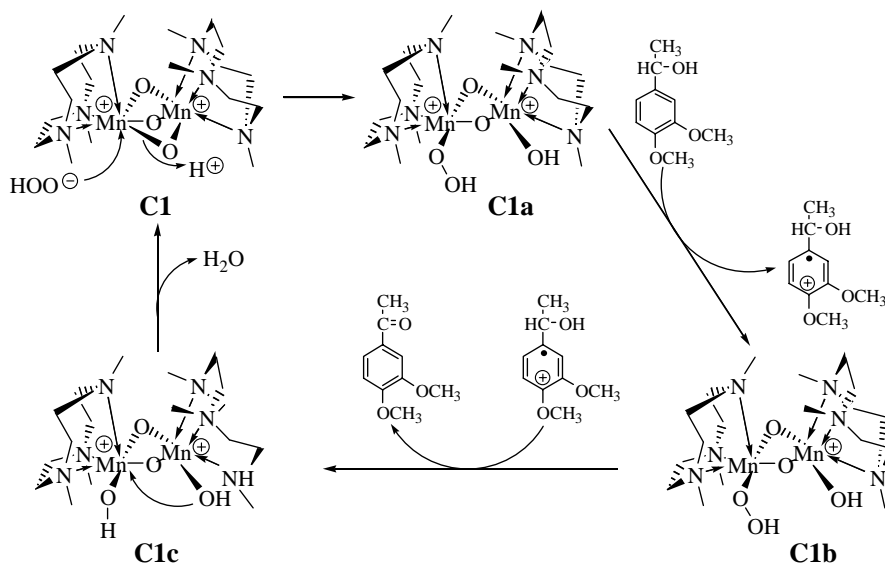


Fig. 11. Catalytic cycle for the C-1-catalyzed oxidation of 1-(3,4-dimethoxyphenyl)ethanol (**1**) with hydrogen peroxide.

**4** with concomitant release of  $H^+$  to the resulting  $Mn(IV)-O^-$  group in a concerted reaction producing the catalyst intermediate **C-1c** that contains two  $M(IV)-OH$  groups. Thus, the  $Mn(III)$  nucleus is oxidized back to the oxidation state of  $Mn(IV)$ . An elimination of a water molecule from the catalyst intermediate **C-1c** then completes a catalytic cycle. The catalytic cycle for the **C-2**-catalyzed oxidation is the same except for difference in ligand of the catalyst. The proposed catalytic cycle is consistent with the results of Gilbert et al. [15] and Hage et al. [16].

### 3.2.2. Oxidation of 1-(3,4-dimethoxyphenyl)-1-propene (**2**)

In the **C-1**-catalyzed oxidation of **2** with hydrogen peroxide, *E*-1-(3,4-dimethoxy-phenyl)propane-1,2-epoxide (**5**), *Z*-1-(3,4-dimethoxyphenyl)-propane-1,2-epoxide (**6**), 1-(3,4-dimethoxyphenyl) propane-1,2-diol (**7**), and 3,4-dimethoxybenzaldehyde (**8**) were identified in the reaction mixture (Fig. 2). However, in the reaction mixture of the corresponding **C-2**-catalyzed oxidation, compound **6** was not identified, probably because it was produced in such a trace amount at the end of reaction that did not be detected by GC analysis. The formation of **5** and **6**, diastereoisomers, indicates that radical species are involved in the **C-1**-catalyzed oxidation of **2**, which will be discussed below. Both in the **C-1**- and **C-2**-catalyzed oxidation of **2** with hydrogen peroxide, the substrate also undergoes the single-electron transfer from aromatic ring to the  $Mn(IV)$  nuclear of  $Mn(IV)-OOH$  group of the catalyst intermediate **C-1a** (see Fig. 11 for structure) as in the corresponding oxidation of compound **1** to produce a corresponding aryl cation radical, the  $\pi$ -orbital of which is overlapped with that of the conjugated double bond and the catalyst intermediate **C-1b**. The resulting  $Mn(III)-O-OH$  group of **C-1b** then undergoes homolytic cleavage of the  $-O-OH$  bond with concomitant transferring of an electron from the  $e_g(\sigma^*)$  orbital to the resulting  $Mn(III)-O^\bullet$  radical, producing  $Mn(IV)-O^-$  group in the catalyst intermediate and hydroxyl radical ( $HO^\bullet$ ). A cross-radical combination between the hydroxyl radical ( $HO^\bullet$ ) and the  $C-\beta$ -centered cation radical **2a** then produces  $\beta$ -hydroxyquinonemethide cation ion intermediate **2b** that immediately undergoes intramolecular nucleophilic attack of the resulting  $\beta$ -hydroxyl group on  $C-\alpha$  with concomitant release of

$H^+$  to the resulting  $Mn(IV)-O^-$  group in a concerted reaction, producing the catalyst intermediate **C-1c**, *E*-1-(3,4-dimethoxyphenyl)propane-1,2-epoxide (**5**) and *Z*-1-(3,4-dimethoxy-phenyl)propane-1,2-epoxide (**6**) (Fig. 2). Evidently, the catalytic cycle for the formation of epoxides **5** and **6** from **2** is analogous to that for the formation of **4** from **1** (Fig. 11).

The epoxides **5** and **6** then undergo non-catalytic hydrolysis via nucleophilic attack of hydroxide anion ( $HO^-$ ) on  $C-\alpha$ , anti-Markovnikov addition, to produce 1-(3,4-dimethoxy-phenyl)propane-1,2-diol (**7**) (Fig. 2). The epoxides **5** and **6** also undergo anti-Markovnikov nucleophilic attack of hydroperoxide anion ( $HOO^-$ ) to give the  $\alpha$ -hydroperoxyl- $\beta$ -hydroxide anion intermediate **5a** that immediately decomposes to give 3,4-dimethoxy-benzaldehyde (**8**), acetaldehyde and hydroxide anion ( $HO^-$ ). These results show that the **C-1** and **C-2** are very good catalysts for epoxidation of double bonds conjugated to aromatic groups. Hege et al. [16] showed that epoxidation reactions with  $H_2^{18}O_2$  using a similar catalyst result in producing the corresponding epoxides that contained 100%  $^{18}O$ . This shows that  $H_2O_2$  is the source of oxygen, not water, which is in agreement with the proposed reaction mechanism.

### 3.2.3. Oxidation of *E*-1,2-diphenylethene (**3**)

The **C-1**- and **C-2**-catalyzed oxidations of **3** with hydrogen peroxide produce the corresponding *E*-1,2-diphenyletheneoxide (**9**) (Fig. 2). The catalytic cycle of the reaction is the same to that of the corresponding oxidation of **2**. However, 1,2-diphenylethane-1,2-diol and benzaldehyde are not identified in the resulting reaction mixtures, formation of which are expected from nucleophilic attack of **9** by hydroxide anion ( $HO^-$ ) and hydroperoxide anion ( $HOO^-$ ), respectively.

## 4. Conclusions

Lignin model compounds, 1-(3,4-dimethoxyphenyl)ethanol (**1**), 1-(3,4-dimethoxyphenyl)-1-propene (**2**) and *E*-1,2-diphenylethene (**3**), readily undergo oxidation with hydrogen peroxide at reaction temperatures below  $80^\circ C$  when  $[LMn(IV)(\mu-O)_3Mn(IV)L](PF_6)_2$  (**C-1**) and  $[L'Mn(IV)(\mu-O)_3Mn(IV)](ClO_4)_2$  (**C-2**) are used as catalyst. The disappearance rate of **1**

in the first phase of **C-1**-catalyzed oxidation increases up to 50 °C then decreases with increasing reaction temperature. Similarly, the disappearance rate of **2** in the first phase of **C-1**-catalyzed oxidation increases up to 60 °C then decreases with increasing reaction temperature. The cause is not known for the slow down of the disappearance rate at reaction temperature range higher than 50–60 °C in the **C-1**-catalyzed oxidation of **1** and **2**. In general, **C-1** is more effective as catalyst in the oxidation of **1** and **2** but less effective in the oxidation of than **C-2** does. The **C-1**- and **C-2**-catalyzed bleaching of pine Kraft-AQ pulps with hydrogen peroxide showed that **C-1** is more effective than **C-2** as catalyst in the bleaching, the result of which will be published elsewhere in the near future [17].

In the **C-1**- and **C-2**-catalyzed oxidation, **1**, is oxidized to the corresponding  $\alpha$ -carbonyl derivative, while **2** readily undergoes epoxidation of the conjugated double bond to produce the epoxides **5** and **6**. The anti-Markovnikov nucleophilic addition of hydroxide and hydroperoxide anions on **5** and **6** then produced  $\alpha,\beta$ -diol **7** and benzaldehyde derivative **8**, which are non-catalytic reactions. The compound **3** also undergoes epoxidation of aliphatic double bond producing the epoxide **9**. However, none of the corresponding  $\alpha,\beta$ -diol and benzaldehyde derivative is detected in the reaction mixture. Based on the kinetic data and reaction products, the catalytic cycles of the **C-1**- and **C-2**-catalyzed oxidation of **1-3** are postulated. It is initiated by nucleophilic attack of hydroperoxide anion on one of the Mn(IV) nuclei with concomitant cleavage of the one of the three  $\mu$ -O bonds. This gives the catalyst intermediate **C-1a** with one Mn(IV) nuclear being bonded to  $-\text{OOH}$  group, and the other Mn(IV) nuclear to  $-\text{OH}$  group. The Mn(IV) nuclear of Mn(IV)-OOH group then abstract a single electron from the aromatic ring of substrate to produce a corresponding aryl cation radical and the catalyst intermediate **C-1b**. The resulting Mn(III)-O-OH group of **C-1b** then undergoes homolytic cleavage of the  $-\text{O}-\text{OH}$  bond with concomitant transferring of an electron from the  $e_g(\sigma^*)$  orbital to the resulting Mn(III)-O $\cdot$  radical, producing Mn(IV)-O $^-$  group in the catalyst intermediate and a hydroxyl radical (HO $\cdot$ ). The latter then abstracts a  $\alpha$ -hydrogen atom from the aryl cation radical producing the corresponding quinonemethide cation intermediates, followed

by rearrangement of the intermediates to give the corresponding  $\alpha$ -carbonyl products with concomitant release of H $^+$  to the resulting Mn(IV)-O $^-$  group to produce the catalyst intermediate **C-1c**. Alternatively, the hydroxyl radical adds to the C- $\beta$ -centered cation radical derived from double bond conjugated to aromatic rings with concomitant intramolecular nucleophilic addition of  $\beta$ -hydroxyl group on C- $\alpha$  to the resulting quinonemethide cation intermediates giving the corresponding epoxides with concomitant release of H $^+$  to the resulting Mn(IV)-O $^-$  group to produce the catalyst intermediate **C-1c**. Thus, the Mn(III) nucleus is oxidized back to the oxidation state of Mn(IV). An elimination of a water molecule from the catalyst intermediate **C-1c** then completes a catalytic cycle.

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