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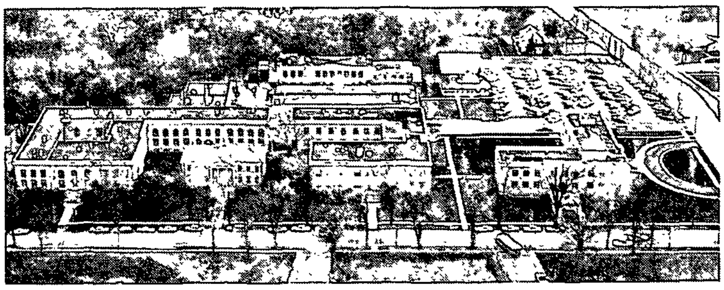

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TRANSITION METAL ION CATALYSIS OF THE REACTION OF A RESIDUAL LIGNIN-RELATED COMPOUND WITH ALKALINE HYDROGEN PEROXIDE

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Transition metal ion catalysis of the reaction of a residual lignin-related compound with alkaline hydrogen peroxide

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ABSTRACT: This paper describes a model study of reactions occurring during delignification of softwood kraft pulp with hydrogen peroxide or oxygen under alkaline conditions. The kinetics of the reaction between 1,1'-methylenebis-(2-hydroxy-3-methoxy-5(2-carboxyethyl)benzene) (MBB) and alkaline hydrogen peroxide (1:5 molar ratio, pH 11, 45°C) were investigated in the absence and presence of catalytic quantities of added transition metal ions. This compound was chosen to be representative of the condensed phenolic structural units believed to be present in the residual lignin of unbleached softwood kraft pulps. The experimental techniques employed allowed independent determinations of the respective amounts of peroxide consumed by the lignin model and lost to decomposition.

Added Fe and Mn salts behaved similarly and catalyzed H_2O_2 decomposition to a greater extent than MBB oxidation. In contrast, the addition of either ferricyanide or Cu(II) salts produced an overall increase in the degradation of the lignin model at lower levels of H_2O_2 decomposition. These findings are discussed with reference to the delignification of pulp by alkaline hydrogen peroxide.

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Introduction

The feasibility of using hydrogen peroxide as a delignifying agent in the first stage of a bleach sequence for alkaline chemical pulps has recently received considerable attention (1-4). This process, like oxygen bleaching, offers pollution abatement as a major advantage, but has the additional advantage of not requiring pressurized equipment.

A number of studies (2,5,6) have shown that the removal of heavy metals from pulp (by pretreatment with acid and/or chelating agents) significantly enhances the extent of peroxide delignification. The negative effect of these metals is believed due to metal ion catalyzed decomposition of hydrogen peroxide.

On the other hand, Agnemo and Gellerstedt (7,8) have demonstrated that peroxide decomposition is necessary for phenolic structures of the type present in lignin to be attacked by hydrogen peroxide. Hydrogen peroxide decomposition involves the intermediate formation of radical species (viz. $O_2^{\overline{\cdot}}$, HO•) (9-11). It is likely that oxygen and these oxy-radicals are the species which attack phenolic lignin units during peroxide delignification (7).

Transition metal ions can be involved in this reaction in a second way. The rate determining step in the oxidation of phenols with oxygen (and H_2O_2) in alkali is believed to be phenoxy radical formation (12-14). Many transition metal ion species are quite effective single-electron oxidants (12,15,16). Landucci (12,16) has demonstrated that the salts of heavy metals commonly found in pulp (Cu, Mn, Fe) catalyze phenoxy radical formation under alkaline conditions and in the presence of oxygen.

It is evident that transition metal ions should play a central role in the reactions of lignin with hydrogen peroxide (and oxygen) in alkali. The present study was directed toward understanding the relationship between transition metal ion catalysis of hydrogen peroxide decomposition and oxidation of a lignin-related compound. The model compound shown below - 1,1'-methylenebis(2-hydroxy-3-methoxy-5(2-carboxyethyl)benzene) or MBB - was selected to represent condensed phenolic units in residual lignin. Hydrogen peroxide was applied to the MBB in an initial 5:1 molar ratio at pH 11 and 45°C. The effects of catalytic quantities of Cu, Mn, and Fe salts (and complexed Fe) on the kinetics of both hydrogen peroxide decomposition and MBB oxidation were studied.

[Drawing here]

Results

H_2O_2 Decomposition kinetics

It is well known that hydrogen peroxide decomposition is extremely sensitive to the presence of trace contaminants. In this study, high-purity reagents, inert reactor surfaces and careful experimental techniques were employed to minimize the introduction of contaminants which could give spurious data. As a result, triplicate hydrogen peroxide decomposition runs (in the absence of MBB) showed very good reproducibility (fig. 1). The level of decomposition observed in these reactions is attributed to a low "background" level of catalysts present in the reaction system in trace quantities.

[fig. 1 here]

The rate expression for hydrogen peroxide decomposition is given by:

$$-d[H_2O_2]/dt = k_1 \, [H_2O_2]^{n_1} \qquad [1]$$

Note that all rate constants evaluated in this study are for constant [HO$^-$] and temperature (45°C). Although the pH of the reaction solutions (with or without MBB present) increased slightly as the H_2O_2 decomposed to oxygen, their pH remained in the interval 11.0-11.4 and the [HO$^-$] was considered constant. Data collected from decomposition runs over the initial [H_2O_2] range of 15-840 m<u>M</u> were analyzed by the initial rate and differential methods (17). Rates were determined graphically on the [H_2O_2]-time plots. Results of this analysis (<u>fig. 2</u>) indicate that the reaction order (n_1) changes from 2.5 to 2.0 as the hydrogen peroxide concentration is decreased below about 60 m<u>M</u>.

[fig. 2 here]

The effects of added transition metal ions (Cu, Mn, Fe) on the kinetics of hydrogen peroxide decomposition ($[H_2O_2]o$ = 150 m<u>M</u>) were also investigated. On the basis of previous studies (7,9,18), first order kinetics (n_1 = 1.0) were anticipated for decomposition in the presence of metals at sufficiently high levels (> 2 μ<u>M</u>). In each case the data showed an excellent fit (correlation coefficient, r > 0.99) to the integrated form of eq. [1] with n_1 = 1.0. These results confirm the suspected first order kinetics for H_2O_2 decomposition in the presence of the metal ions.

The rate constants found for hydrogen peroxide decomposition (k_1) in the presence and absence of added transition metal ions are tabulated in table I.

[table I here]

Hydrogen peroxide decomposition during each MBB oxidation run (table II) was monitored (independently of its consumption by MBB) by measuring the volume of oxygen evolved. The rate law for decomposition under these conditions was assumed to be:

$$d[Ox]/dt = k_2 \, [H_2O_2]^{n_2} \qquad [2]$$

[table II here]

The term [Ox] represents the concentration of decomposed H_2O_2 as measured by oxygen evolution (2 moles of H_2O_2 decompose to 1 mole of oxygen). The effects that the additives had on the decomposition and total consumption of H_2O_2 in the MBB oxidation runs are shown in fig. 3 and 4, respectively.

[fig. 3 and 4 here]

The data in fig. 3 were analyzed by the differential method, with the rates (d[Ox]/dt) determined graphically. The results, depicted in fig. 5, show that the reaction order (n_2) for the Control, Cu, and Mn reactions were essentially the same as the orders (n_1) found in the absence of MBB (2, 1, and 1, respectively). The presence of MBB in the Fe reaction caused the reaction order to increase from 1.0 (n_1) to 1.5 (n_2). A 1.5 order (n_2) was also found in the reaction catalyzed by ferricyanide ions (FC).

[fig. 5 here]

Upon addition of H_2O_2 and alkali, the additives in the Mn, Cu, and Fe reactions formed insoluble hydroxides and oxyhydroxides of higher oxidation states (viz. MnO_2, CuO, Fe_2O_3) (19). As evident from the high initial rates of H_2O_2 decomposition in these reactions (dashed lines, fig. 5), the metal ion species were probably initially present in a physical form and/or oxidation state which exhibited a higher catalytic activity.

The rate constant, k_2, for each oxidation run was evaluated using the integral method. Integration of eq. [2] gives:

$$[Ox] = k_2 \int_0^t [H_2O_2]^{n_2} dt \qquad [3]$$

The integral was approximated by applying Simpson's Rule to the $[H_2O_2]$-time data (fig. 4). Plots of eq. [3] for the oxidation runs (Control, FC, Fe, Cu, and Mn with reaction orders, n_2, of 2.0, 1.5, 1.5, 1.0, and 1.0, respectively) showed excellent linearity ($r > 0.99$). Table III lists the rate constants, k_2, evaluated in this analysis.

[table III here]

MBB Oxidation kinetics

The MBB concentration-time curves in fig. 6 represent the net effect of the metal ion additives on the two overall reactions: hydrogen peroxide decomposition and MBB oxidation. In order to compare the catalytic effect of the metals on the MBB oxidation rate, the same general kinetic model was applied to the data from each reaction.

[fig. 6 here]

The model, defined by eq. [4] and [5], represents a useful but simplified description of the complex reaction systems under study. A first order dependence on [MBB] was assumed on the basis of a similar kinetic study by Agnemo and Gellerstedt (7). As a first assumption, the order with respect to $[H_2O_2]$, n_3, was set equal to one. The first term of eq. [5] represents peroxide decomposition; the values k_2 and n_2 from table III were used. The second term represents H_2O_2 consumption by MBB (and its products). The overall reaction stoichiometry is defined by the ratio, k_4/k_3.

$$-d[MBB]/dt = k_3 [MBB][H_2O_2]^{n_3} \qquad [4]$$

$$-d[H_2O_2]/dt = k_2 [H_2O_2]^{n_2} + k_4 [MBB] [H_2O_2]^{n_3} \qquad [5]$$

A computer program for parameter estimation from multiresponse data (20) was employed to obtain optimal values for the rate constants, k_3 and k_4. The experimental data from the Control, Fe, FC, and Mn reactions showed a good fit to the resulting calculated $[H_2O_2]$-time and [MBB]-time curves using the above model.

For the Cu reaction the model accurately described the experimental data only when a zero order dependence on $[H_2O_2]$ was assumed (i.e., $n_3 = 0$). Table IV summarizes the rate constants found by this analysis for the five reactions.

[table IV here]

Application of the differential and integral methods of kinetic analysis to the same data gave results which were in qualitative agreement with the above findings (21). For the Control and FC reactions a value of $n_3 = 1.3$ was found. The ratio of rate constants, k_3(FC)/k_3 (Control), with $n_3 = 1.3$ was 2.0 - the same ratio found above for $n_3 = 1.0$ (table IV).

In the initial part of the Fe and Mn reactions, the differential method indicated an apparent order, n_3, of ca. 5.0 and 1.9, respectively. After ca. 40% of the H_2O_2 had been consumed, the reaction order (n_3) for both reactions abruptly decreased to ca. 0.5 over the remainder of each reaction. As explained above for peroxide decomposition in the presence of MBB, this effect is probably due to a change in the nature of the metal catalysts as the reactions progressed. The ratio of rate constants, $k_3(Mn)/k_3(Fe)$, was 2.5 over the region where n_3 = 0.5. This is equal to the ratio found above for n_3 = 1.0 (table IV). Thus the kinetic model analysis provides a convenient, qualitative means for comparing the MBB oxidation rates (k_3's) in the Control, Mn, Fe, and FC reactions.

For the Cu reaction, application of the differential and integral methods also demonstrated that the rate of MBB oxidation was independent of $[H_2O_2]$ (21). The rate constant found was in agreement with the corresponding value in table IV.

Discussion

H_2O_2 Decomposition

The results presented above illustrate some of the complexities associated with the chemistry of hydrogen peroxide decomposition. The bulk of the literature concerning peroxide decomposition indicates that this reaction proceeds *via* a radical chain mechanism catalyzed by transition metal ion species (9,22-24). Fig. 7 depicts a set of reactions which we believe are important in describing hydrogen peroxide decomposition in alkali (21).

[fig. 7 here]

The observed changes in the reaction order, n_1, with changes in the H_2O_2 or metal ion concentration are consistent with a complex reaction proceeding by two or more parallel paths (25). Other researchers have reported changes in this reaction order with changes in pH or metal ion concentration (9). In the presence of Fe salts the addition of MBB also caused a change in the order ($n_1 = 1.0$, $n_2 = 1.5$).

Hydrogen peroxide decomposition was accelerated by MBB in the Control, Mn, and Cu reactions (cf. tables I and III). A similar acceleration was also observed in a study in which glucose was added to alkaline H_2O_2 (26). It is probably due to the organic substrate acting as a chain transfer agent in the radical decomposition reaction. For example, the single electron oxidation of MBB by M^+ provides an additional route for M to be formed which, as shown in fig. 7, is involved in the chain mechanism for peroxide decomposition (step 1).

MBB Oxidation

At the levels added the metal ions can be listed in order of decreasing catalytic activity with respect to MBB oxidation as follows:

Cu > Mn > FC > Fe (> Control)

Landucci (12) found the same ranking for these additives with respect to their ability to catalyze phenoxy radical formation. This provides strong evidence for the contention that the important, rate-limiting step in the degradation of phenolic lignin units in alkaline hydrogen peroxide is phenoxy radical generation.

On the basis of the results of this study and others (7,12,13) the reaction scheme depicted in fig. 8 may be considered to represent the mechanism of destruction of phenolic lignin units by alkaline hydrogen peroxide. The single-electron oxidation of the phenolate anion (step 2, fig. 8) results in the formation of a resonance-stabilized phenoxy radical. Reaction with superoxide and/or oxygen (step 3, fig. 8) gives a cyclohexadienone hydroperoxide which is degraded to lower molecular weight products by ionic mechanisms involving attack by hydroxyl and hydroperoxy anions (27-29). The mechanism of *fig. 8* is equally applicable to oxygen bleaching since all of the same species are present there.

[fig 8. here]

The observed independence of oxidation rate and H_2O_2 concentration for the Cu reaction can be explained in terms of this mechanism. It is postulated that the Cu catalyst effectively competes with the phenoxy radical for superoxide ions. Thus reaction of phenoxy radicals (which are generated at high rates by the Cu catalyst) with oxygen in step 3 (*fig. 8*) becomes the favored pathway to the formation of cyclohexadienone hydroperoxide intermediates. Since the decomposing hydrogen peroxide maintains a saturated solution of oxygen (*i.e.*, constant concentration), the reaction rate depends only on the MBB concentration.

The same mechanism may have operated to a lesser degree in the Mn and Fe catalyzed reactions. These two systems exhibited a one-half order with respect to $[H_2O_2]$ (over 60% of each reaction) which is less than the 1.3 order for the Control reaction.

A large number of metal ions and their complexes are known to catalyze superoxide dismutation:

$$H_2O + 2O_2^{\overline{\cdot}} \longrightarrow HO_2^- + O_2 + HO^-$$

For example, hydrated Cu(II) ions have been shown to catalyze this reaction at diffusion controlled rates [$k \sim 10^{10}\,\underline{M}^{-1}\,s^{-1}$ (30)]. However, not all metal species are this active. Superoxide dismutation in the presence of ferricyanide/

ferrocyanide ions occurs at much slower rates [k ~ 10^3 $\underline{M}^{-1}$ s^{-1} (31)]. This likely explains why the dependence of MBB oxidation rate on [H_2O_2] was the same in both the Control and FC reactions.

Conclusions and practical significance

The results of this study are consistent with our present understanding of the complex mechanisms of H_2O_2 decomposition (fig. 7) and phenol degradation by H_2O_2 (or oxygen) under alkaline conditions (fig. 8). The kinetics of these two reactions were shown to be strongly influenced by different transition metal ions added at catalytic levels.

The relationship between the catalysis of H_2O_2 decomposition and phenol oxidation by the metal ion species is illustrated in fig. 9. In this figure, the level of peroxide decomposed is plotted as a function of the amount of MBB reacted. The slope of the lines in the plot represents the ratio of the rates of H_2O_2 decomposition to MBB oxidation. The Cu reaction gave a nonlinear response due to the independence of MBB oxidation rate on [H_2O_2].

[fig. 9 here]

Fig. 9 graphically demonstrates that the added transition metal ions catalyzed H_2O_2 decomposition and the oxidation of the lignin model to different extents. In the context of peroxide delignification of pulp, these results suggest that the presence of some metals (e.g., Fe and Mn) waste H_2O_2 through increased decomposition to oxygen. However, results of the Cu and FC reactions indicate that not all metal species may be considered detrimental. For instance, it might be possible to increase the extent and rate of delignification for a given H_2O_2 charge by controlling the levels and types of metal ion species in the pulp. As a further extension, it may be feasible to increase selectivity by means of catalysts which preferentially direct peroxide attack to the lignin fraction, thus minimizing damage to the carbohydrates.

Experimental

Materials

Synthesis of model compound. The model compound, 1,1'-methylenebis-(2-hydroxy-3-methoxy-5(2-carboxyethyl)benzene) (MBB), was prepared by refluxing hydroferulic acid (130 mmol) and formaldehyde (260 mmol) in 2.2N NaOH (120 mL) under a helium atmosphere for 3 hours (21). [The hydroferulic acid was prepared by the catalytic hydrogenation (10% Pd on charcoal and atmospheric H_2 pressure) of commercially available ferulic acid (4-hydroxy-3-methoxy-cinnamic acid).] After cooling and acidifying the refluxed solution, the crude MBB was isolated and purified via column chromatography [silica gel 60 adsorbent and dichloromethane:acetic acid (100:1 —> 10, v/v) solvent system]. The recovered product was recrystallized from distilled water to give finely divided white crystals: m.p. 168-169°C. Analyses by GLC and TLC showed the product to be pure. 'H-NMR (100 MHz, $CDCl_3$): δ 2.57(m, 4H, β-CH_2), 2.87(m, 4H, α-CH_2), 3.84 (s, 8H, OCH_3, and Ar-CH_2-Ar), 6.58(d, 6H, Ar, and ArOH). ^{13}C NMR (DMSO d6, fully decoupled): δ 28.8, 30.2, 35.6, 55.5, 109.2, 121.4, 126.8, 130.5, 141.6, 146.7, 173.4.

Chemicals. Ultrapure grades of 30% NaOH solution (Alfa Division, Ventron Corp., Danvers, MA) and 30% hydrogen peroxide (J. T. Baker Chemical Co., Phillipsburg, NJ) were used as received. Triply-distilled (3-D) water (21) was used in preparing all reaction solutions. The following analytical reagent grade chemicals (J. T. Baker Chemical Co.) were used as the metal ion catalysts: $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot H_2O$, $FeSO_4 \cdot 7H_2O$, $K_3Fe(CN)_6$.

Reaction procedures

Reactor system. The reactor consisted of a Teflon-lined brass bomb (ca. 300 mL capacity) equipped with an inert valve system which permitted addition of reactants and removal of samples. The gas tight reactor also contained a sealed reference combination pH electrode (Sensorex, Westminster, CA). The reaction solutions were magnetically stirred and maintained at 45 ± 0.2°C by a water bath. After each kinetic run, all reactor surfaces which came into contact with the solution were thoroughly cleaned (21).

Kinetic runs. Reaction solutions for the oxidation runs were prepared by weighing appropriate quantities of MBB and 3-D water into the reactor. Metal ions, when present, were added at this point as 1 mL aliquots of stock metal ion solutions. The reaction solution was continuously purged with nitrogen as 30% NaOH was added to dissolve the model substrate (pH 8-9). After reaching thermal equilibrium, the nitrogen flow was stopped and the reaction was initiated by injecting a weighed amount of 30% H_2O_2 into the reactor followed by sufficient 30% NaOH to bring the pH to 11.0 ± 0.05. Hydrogen peroxide decomposition runs were performed as above except MBB was not added.

Analyses

At different reaction times, samples (2 x 1.00 mL) were withdrawn from the reactor and analyzed for H_2O_2 by iodometric titration (32). Unreacted MBB was determined via quantitative GLC of its trimethylsilyl (TMS) derivative using n-octacosane as an internal standard. For this analysis, reaction samples (2 x 1 mL) were added gravimetrically to vials containing a quench solution (0.3 mL of 1.4M KH_2PO_4 and 0.3 mL of 0.75M $NaAsO_2$). After workup and derivatization (21), each sample was analyzed in triplicate by a Perkin-Elmer model 3920 gas chromatograph containing a 3 ft x 0.25 in (2 mm ID) glass column packed with 3% OV-1 on 80/100 mesh Chromosorb W-HP. The column was maintained at 250°C, and the detector and injector at 290°C. The carrier gas was prepurified N_2 (32 mL/min).

Hydrogen peroxide decomposition was followed over the entire course of each MBB oxidation reaction. This was accomplished by measuring the volume of evolved oxygen via a gas buret attached to the gas-exit port of the reactor. In the absence of MBB the observed rate of oxygen evolution and H_2O_2 disappearance (measured by iodometric titration) were found to agree within 3% error (21).

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TABLE I

HYDROGEN PEROXIDE DECOMPOSITION KINETICS IN THE ABSENCE OF MBB METAL IONS ADDED AS THE SALTS: $MnSO_4$, $CuSO_4$, $FeSO_4$ CONDITIONS: pH 11.0-11.4, TEMPERATURE 45°C

Metal ion additive	Additive level, μM	Reaction order, n_1	Rate constant,[a] k_1
--	--	2.0	1.36 ± 0.51
--	--	2.5	1.69 ± 0.34
Fe	18.2	1.0	3.50 ± 0.09
Fe	285	1.0	5.80 ± 0.33
Cu	1.8	1.0	8.45 ± 0.07
Cu	9.1	1.0	8.72 ± 0.26
Cu	18.2	1.0	8.83 ± 0.49
Cu	285	1.0	26.4 ± 3.1
Mn	9.1	1.0	4.85 ± 0.06
Mn	18.2	1.0	7.33 ± 0.14
Mn	285	1.0	202 ± 58

---

[a] Units (order): $\text{min}^{-1} \cdot 10^{-3}$ (1.0), $\text{mM}^{-1} \cdot \text{min}^{-1} \cdot 10^{-5}$ (2.0), $\text{mM}^{-1.5} \cdot \text{min}^{-1} \cdot 10^{-6}$ (2.5). ± 95% confidence limits based on triplicate runs for the controls and single runs for the rest.

[b] In the absence of additives the order was 2.0 below ca. 60 mM H_2O_2 and 2.5 above this concentration.

TABLE II

LEVELS OF METAL ION ADDITIVES. REACTION CONDITIONS: $[MBB]_o$ = 20 mM, $[H_2O_2]_o$ = 100 mM, pH 11.0-11.4, 45°C

Reaction	Additive	Level, μM
Control	--	--
Cu	$CuSO_4$	12
Mn	$MnSO_4$	21
Fe	$FeSO_4$	300
FC	$K_3Fe(CN)_6$	300

TABLE III

HYDROGEN PEROXIDE DECOMPOSITION KINETICS IN THE PRESENCE OF MBB. METAL IONS ADDED AS THE SALTS: $MnSO_4$, $CuSO_4$, $FeSO_4$ (pH 11.0-11.4, 45°C)

Reaction	Additive conc., μM	Reaction order, n_2	Rate Constant[a], k_2
Control	--	2.0	5.42 ± 0.20
Fe	300	1.5	11.6 ± 1.1
FC	300	1.5	7.28 ± 0.57
Mn	21	1.0	19.5 ± 0.6
Cu	12	1.0	10.8 ± 0.3

---

[a] Units (order): $mM^{-1} \cdot min^{-1} \cdot 10^{-5}$ (2.0), $mM^{-0.5} \cdot min^{-1} \cdot 10^{-4}$ (1.5), $min^{-1} \cdot 10^{-3}$ (1.0). ± 95% confidence limits.

TABLE IV

RATE CONSTANTS EVALUATED BY THE KINETIC MODEL ANALYSIS

Reaction	Constants, $\underline{mM}^{-1} \cdot min^{-1}$		k_4/k_3	Relative k_3[a]
	$k_3 \times 10^5$	$k_4 \times 10^4$		
Control	2.69	2.06	7.7	1.00
Fe	3.60	2.30	6.4	1.34
FC	5.39	3.78	7.0	2.00
Mn	8.60	7.23	8.4	3.20
	Constants, min^{-1}			
Cu	5.9	4.95	8.4	--

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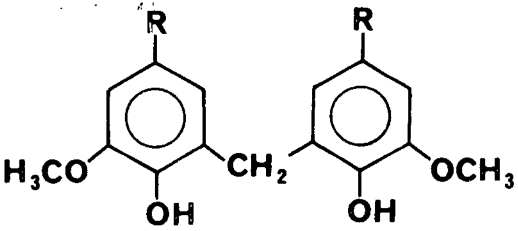
[a] Ratio of k_3 for the given reaction to k_3 for the control.



MBB R = $-CH_2-CH_2-COOH$

Drawing (page 3)

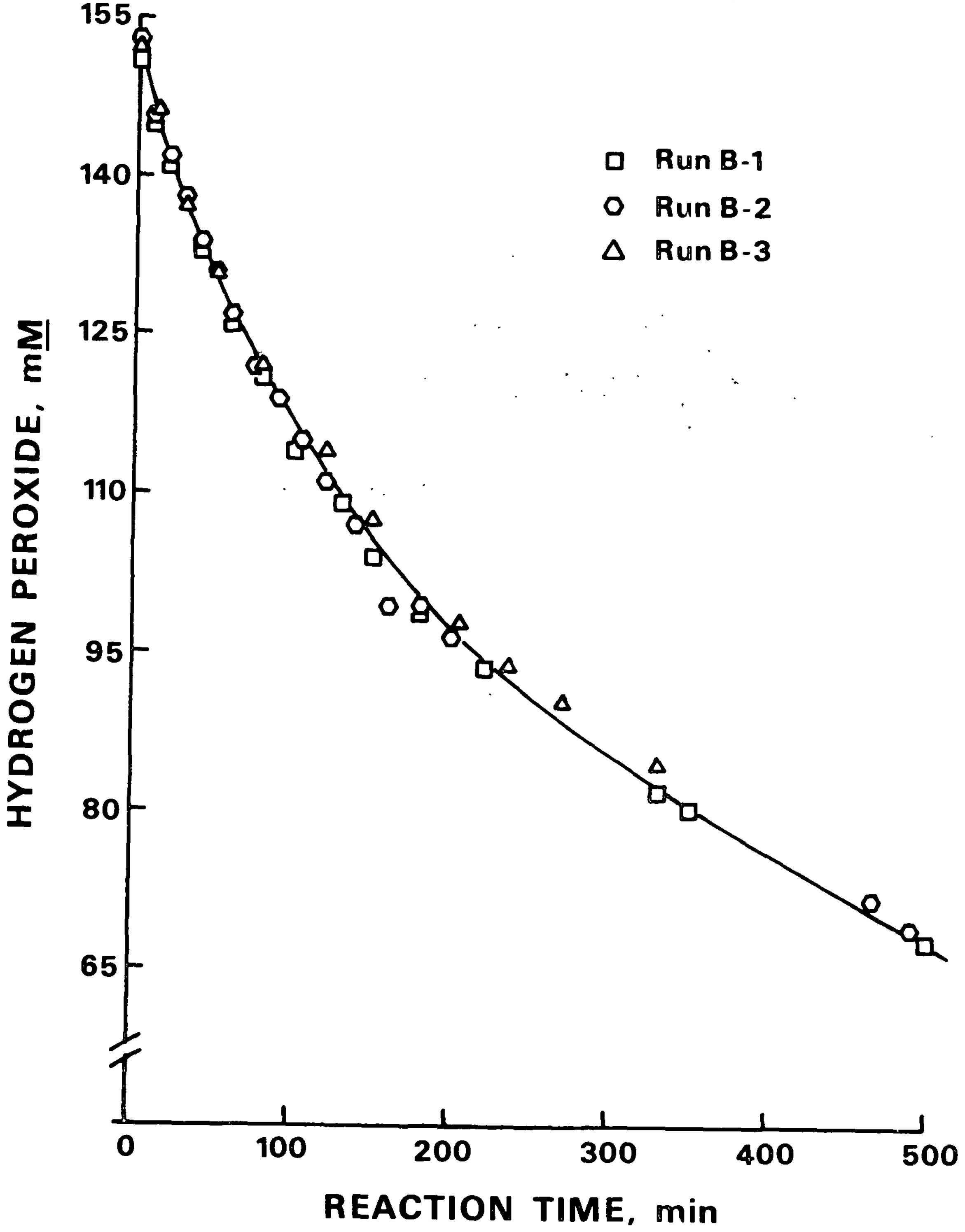


Fig. 1. Hydrogen peroxide decomposition in the absence of MBB (45°C, initial pH 11.0).

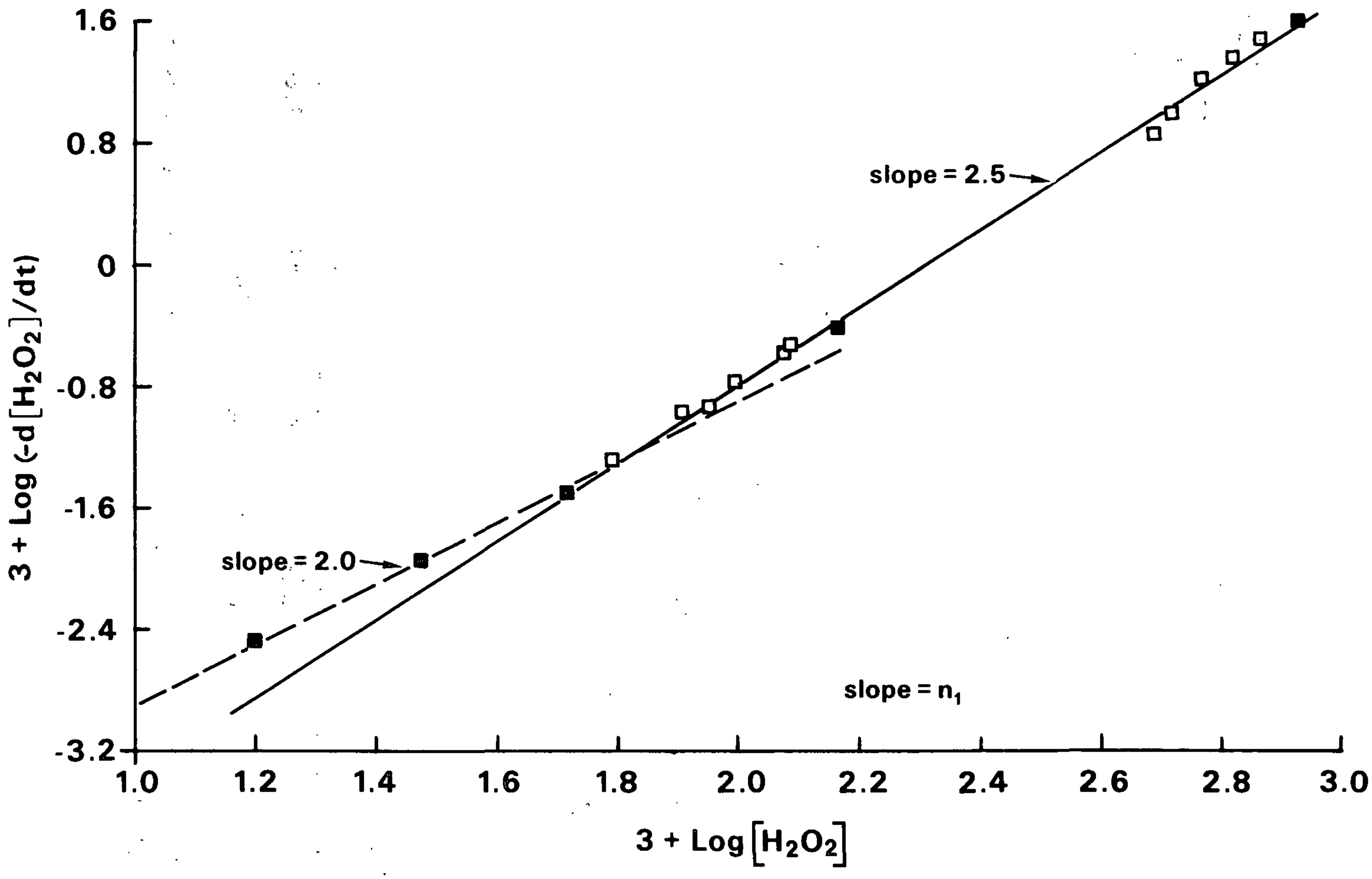


Fig. 2. Kinetic plot of hydrogen peroxide decomposition data without additives (pH 11.0-11.4, 45°C). Data plotted according to the differential method using initial rates (■), and rates at various reaction times (□).

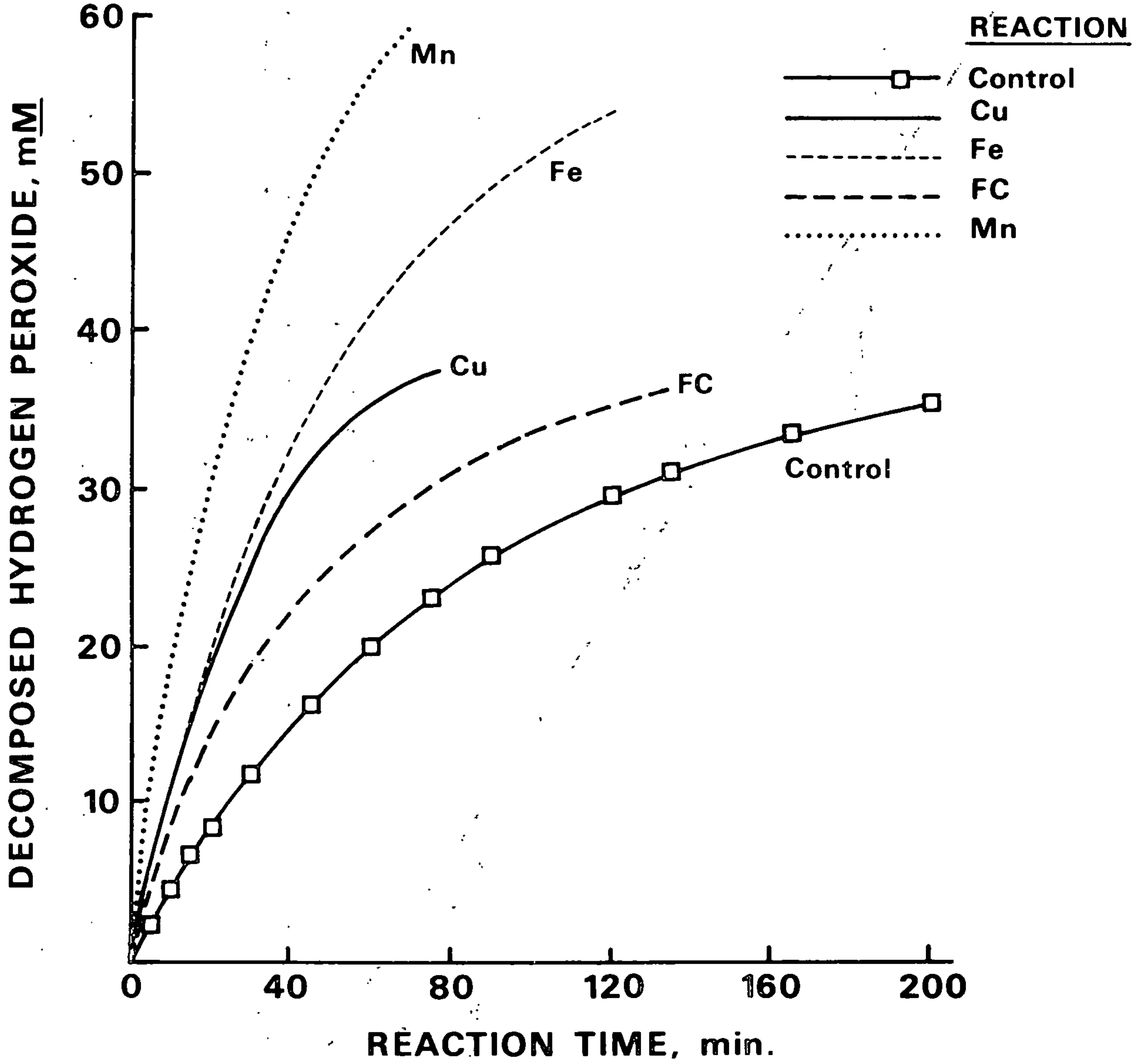


Fig. 3. Effects of added metal ions on H_2O_2 decomposition during the MBB reactions (conditions given in Table II).

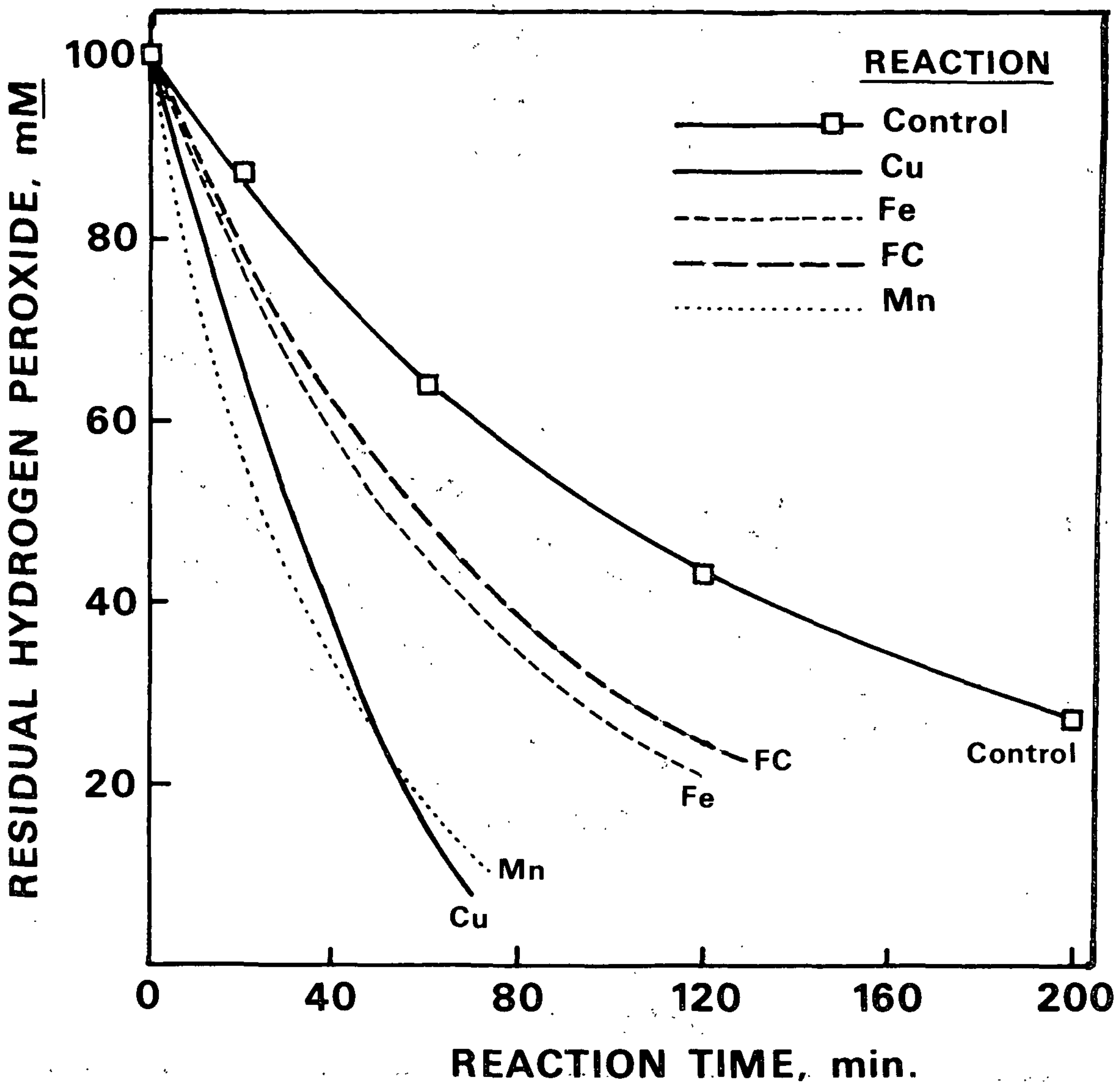


Fig. 4. Effects of added metal ions on the residual level of H_2O_2 during the MBB reactions (conditions given in Table II).

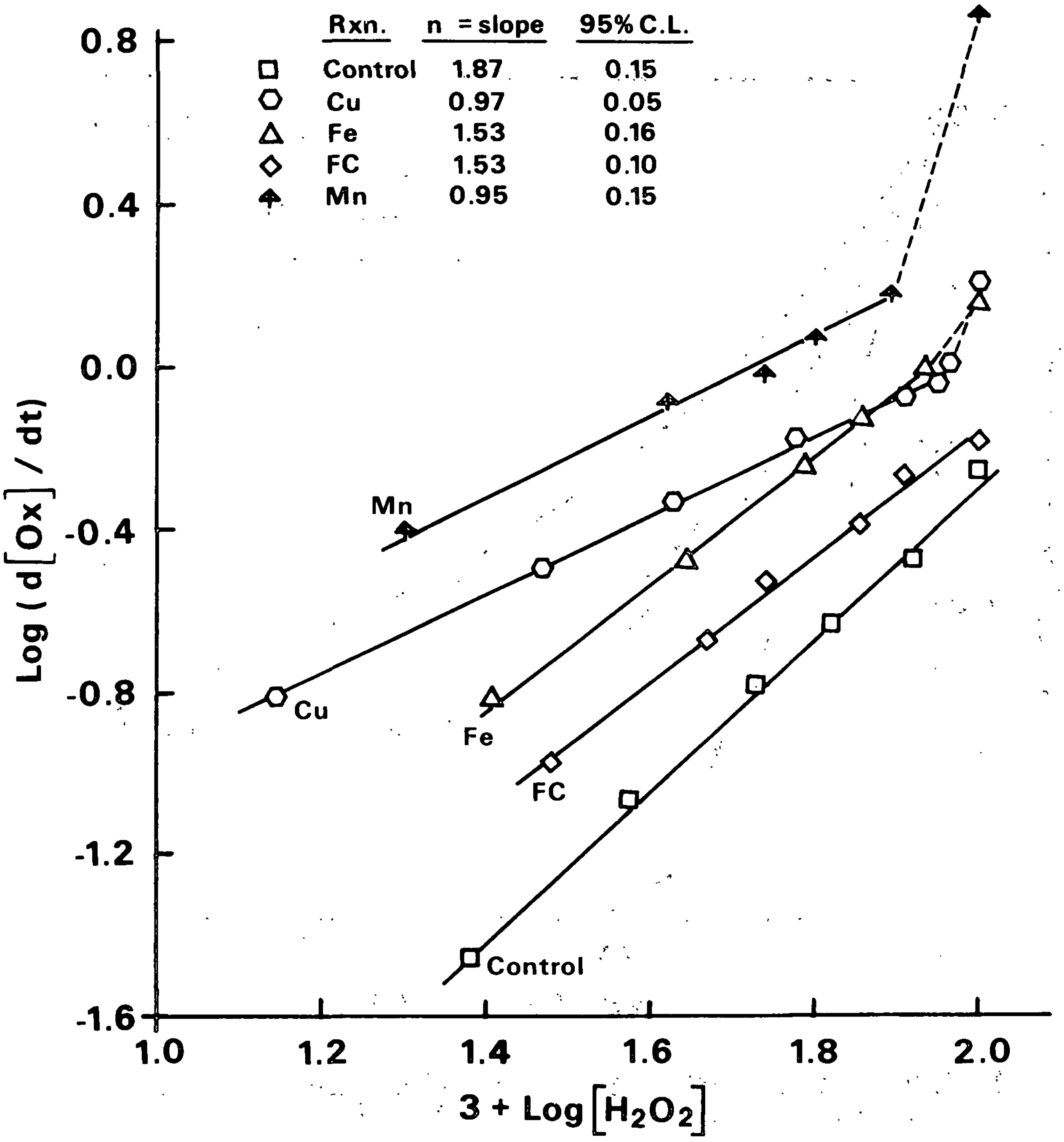


Fig. 5. Kinetic plot of hydrogen peroxide decomposition data for the Control, Cu, FC, Fe, and Mn reaction runs (conditions given in Table II). Data plotted according to the differential method.

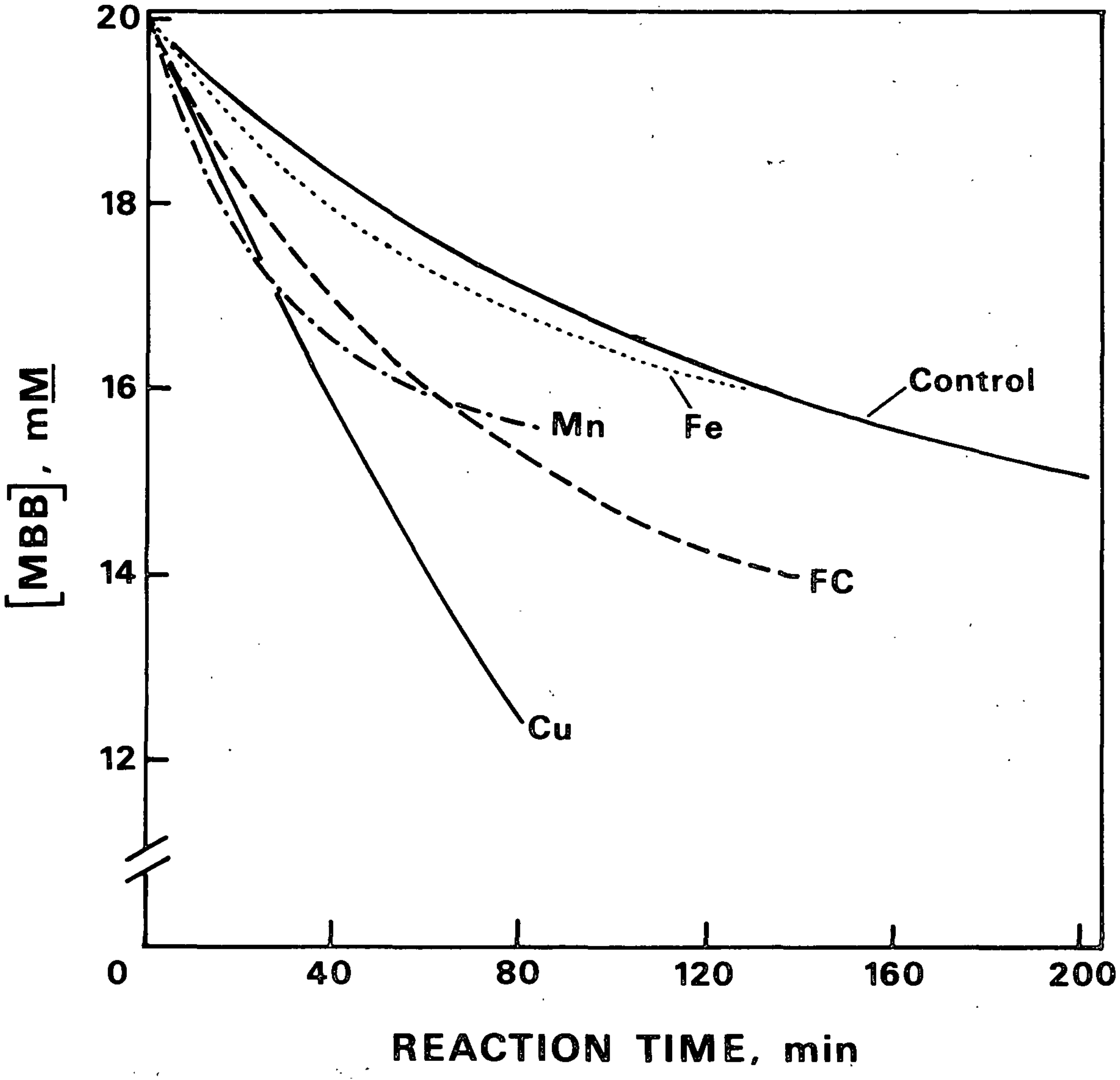


Fig. 6. Effects of added metal ions on the degradation of MBB in alkaline hydrogen peroxide (conditions given in Table II). The curves are the results from the computer model (see text).

$$H_2O_2 + M \longrightarrow HO^{\bullet} + HO^{-} + M^{+} \tag{1}$$

$$H_2O_2 + HO^{-} \rightleftarrows HO_2^{-} + H_2O \tag{2}$$

$$HO_2^{-} + M^{+} \longrightarrow HO_2^{\bullet} + M \tag{3}$$

$$HO_2^{\bullet} + HO^{-} \rightleftarrows O_2^{\overline{\bullet}} + H_2O \tag{4}$$

$$O_2^{\overline{\bullet}} + M^{+} \rightleftarrows O_2 + M \tag{5}$$

$$O_2^{\overline{\bullet}} + HO^{\bullet} \longrightarrow O_2 + HO^{-} \tag{6}$$

$$2\,O_2^{\overline{\bullet}} + H_2O \longrightarrow O_2 + HO_2^{-} + HO^{-} \tag{7}$$

$$HO^{\bullet} + HO_2^{-} \longrightarrow H_2O + O_2^{\overline{\bullet}} \tag{8}$$

$$HO^{\bullet} + M \longrightarrow HO^{-} + M^{+} \tag{9}$$

$$HO^{\bullet} + HO^{\bullet} \longrightarrow H_2O_2 \tag{10}$$

Fig. 7. Proposed metal-catalyzed radical chain mechanism for decomposition of hydrogen peroxide in aqueous alkali.

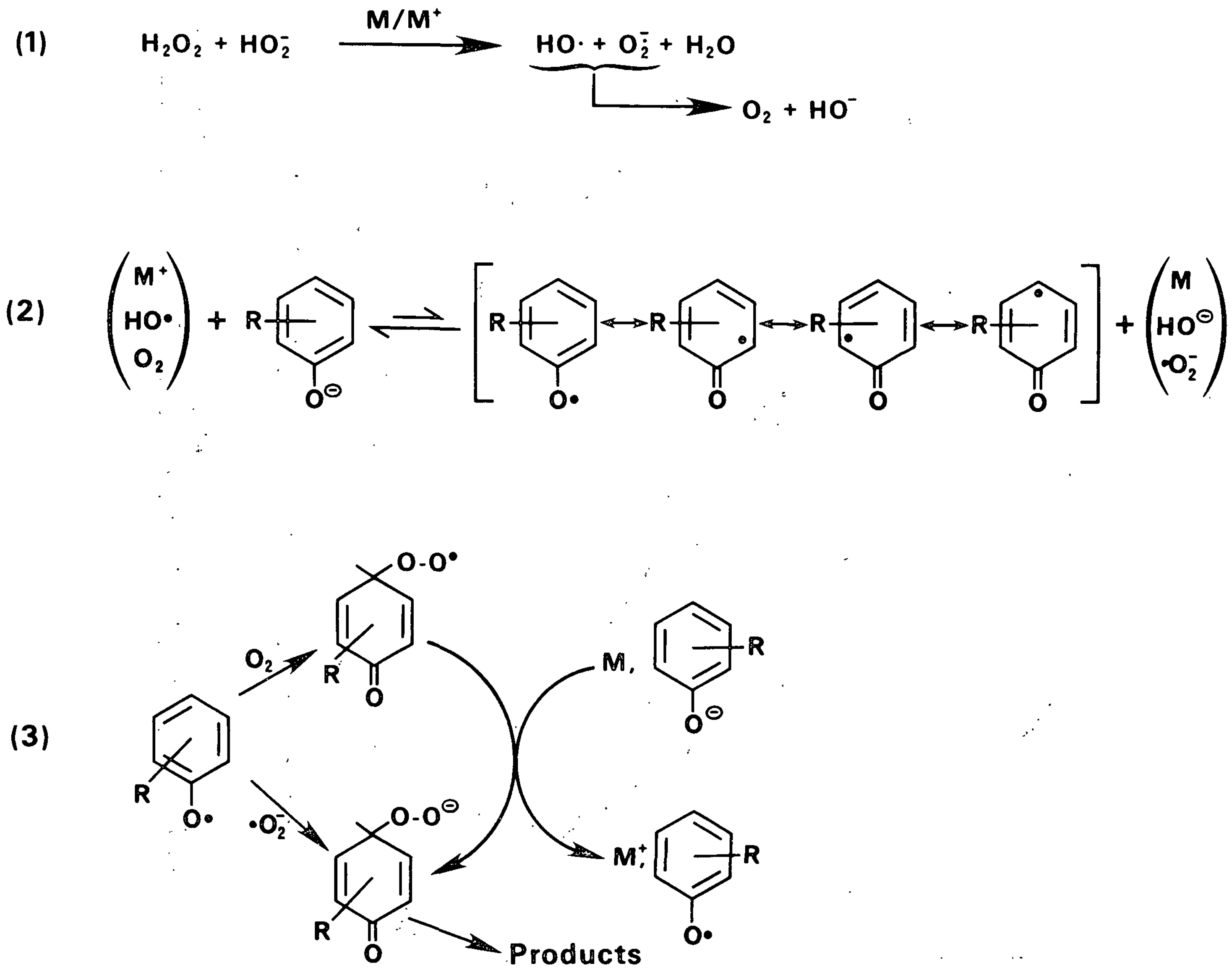


Fig. 8. Proposed oxidation scheme for substituted phenols under alkaline oxygen and/or hydrogen peroxide conditions.

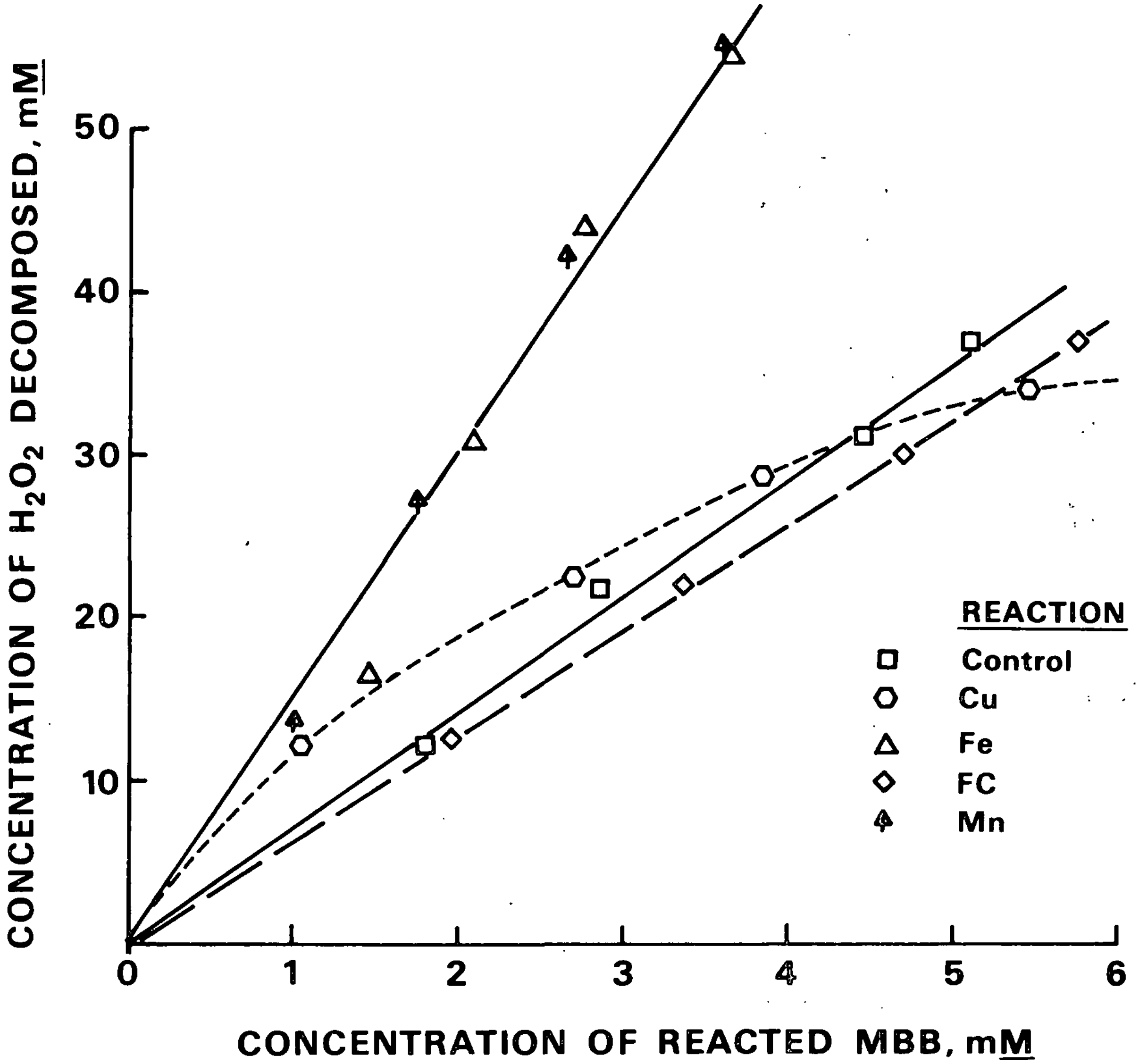


Fig. 9. Influence of metal ions on the relationship between peroxide decomposition and MBB oxidation (reaction conditions given in Table II).