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The effect of over-oxidation on periodate oxidation of cellulose was studied. It was found that the over-oxidation process has a significant effect on the overall reaction. An integrated rate equation was formulated. The oxidation of internal glucose units is second-order overall, first order with respect to both periodate and cellulose; while the oxidation of the reducing end group is first order overall, that with respect to periodate.

It was also found that prolonged oxidation degrades cellulose to a considerable extent, which is thought to be the direct result of random chain scission. The periodate breaks up cellulose polymer into fragments, some of which are so small that they go into the solution.

Periodate Oxidation of Cellulose - A Complete Kinetic Study

by

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Typed by Bhaskar A. Chandan for Bhaskar A. Chandan

To My Parents

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CHAPTER 1: INTRODUCTION

1.1 Chemicals from Biomass

Almost all organic chemicals and the synthetic organic polymeric materials derived from them are obtained from petroleum and natural gas. This dependence is so great that the term petrochemicals has become synonymous with the chemical industry.

Oil and gas are no longer inexpensive and are increasing in price with time. Furthermore, there is an increasing awareness of the finite nature of these fossil liquid and gaseous hydrocarbons and their ultimate depletion. The search for alternate sources of fuels and chemicals is accelerating and increasing attention is being focused on renewable resources as alternate sources. Indeed, it has been projected that biomass will be a major source of organic chemicals within 20 to 30 yr [1].

Biomass is the only renewable carbon source. It is naturally abduant and easily accessible. As a fuel source, biomass is a bad choice due to its high oxygen content and hence low heating value [2]. However, the relative abundance of oxygen in cellulosic material makes these materials particularly attractive as sources for certain oxychemicals which are widely produced and used

throughout the chemical process industries. Table 1-1 [3] shows the top oxychemicals produced in the U.S in 1986. All these oxychemicals can be produced from renewable materials. As seen from the table, the production of ethylene glycol (almost five billion lb/yr) far exceeds that of other oxychemicals. The production and sales of ethylene glycol in the USA over the past 10 yr, and its unit price is shown in Fig. 1-1 [3].

Before the era of petrochemicals, various chemicals were produced from biomass by such techniques as extraction, fermentation, and pyrolysis.

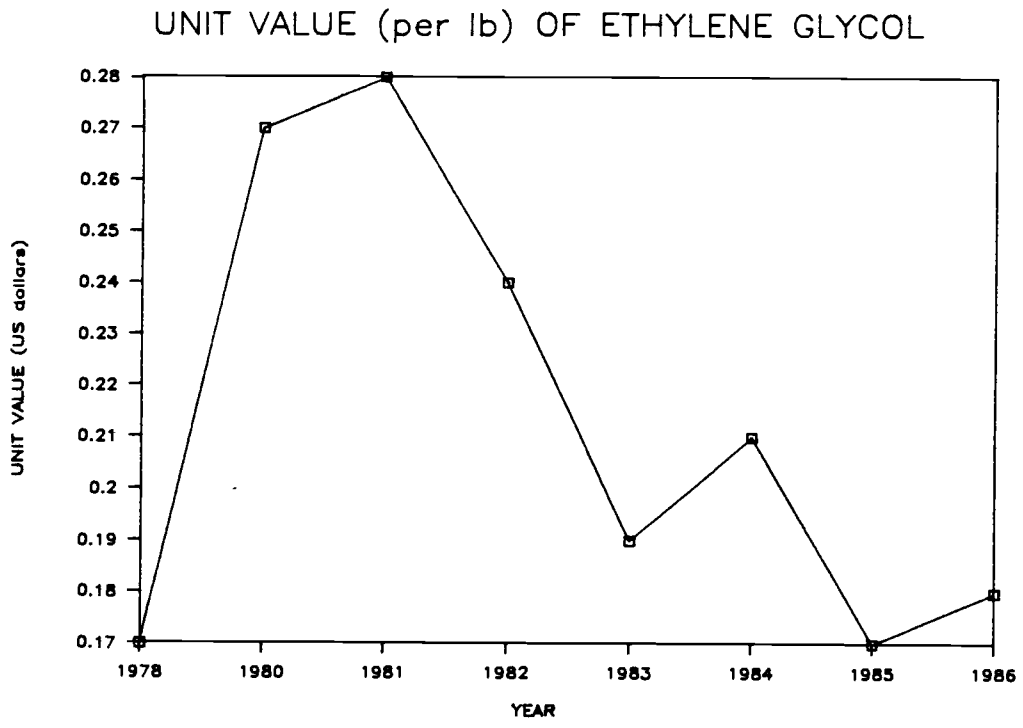
Extractives are those components that can be dissolved from the wood and bark without destroying the cellulose structures. There are three major types of extractives: aliphatic compounds (mainly fats and waxes), turpenes and terpenoids, and flavanoids and related materials. The resinous exudates from the pine trees provided the raw material for the naval store industry, the oldest chemical industry in North America. The exudates were later distilled to provide turpentine and rosin. Extracts from the heartwood of certain hardwoods provided tannins [4].

Chemicals which have been produced by fermentation include ethanol, glycerol, butanol, acetone, lactic acid, acetic acid, oxalic acid, citric acid, itaconic acid, etc. The production of ethanol for beverages is still a major

Table 1-1

Top Oxychemicals Produced in the US in 1986 [3]

Oxychemical	1986 US Production in million lb
Ethylene Glycol	4,771
Propylene Glycol	573
Sorbitol	185
Ethanol, synthetic	529
Acetic Acid	2,728
Acetone	1,910



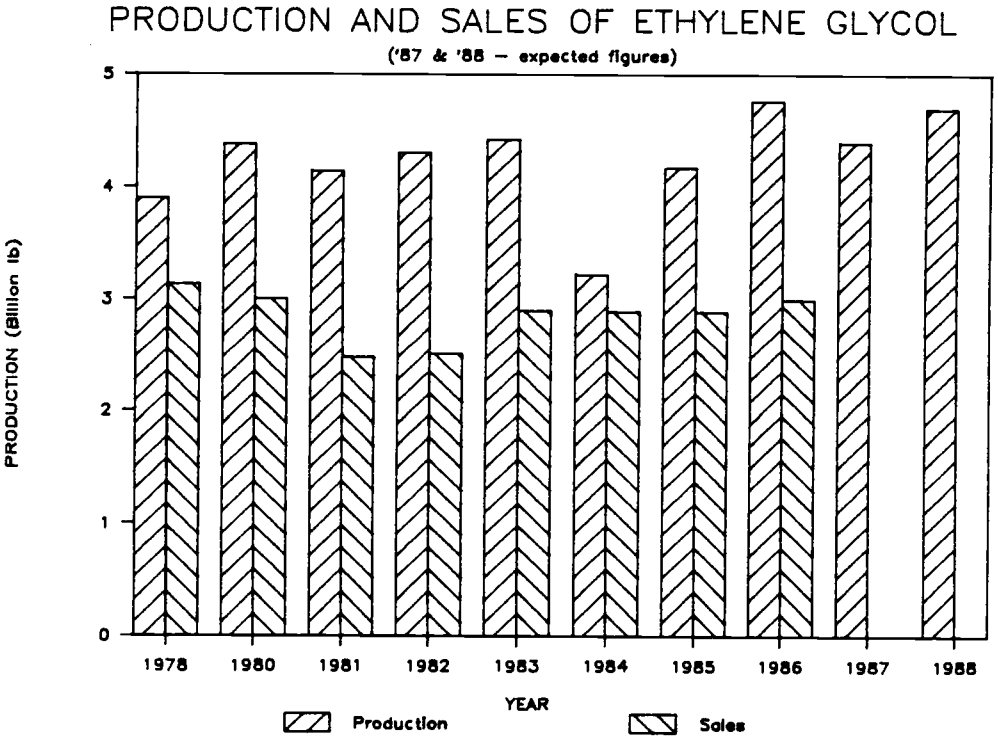


Figure 1-1: Production, Sales and Unit Value of Ethylene Glycol from 1978 to 1988 [3]

industry. About 300 million lb of organic and amino acids are derived annually from a sugar or grain base by fermentation.

The destructive distillation of wood to produce charcoal was once an important industry [5]. A number of volatile organic chemicals can be recovered from the distillate of wood pyrolysis. Acetic acid, methanol, and acetone were formerly obtained from wood distillation. In addition, various wood tar oil fractions, used for medicinals, smoking meats, disinfectants and weed killers were also recovered [2].

In addition to the above mentioned processes, there are a number of chemical processes which can utilize the sugars obtained from the hydrolysis of cellulose and hemicellulose. Chief among these is the sulfuric acid catalyzed dehydration of xylose and other pentoses to furfural [6]. The same process when applied to hexoses results in the formation of hydroxymethyl furfural, which can react further to form levulinic acid [7]. Another useful reaction of the sugars is their hydrogenation to the corresponding alditols. Hydrogenation of glucose produces sorbitol, an intermediate in vitamin C manufacture as well as a useful sweetening agent. Similarly, xylose is hydrogenated to form xylitols which is also a commonly used sweetening agent, particularly in the chewing gum industry due to the cooling sensation felt

on initial chewing because of its endothermic heat of solution.

An entirely different approach for conversion of biomass to chemicals involves selective chemical conversion of cellulose and hemicellulose in their polymeric forms, followed by hydrolysis of their derivatives. In late 1950's and early 1960's, a great deal of research was done on dialdehyde starch, which had become available as an industrial chemical. Work by Otey, et al. [8] showed that ethylene glycol and erythritol can be obtained from dialdehyde starch by hydrolysis and an industrial process was developed. However, the process was never commercialized, probably due to the high cost of the chemicals involved and the cheap availability of these chemicals derived form petroleum sources.

Within the last decade, researchers at Laboratory of Renewable Resources Engineering (LORRE), Purdue University, have been working on the conversion of cellulose and hemicellulose from biomass (wood, corn, artichoke, etc.) to useful oxychemicals. The overall reaction scheme adopted is as shown in Figure 1-2 [9, 10]. Cellulose or xylan is first oxidized by sodium metaperiodate or periodic acid to its respective dialdehyde species. The internal glucose units will each consume one equivalent of periodate, while the end groups will consume two equivalents of periodate. While the

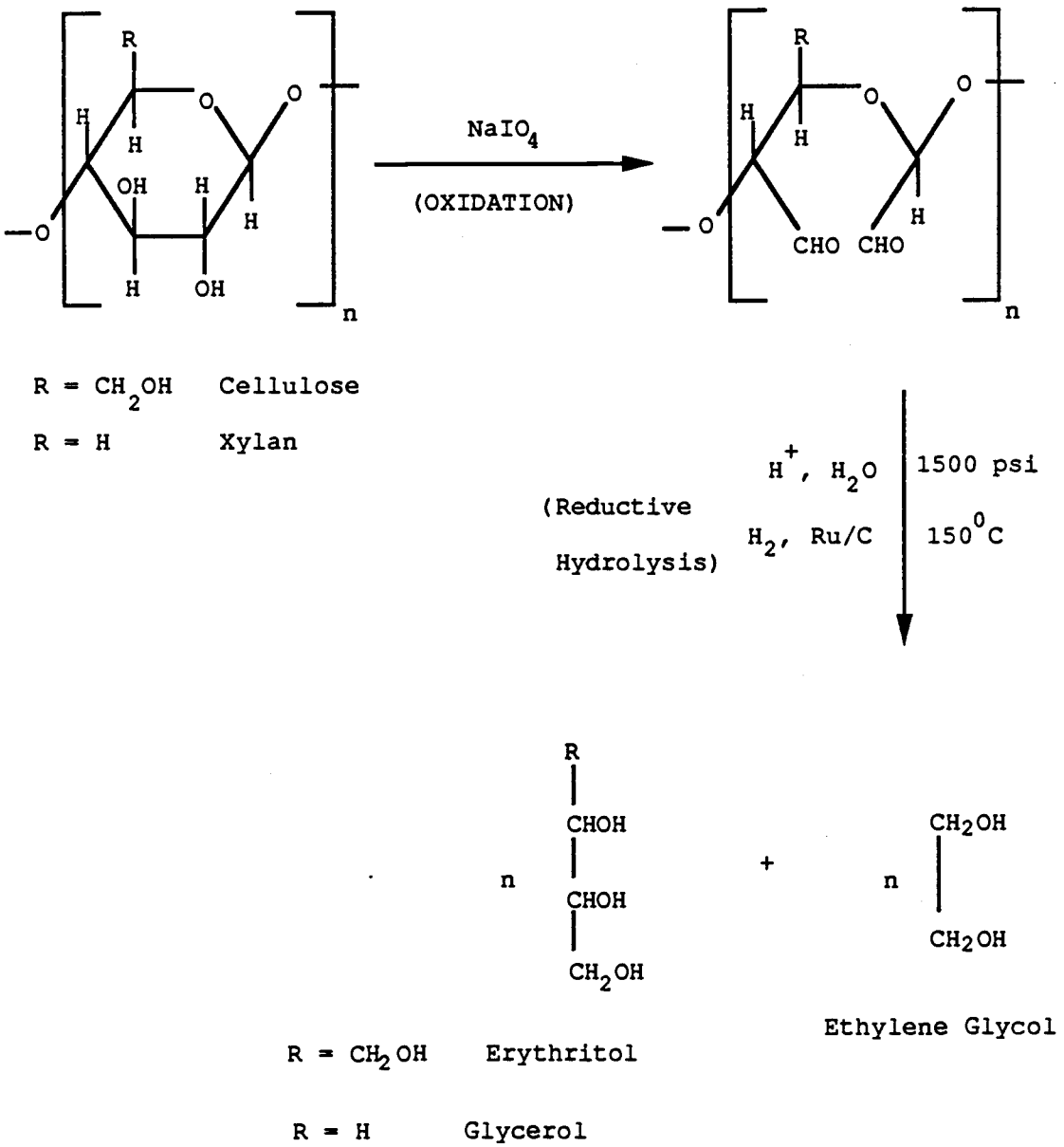


Figure 1-2: Overall Scheme for the Chemical Conversion of Cellulose and Xylan to Oxychemicals.

oxidation of the non-reducing end group will stop after consumption of two equivalents of periodate, the reducing end group may further be oxidized by periodate by a process which is often termed as "over-oxidation" [11], as shown in the next chapter. The rate and extent of this reaction will depend on the conditions employed.

In the next step (see Fig. 1-2), the dialdehyde species formed from the internal glucose unit is subjected to reductive hydrolysis at high pressure (1500 psi) in the presence of ruthenium-on-carbon catalyst, resulting in the reduction of the aldehyde groups to hydroxyl group. The polymer chain is thus broken to ultimately yield ethylene glycol and erythritol or glycerol (from cellulose or xylan, respectively).

As reported by Durrence [9], the major cost factor in the LORRE scheme is the cost of periodate. He conducted his studies under the assumption that there is negligible over-oxidation and has suggested second-order kinetics for periodate oxidation of cellulose, first-order with respect to both periodate and cellulose concentrations. Hough, et al. [12, 13] have reported that the reducing end group oxidation (over-oxidation) is so slow between pH 3 and pH 5, that it can be neglected. While this is probably true at lower temperatures, at temperatures above 40°C this oxidation may become significant and thus it should not be ignored.

For the conversion of cellulose to ethylene glycol to be of practical importance, the reaction rate for the oxidation step must be significantly high. For this to happen, cellulose has to be made more accessible, by either increasing the temperature or by pretreating the cellulose, both of which may lead to greater cellulose degradation, and consequently, higher periodate consumption and lower than expected yields. Thus, the unique effect of the end group oxidation must be included in the study of the oxidation of cellulose.

1.2 Objectives and Method of Approach

Preliminary studies with cellulose at Oregon State University showed that because of over-oxidation the simple model proposed by Durrence [9] does not accurately account for periodate consumption and dialdehyde cellulose formation. Thus, the principle objective in this work was to include the effect of cellulose degradation in the kinetic modeling of the oxidation step so that better estimates can be made for the formation of dialdehyde cellulose and the consumption of periodate. Also, a study of this sort was expected to provide some insight into the periodate oxidation of cellulose and the reactivity and accessibility of cellulose under the employed conditions.

The following two reactions take place when cellulose

is reacted with sodium m-periodate,

$$R'\text{-}(C_6H_{10}O_5)_{n-2}\text{-}R + (n-2)\ IO_4^- \text{------>}\ R'\text{-}(C_6H_8O_5)_{n-2}\text{-}R + (n-2)\ IO_3^- + (n-2)\ H_2O \quad (1.1)$$

$$(G)_{n-1}\text{-}C_6H_{11}O_6 + 6\ IO_4^- \text{----->}\ (G)_{n-2}\text{-}R + HCHO + 4\ HCOOH + CO_2 + 6\ IO_3^- \quad (1.2)$$

where

R' and R = non-reducing and reducing end groups, respectively,

G = anhydroglucose units - $C_6H_{10}O_5$ (including non-reducing end groups, i.e., R')

n = cellulose chain length (i.e., number of glucose residues)

IO_4^- = periodate ion

The former is the desired ideal reaction which results only in the formation of dialdehyde cellulose, while the latter is the undesirable over-oxidation reaction. As the formic acid produced is four times in excess of the other two products, its measure should be selected to investigate the extent of over-oxidation. Of the various analytical methods used to measure the concentration of formic acid in a solution, the HPLC method using an appropriate column is one of the more convenient, easy to use and accurate methods. The periodate concentration in the solution was followed by measuring the absorption of

the diluted reaction solution using an ultra violet spectrophotometer at a wavelength of 223 nm.

Periodate is consumed in two reactions - (1.1) and (1.2). The rate equations thus obtained are nonlinear in nature and their solution requires numerical methods. Durrence's [9] study suggests that reaction (1.1) is second order, while the order of the reaction (1.2) can be obtained by fitting a model based on theory to experimental data.

CHAPTER 2: LITERATURE SURVEY

2.1 Constituents of Biomass

In the leaf of a plant, the simple compounds carbon dioxide and water are combined to form simple sugars, predominantly consisting of D-(+)-glucose (usually abbreviated to simply "glucose"), by the process of photosynthesis using energy in the form of sunlight. Thousands of glucose molecules can then be combined to form the much larger molecules of cellulose, a polymer which constitutes the supporting framework of the plants. Glucose molecules can also be combined, in somewhat different way, to form the larger molecules of starch. When eaten by animal, the starch (and even cellulose in some animals) is broken down into the original glucose units, which is carried by the blood stream to the tissues, where it is ultimately oxidized to carbon dioxide and water, with the release of the energy originally supplied as sunlight [14].

The other sugars formed by photosynthesis can be combined in a more complex manner to form the second major component of the plant matter, hemicellulose. The third major component of plant matter is lignin, which is formed to give the plant rigidity. The amount of each of these

varies considerably, depending on the species of the plant. Thus, according to the species, wood contains on dry basis between 40 and 55% cellulose, 25 and 40% hemicellulose, and 15 and 35% lignin. The chemical composition of a few wood species is shown in Table 2-1 [15].

As glucose forms the fundamental repeating unit in both starch and cellulose and as it is the most common and extensively studied sugar, a few words about glucose would help to better understand the structures of cellulose, starch and hemicellulose.

2.1.1 (+)-Glucose

Glucose, cellulose, starch and hemicellulose belong to the class of organic compounds known as carbohydrates. Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones or compounds that can be hydrolysed to them.

Because it is the unit of which starch, cellulose, and glycogen are made up, and because of its special role in biological processes, glucose is by far the most abundant monosaccharide - there are probably more glucose units in nature than any other organic group - and thus, by far, the most important monosaccharide.

Glucose constitutes one of the possible sixteen stereoisomers (eight pairs of enantiomers) which make up

Table 2-1

Chemical Composition of a Few Wood Species [15]

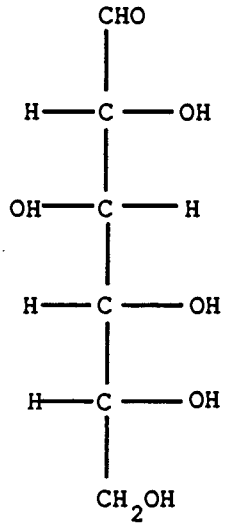
Common name	Total extractive (wt%)	Lignin (wt%)	Cellulose (wt%)	Hemicellulose (wt%)
Softwoods:				
Balsam fir	2.7	29.1	38.8	28.5
Douglas fir	5.3	29.3	38.8	26.3
White spruce	2.1	27.5	39.5	30.6
Scots pine	3.5	27.7	40.0	28.5
Hardwoods:				
Red maple	3.2	25.4	42.0	28.9
Sugar maple	2.5	25.2	40.7	30.8
Paper birch	2.6	21.4	39.4	34.5
Balsa	2.0	21.5	47.7	27.6

the family of aldohexoses. All the sixteen of these possible stereoisomers are now known, through either synthesis in the laboratory or isolation from natural sources. All the aldohexoses undergo similar type of reactions, and the chemistry is essentially the same.

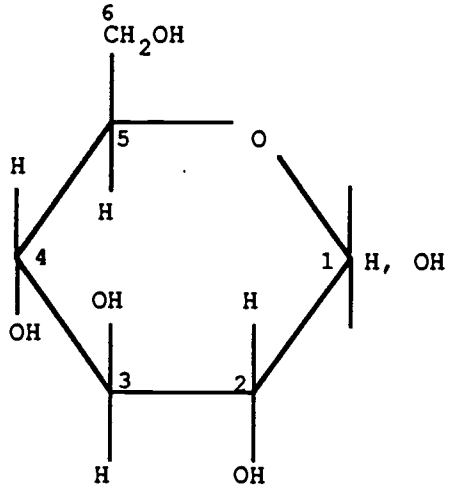
The structure of the glucose molecule is now well established. The straight chain configuration of the glucose molecule is as shown Fig. 2-1 (A). In solution glucose is present largely as a ring structure, pyranose, which results from reaction of the C-1 aldehyde in glucose with the C-5 hydroxyl (resulting in a hemiacetal carbon atom at the C-1 position), and is usually represented as shown in Fig. 2-1 (B) (note the standard numbering scheme for six carbons and the α,β labels for the position of the -OH group on the number 1 carbon). But glucose is best represented by chair confirmation as shown in Fig. 2-1 (C) Of the two isomeric forms of the glucose molecule (α and β), the β isomer is more stable. In fact, it is the most stable stereoisomer of the aldohexose family. This stability results from the fact that in the chair confirmation, the -OH groups in the β isomer are as far apart as possible and there is very little ring strain.

2.1.2 Cellulose

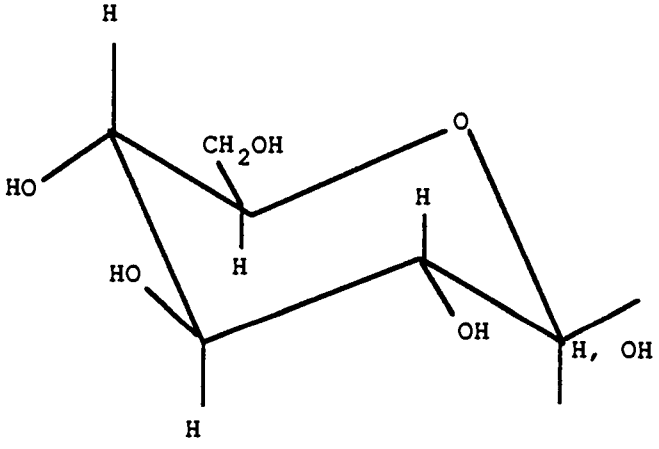
It is generally accepted that cellulose is a linear



(A) Straight Chain



(B) Pyranose Forms



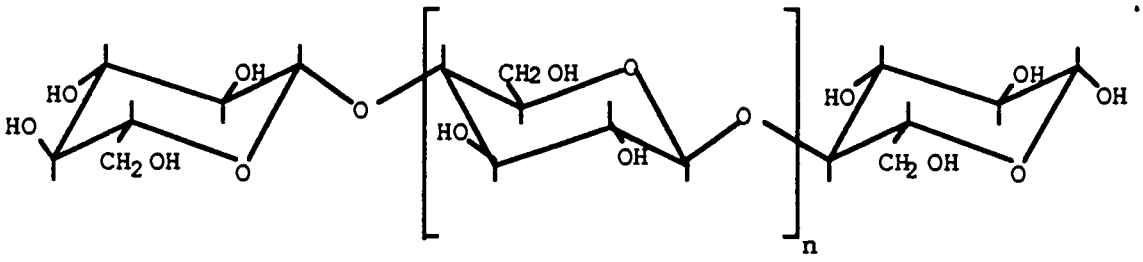
(C) Chair Conformation

Figure 2-1: Structure of Glucose

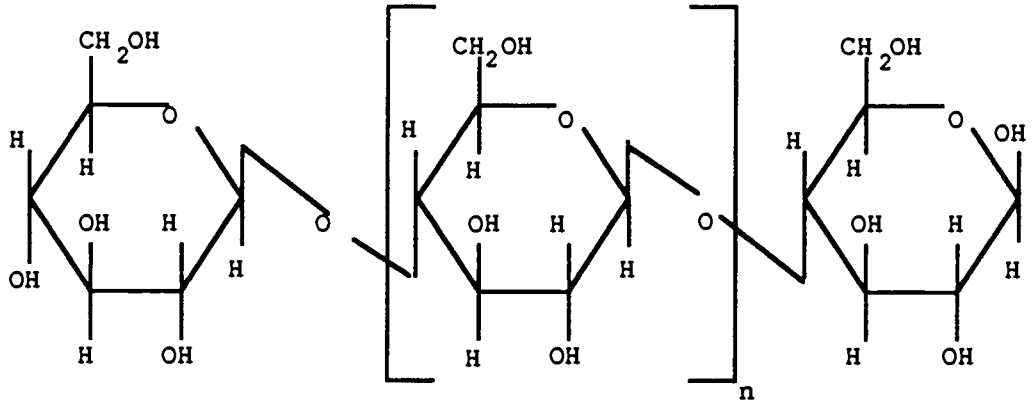
condensation polymer consisting of D-anhydroglucopyranose units (often abbreviated as anhydroglucose units) joined together by β-1,4-glycosidic bonds. It is thus a 1,4-β-D-glucan. On the other hand, starch is similar to cellulose except that, in starch, the anhydroglucose units are joined by α-1,4-glycosidic bonds. The β-1,4-glycosidic bond in cellulose is more stable than the α-1,4-glycosidic bond in starch, and thus cellulose is more stable towards hydrolysis, and generally less reactive than starch. But due to the structural similarity between the two, starch and cellulose undergo similar type of reactions.

In cellulose, the pyranose rings are in the $^4C_1$ confirmation, which means that the $-CH_2OH$ and -OH groups, as well as the glycosidic bonds, are all equatorial with respect to the mean planes of the rings as illustrated in Fig. 2-2 (A). The older Haworth projection formula [16] shown in Fig. 2-2 (B) is still frequently used because it is easier to write quickly and is adequate to describe many of the reactions and properties of cellulose. Its chief shortcoming is that it obscures some important stereochemical features of the molecule. For example, the projected angle between either pair of secondary alcohol groups is 60° when viewed along the bond joining the carbon atoms to which they are attached; not 180° as might be thought from Fig. 3 (B).

The degree of polymerization or DP (sometimes



(A) Cellulose



(B) Haworth Formula

Figure 2-2: Structure of Cellulose

referred to as chain length) of cellulose varies for different wood species and different pretreatment steps. It can be as high as 15,000 in native cotton cellulose to as low as 100 for regenerated cellulose (see Table 2-2).

The crystalline regions of cellulose in its native form are stabilized by hydrogen bonding. Each glucose residue participates in three hydrogen bonds [16]. Two of these bonds are between neighboring residues along the cellulose chain (between C-3 and C-5 oxygen on one side of a cellobiose repeating unit, and C-2 oxygen donating a proton to C-6 oxygen on the other side). The third occurs between adjacent chains, wherein C-6 oxygen in a corner chain donates a proton to C-3 oxygen of the adjacent corner chain. Due to the stability imparted by these hydrogen bonds, the crystalline regions of cellulose generally react very slowly. In most processes, the crystalline structure must be disrupted before the reaction can proceed at a reasonable rate. Transition metal complexes, concentrated acids and zinc chloride are effective in disrupting this hydrogen bonding network.

Since α-cellulose is often used as a model compound, it would be worthwhile to give its definition. Material which, after being mercerized with sodium hydroxide, is insoluble in the alkali when diluted to about 8% is defined as α-cellulose [16, 17]. That material which is soluble in alkali but is precipitated on acidification is

Table 2-2

Degree of Polymerization (DP) for Different Types of Cellulose [15]

Type of Cellulose	Average DP
Cotton Cellulose (native state)	15,000
Wood Cellulose (native state)	10,000
Purified Cotton Linters	1750-3350
Commercial Wood Pulp	650-1250
Regenerated Cellulose (Rayon)	100-500

known as β-cellulose, and that which remains in solution on acidification is Γ-cellulose. Note that the names do not define chemical nature. α-Cellulose is mainly cellulose with traces of hemicellulose, and the term is now reserved for what is now universally called cellulose.

2.1.3 Hemicellulose

The hemicelluloses are not forms of cellulose. They comprise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. Delignified wood is often referred to as holocellulose. The hemicellulose can be extracted from holocellulose with aqueous alkali or dilute acid at mild temperature.

Hemicellulose differ from cellulose in several important respects. Cellulose is composed entirely of glucose units, but the hemicelluloses contain a number of different sugars including both hexoses (glucose, mannose, galactose) and pentoses (xylose, arabinose); also the main backbone chain may contain more than one kind of sugar. The molecular chains are much shorter than they are in cellulose, and the chain molecules are frequently branched, either through attachment of side chains to a main chain or by more extensive branching. The union between the individual sugars residues is not always

through the 1 and 4 positions, as in cellulose. The hemicelluloses may contain other groups, particularly uronic acid and acetyl groups, that are not present in cellulose.

Most commonly occurring hemicelluloses are galactoglucomannan and xylans. The former comprises of a backbone of β-anhydromannopyranose units and β-anhydroglucopyranose units linked 1 → 4, with side chains of α-D-galactopyranose units linked 1 → 6. While the xylans comprises of a backbone of β-D-anhydroxylopyranose units linked 1 → 4, with side chain of either 4-O-methyl-α-D-glucuronic acid (linked 1 → 2) or α-L-arabinofuranose (linked 1 → 3) or both.

2.1.4 Lignin

Lignins are complex hydrocarbon polymers which are predominantly aromatic, with some aliphatic constituents. Their chief monomer units are various ring-substituted phenylpropanes linked together in ways still only partially understood [16]. Their detailed structures differ widely from one source to another. They are all very inert and they do not hydrolyse to monomeric units. Lignins lack a highly regular structures. They have as yet been put to relatively little industrial use, except as fuel, though it is likely that processes for conversion

of lignin to phenol and other aromatics will gradually develop.

2.2 Periodate Oxidation

Periodate is a specific oxidizing agent for compounds containing two or more -OH or =O groups or a hydroxyl and an amino group attached to adjacent carbon atoms and is characterized by the cleavage of the carbon-carbon bond as illustrated in Fig 2-3. It is available commercially in three forms: orthoperiodic acid (H_5IO_6), which is highly soluble in water, sodium metaperiodate ($NaIO_4$), which is moderately soluble in water (12.6 g per 100 g water at 25°C), and potassium metaperiodate (KIO_4), which is only sparingly soluble (0.51 g per 100 g water at 25°C).

Upon dissolution in water, the exchange of oxygen between periodate and water is at least one thousand times faster than that of iodate [18]. Thus, it is widely accepted that IO_4^- is the only anhydrous species present in aqueous solution, and it can be assumed that periodate reacts as a single species.

Periodate solutions are stable at room temperature in the absence of light, but they are unstable in the presence of light. The instability of the pure solutions in light is due to the autoreduction of periodate to iodate and ozonized oxygen. Head and co-workers [19, 20]

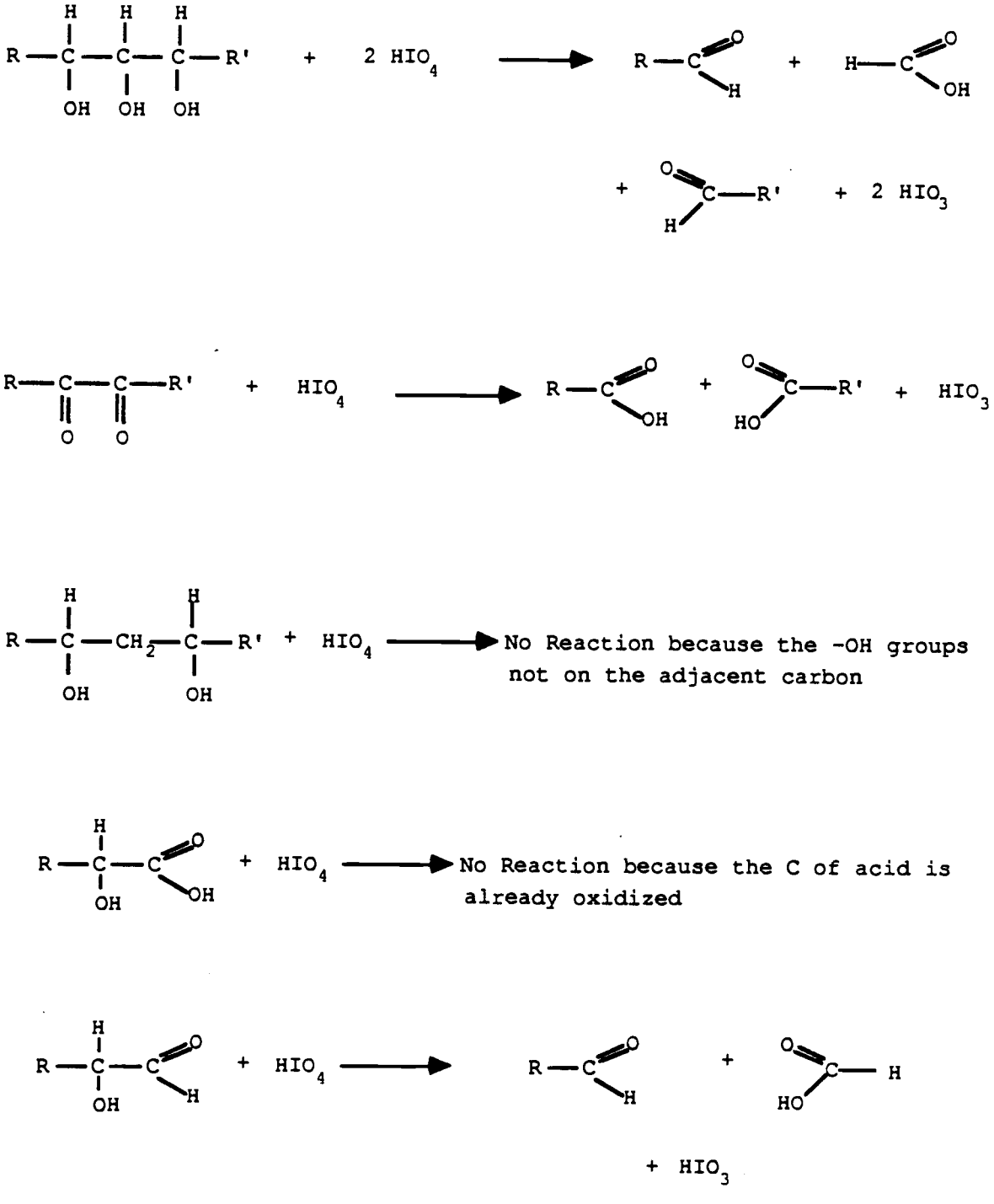


Figure 2-3: Periodate Oxidation of a Few Compounds

have studied the effect of daylight on periodate oxidation of simple compounds and carbohydrates at room temperature. They have shown that light accelerates the periodate oxidation of a number of simple organic compounds (like formic acid and formaldehyde). The reactions in the dark are continuous over long periods, and there is no evidence that they differ, except in speed, from the reactions in light. Their results indicate that the periodate oxidation of formic acid and formaldehyde in the dark is negligible and can be ignored for small reaction times of less than two days. Light has more serious implications in the oxidation of carbohydrates. It is doubtful whether the initial stage (also called "Malaprade oxidation") of the oxidation is affected, but the rates of the subsequent "over-oxidation" reactions are greatly increased [20]. It was also shown that considerably more formic acid is produced in daylight than in the dark, but there is not much difference in the formaldehyde yields. Thus, to reduce the extent of side reactions (both over-oxidation of the cellulose and the oxidation of the products thus formed) the periodate oxidation of cellulose should be performed in the dark.

2.2.1 Periodate Oxidation of Mono and Disaccharides

Most of the unsubstituted carbohydrates have adjacent

carbon atoms which have two or more -OH or =O groups on them, and thus they undergo oxidative cleavage by periodate. This type of reaction, which is one of the most useful tools in research on carbohydrate chemistry, was first introduced by Malaprade in 1928 [21]. The term "Malaprade oxidation" is usually used to describe an ideal oxidation that involves only the cleavage of 1,2-diols and analogous substances with no side reactions, such as hydrolysis of the unstable products.

Periodate oxidation of simple sugars, such as glucose, is characterized by cleavage of each carbon-carbon bond, resulting in the formation of five equivalents of formic acid (from the secondary alcohol groups and the aldehyde group) and one equivalent of formaldehyde (from the primary alcohol group). Fig. 2-4 (A) shows the sites for periodate oxidation.

For simple furanosides such as methyl β-D-glactofuranoside, Fig. 2-4 (B), two equivalents of periodate are consumed with the formation of one equivalent of formaldehyde. For simple glucosides such as methyl α-D-glucopyranoside, Fig. 2-4 (C), two equivalents of periodate are consumed, resulting in cleavage of only two carbon-carbon bonds, thus giving a 2,4-dialdehyde (D) and one equivalent of formic acid [14]. Similarly periodate oxidation of methyl α-D-glucuronopyranose (E) yields a 1,3-dialdehyde (F) and one equivalent of formic

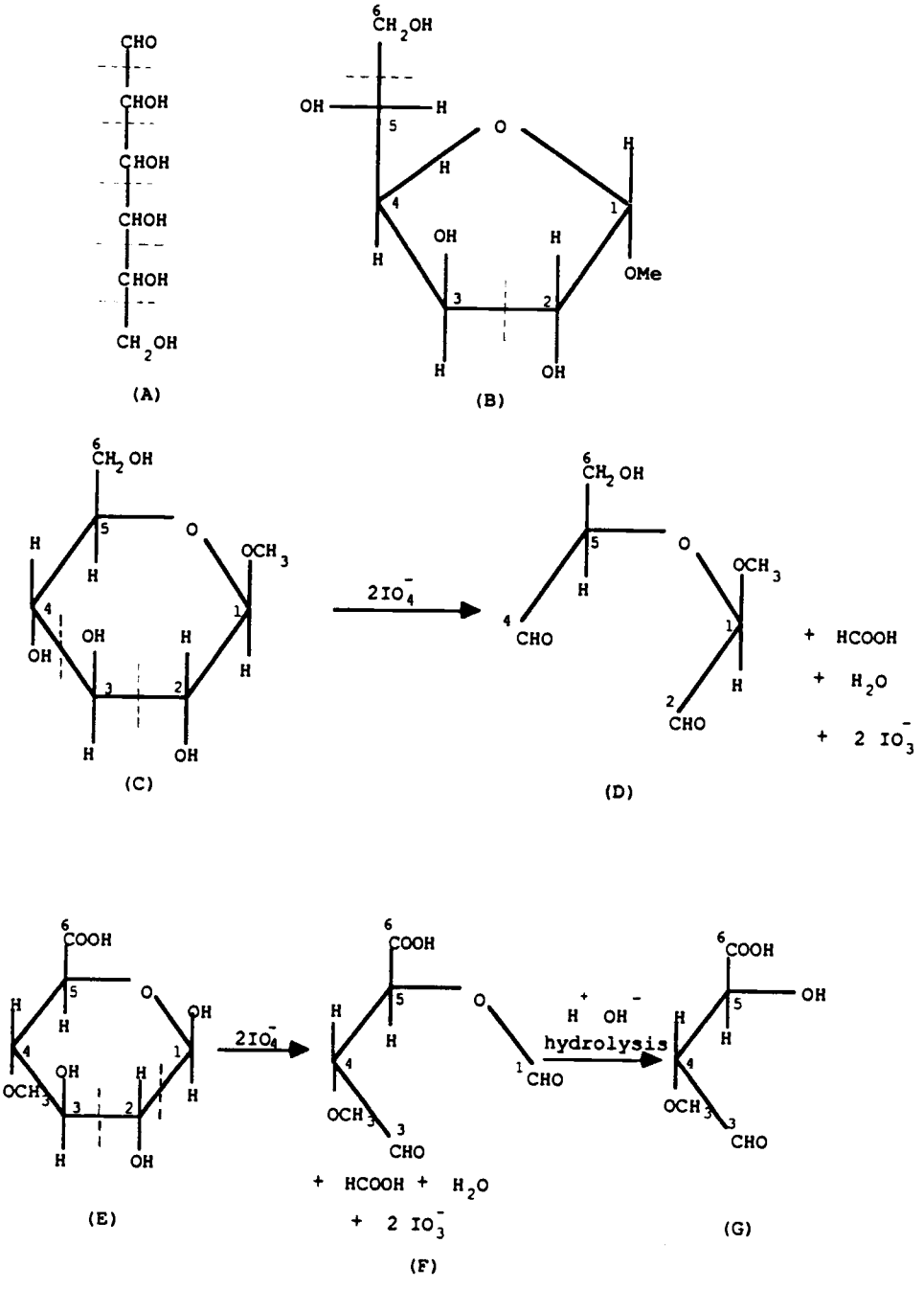


Figure 2-4: Periodate Oxidation of Mono- and Disaccharides

acid. Under favorable conditions, the dialdehyde (F) may undergo hydrolysis to yield the formyl ester (G) and one equivalent of formic acid. For structures such as (G), no further periodate is consumed, because the -COOH group at C-6 will block any further oxidation.

Periodate oxidation of disaccharides has also been extensively studied. Oxidation of cellobiose [22], lactose and maltose [23] by periodate can be represented by the equation,

$$C_{12}H_{22}O_{11} + 11\ IO_4^- \text{------>}\ 9\ HCOOH + 2\ HCHO + CO_2 + 11\ IO_3^- \qquad (2.1)$$

2.2.2 Periodate Oxidation of Polysaccharides

Periodate oxidation of polysaccharides depends on a number of factors: the type of sugar residues involved (hexose or pentose; pyranose or furanose), the type of linkages between sugars, the degree of polymerization of the species, and the frequency of branching. The non-reducing terminal units in polysaccharide or (1 → 6) linked non-terminal units having three adjacent hydroxyl groups will be cleaved by two molecular proportions of periodate to give one molecular proportion of formic acid. Non-terminal units joined by (1 → 2) or (1 → 4) bonds undergo cleavage by one molecular proportion of periodate,

but no formic acid is generated. Units which do not possess adjacent hydroxyl groups such as non-terminal units joined by (1 → 3) bonds or units involved in branching at C-2 and C-3 are not affected by periodate [24].

The periodate oxidation of cellulose results in the formation of dialdehyde cellulose with modified end groups (see Fig. 2-5). The reducing and the non-reducing end groups each consume two equivalents of periodate, with formation of one equivalent of formic acid each, while the internal glucose residues consumes only a single equivalent of periodate, but no formic acid is formed. The overall reaction for the an internal glucose unit is given by the following equation,

$$R'\text{-}(C_6H_{10}O_5)_{n-2}\text{-}R + (n-2)\ IO_4^- \text{------>}\ R'\text{-}(C_6H_8O_5)_{n-2}\text{-}R + (n-2)\ IO_3^- + (n-2)\ H_2O \quad (2.2)$$

where

R' and R: non-reducing and reducing end groups, respectively

Nevell [25] has proposed that the reaction between the internal glucose unit and periodate takes place through the intermediate ester ion, Fig. 2-6 (B), which decomposes spontaneously to (C) by electronic rearrangement. This unimolecular decomposition is the rate-controlling step. In acid solution the ion acquires a proton to give the

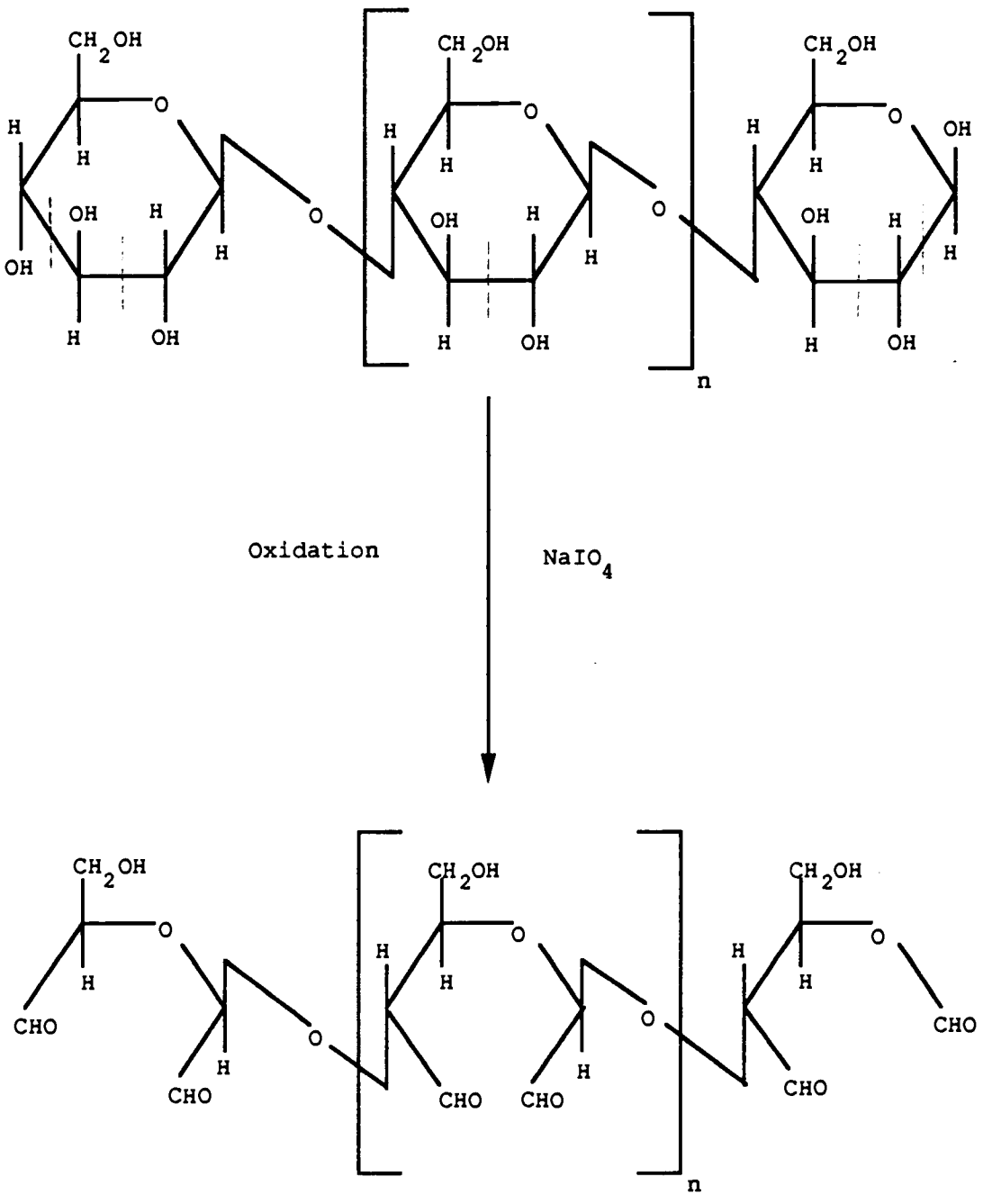


Figure 2-5: Periodate Oxidation of Cellulose

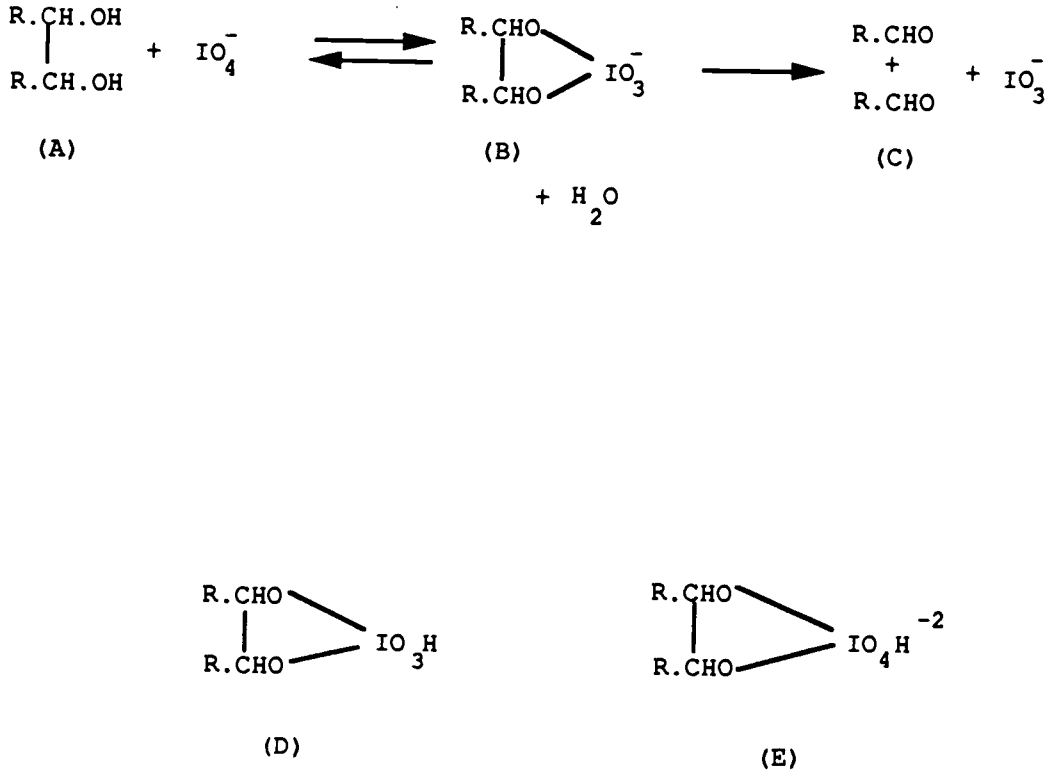


Figure 2-6: Mechanism of Periodate Oxidation of Cellulose

uncharged structure (D) and in alkaline solution it acquires a hydroxyl ion to give the double-charged (E), neither of which can decompose by simple rearrangement. The reaction is therefore retarded in strongly acidic and in alkaline solutions and it is best to work at pH 2 to 5. Alkali is also to be avoided because it degrades 2,3-dialdehyde-containing chains.

The oxidation of the non-reducing end group, and the internal glucose unit will stop after consumption of two and one equivalents of periodate, respectively, while the reducing end group can be further oxidized by periodate, as explained in the following paragraph. The above argument is also applicable to starch.

Periodate oxidation of polysaccharides, whose reducing aldohexose end-group is attached to the penultimate unit by a glycosidic linkage to C-2, C-3, or C-4, leads to the formation of one equivalent of formaldehyde and a substituted malonaldehyde intermediate (see Fig. 2-7 IV) [11]. The latter is further oxidized by a process that has often been termed as "over-oxidation" to give formic acid and one equivalent of carbon dioxide, with the result that the penultimate unit is now exposed to further oxidation. By this process, a linear polymer of aldohexopyranosyl units containing only (1 → 2), (1 → 3), or (1 → 4) glycosidic linkages can be completely eroded from the reducing end-group with the formation of

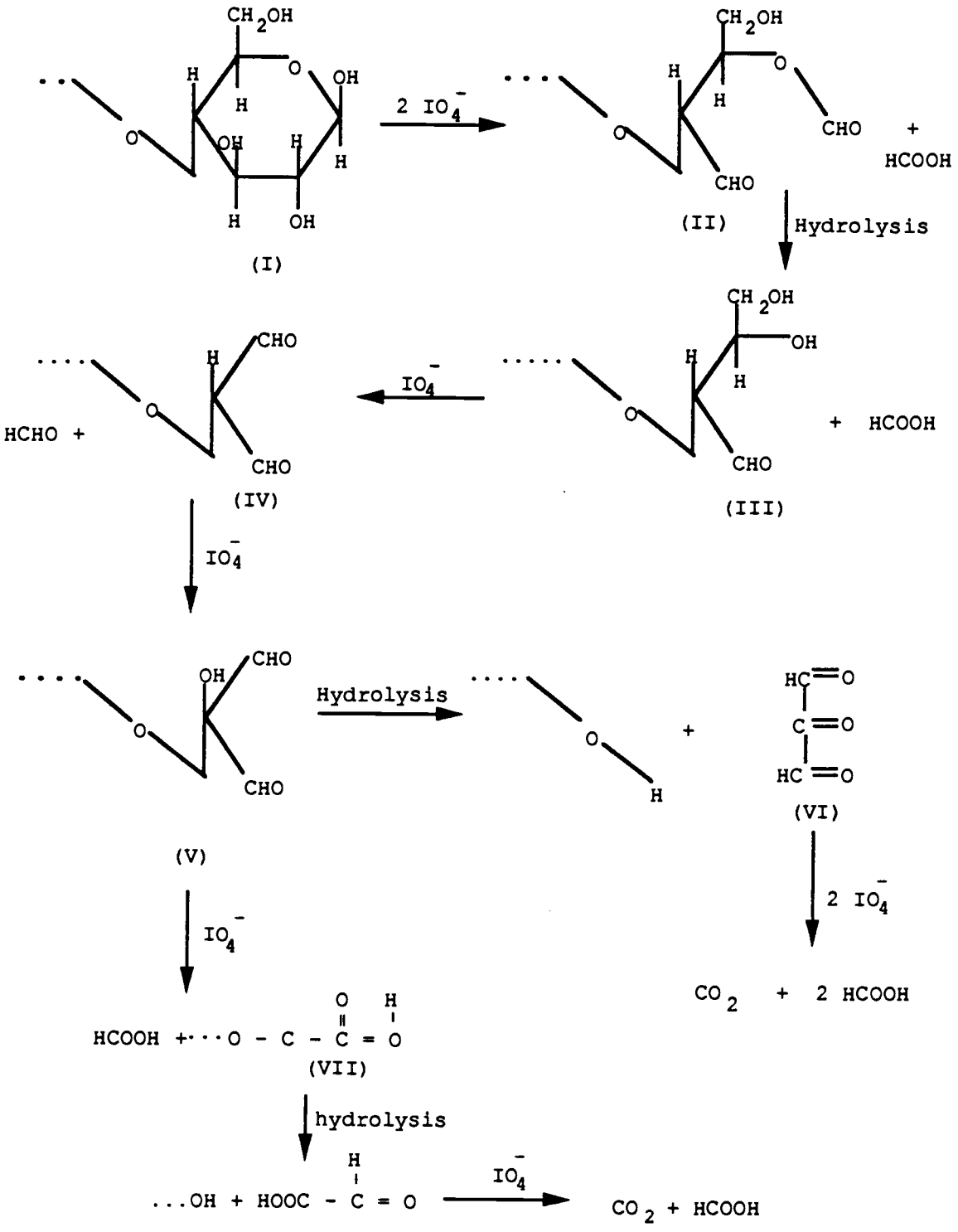


Figure 2-7: Mechanism for Over-oxidation of Cellulose

four equivalents of formic acid, one equivalent of formaldehyde and one equivalent of carbon dioxide per hexosyl unit. The overall reaction is given by,

$$(G)_{n-1}C_6H_{11}O_6 + 6\ IO_4^- \text{ ------> } (G)_{n-2}\text{-R} + HCHO + 4\ HCOOH + CO_2 + 6\ IO_3^- \qquad (2.3)$$

where

G = anhydroglucose units (including non-reducing end groups, i.e., R').

A linear polymer containing (1 → 2) or (1 → 3) linked aldopentosyl unit will be similarly oxidized.

The reaction sequence is illustrated by a 4-O-substituted aldoxehose (see Fig. 2-7 I), as found in maltose, cellobiose, lactose, cellulose, starch, and glycogen, and proceeds by way of the formyl ester (II), which, after hydrolysis to a 2-O- substituted tetrose (III), is cleaved to formaldehyde and a malonaldehyde (IV). Activation of the C-H bond adjacent to the two carbonyl groups in the latter (IV) causes further oxidation to the corresponding hydroxy derivative (V), an acetal that can break down either by hydrolysis to mesoxyaldehyde (VI), or by oxidation to a glyoxylic ester (VII), with the same final result, namely, to give one equivalent of carbon dioxide and two equivalents of formic acid and thus exposing the next unit to further oxidation. Indeed, cellulose left immersed in a large excess of

aqueous periodate eventually breaks up and dissolves completely.

Many workers have undertaken the study of periodate oxidation of cellulose [9, 25, 26, 27, 28, 29, 30, 31], but very few have considered the over-oxidation of cellulose [11,20]. Most of the studies on the oxidation of cellulose have been conducted under the conditions such that over-oxidation is negligible. But under such conditions, the oxidation of cellulose is very slow to be of practical importance. One of the first studies on kinetics of periodate oxidation of cellulose [27] was done at a pH of less than 1, and it did not consider the over-oxidation of cellulose because the mechanism of over-oxidation was not well established at that time.

The rate of formation of formic acid is dependent upon various factors: the concentration of periodate and carbohydrates, the temperature, and in particular, the pH of the reaction mixture. The hydrolysis of the intermediary formyl ester (II) and glyoxyl ester (VII) are usually very slow at about pH 3.6 in 0.015 M periodate solution at 18°C, thereby imposing a rate determining step on subsequent oxidation [11]. At higher and lower pH values, the rate of hydrolysis is increased significantly, the rate being particularly rapid at pH 7. Nevell [25] has conducted the studies of periodate oxidation of cellulose in a buffered solution at 20°C, and has shown

that at low pH values, where the predominating species is the undissociated acid (H_5IO_4) and at higher pH values, where it is paraperiodate ion ($H_3IO_6^{-2}$), the ideal Malaprade oxidation (which results in the formation of only dialdehyde cellulose) is much slower than in the pH range 2.9 to 6.8, where the periodate is mainly in the form of a univalent ion (IO_4^- or $H_4IO_6^-$), and that it is virtually independent of pH in this range. Thus, the pH range of 3 to 5 seems most appropriate for maximizing the desired Malaprade oxidation and minimizing the over-oxidation.

CHAPTER 3: EXPERIMENTAL METHODS

This chapter describes the experimental procedures employed to study the periodate oxidation of cellulose. Table 4-1 gives all the chemicals used for this work, and the supplier from which they were obtained.

3.1 Periodate Oxidation

The oxidations of α-cellulose and starch were carried out under similar conditions. The procedures for oxidation were also similar.

Extreme caution was taken to keep all the apparatus used for the entire work in dark, by covering it with aluminum foil. This was done in order to avoid the photolytic decomposition of periodate to iodate plus an oxygen radical, and thus to reduce the extent of non-specific oxidation, which includes the oxidation of formic acid and formaldehyde to carbon dioxide. The latter oxidation is quite rapid at room temperature, and should be avoided if accurate detection of formic acid concentration is desired.

In a typical run, 50 ml of 0.1 M sodium m-periodate, previously heated to the desired temperature, was added to

Table 3-1

Chemicals Used and Source

Chemical	Source
α-Cellulose	Sigma
Starch	Sigma
Sodium m-Periodate	J.T. Baker
Sodium Borohydride	J.T. Baker

an erlenmeyer flask containing 0.65 g cellulose. The flask was placed in an incubator shaker (Lab-line Orbit), at 180 rpm, to keep the insoluble polysaccharide in suspension. Fong [26] has reported that at 30°C, the diffusional effects are negligible for the shaker speeds of 180 rpm or greater. As the diffusional effects may become significant at higher temperatures, one run was conducted at 320 rpm and 60°C. The temperature fluctuation inside the shaker was ± 1°C, at the maximum. The temperatures employed were between 30 and 60°C. The sodium m-periodate concentrations employed were between 0.05 to 0.2 M (pH 3 to pH 5); this being the expected operating range in which the formyl ester, formed during the over-oxidation, is supposed to be stable [12].

3.2 Analysis of Periodate Consumption

The method of Dixon and Lipkin [32] was followed to determine the periodate concentration in the reaction mixture.

Following the oxidation of α-cellulose (or starch) with sodium m-periodate, the reaction flask was taken out from the shaker at the required time. Approximately 10 ml of the reaction mixture was taken into a syringe and filtered into a vial by using a syringe filter and Gelman Science SUPOR-450, 0.45-μm membrane filter. Approximately

10 ml of filtered solution was transferred into a vial. Again, care was taken to keep all the apparatus in dark. Exactly 1 ml of the filtered solution was taken from the vial and further diluted at a known ratio so as to have a concentration between 0.02 and 0.2 mM (the approximate range in which the Beer Lambert law is obeyed). The exact concentration was then found by measuring the absorbance of this solution at 223 nm using a HP 8451A Diode Array Spectrophotometer (the calibration curve is provided in Fig. 3-1).

It was observed that the interference due to formic acid, formed by the over-oxidation of the cellulose, could become very significant after a certain period of time (depending on the temperature and concentrations employed). For a few readings, the formic acid (which absorbs at 205 nm) peak completely overshadows the periodate peak, thus making it impossible to read the correct absorption at 223 nm for periodate. In such cases, a known amount of sodium m-periodate was added to the sample to increase the periodate concentration, thus giving a unique peak at 223 nm, free from formic acid interference. The concentration of the periodate in the sample was then determined by subtracting the concentration of the added sodium m-periodate from the concentration of the mixture, as obtained from the calibration plot.

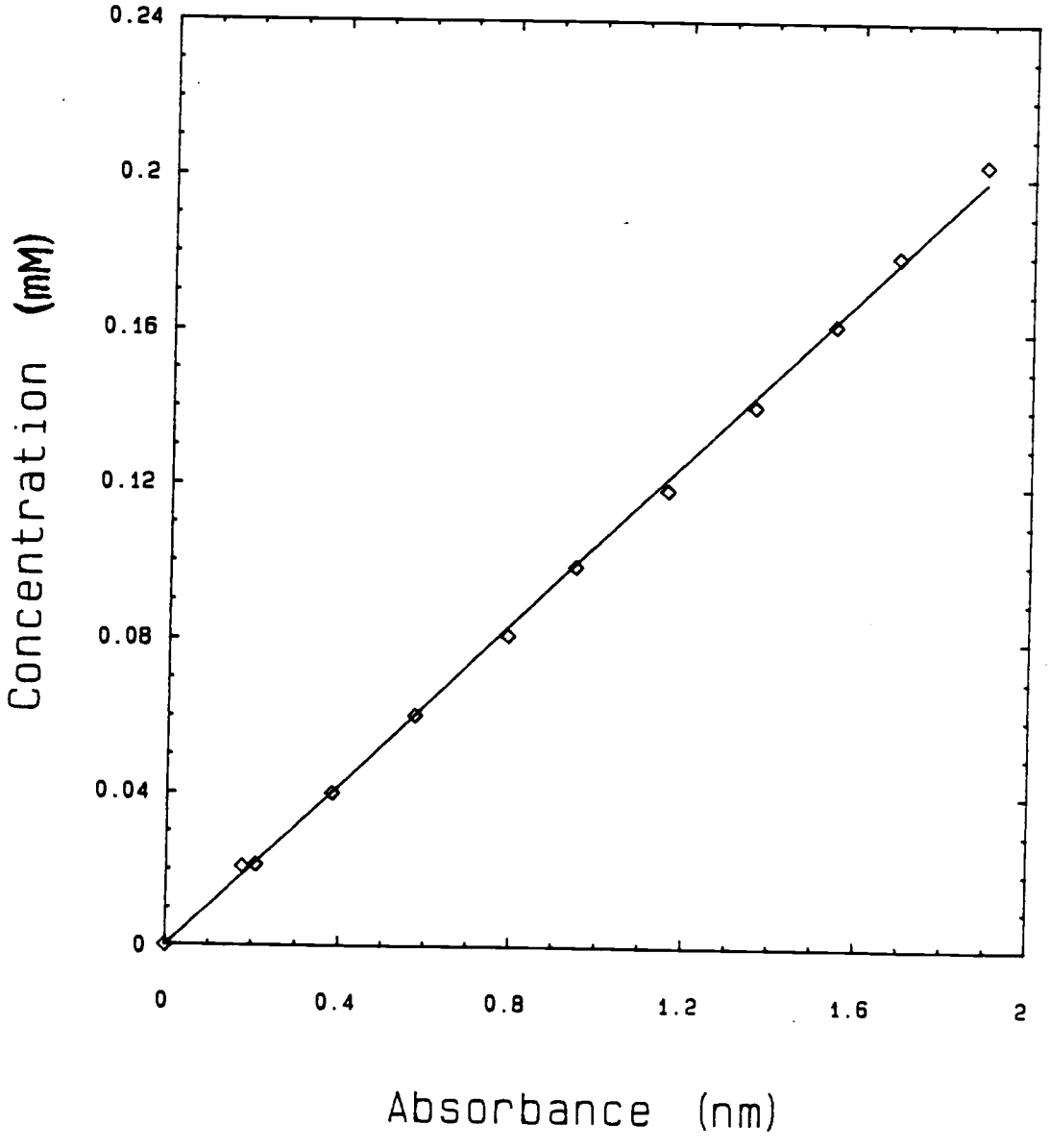


Figure 3-1: Calibration Plot for the Determination of Sodium m-Periodate

3.3 Determination of Formic Acid

The extent of over-oxidation of the polysaccharide was determined by following the concentration of formic acid formed during the oxidation by sodium m-periodate. An ISCO HPLC system, equipped with a Bio-Rad HPX 87H carboxylic acids analysis column, a UV detector set at 210 nm and a HP 3390A integrator, was used for this purpose. Sulfuric acid (0.01 N) was used as the solvent at a flow rate of 0.6 ml/min. The clean and filtered reaction solution, collected in a vial in the previous procedure for analysis of periodate consumption, was used for this purpose. To reduce the risk of damage to the column due to the high concentrations of periodate employed, the injection volume was kept at 10 μl, using a loop provided for the same purpose. To avoid photolytic decomposition of periodate, the syringe washings and HPLC injections were conducted in a dark room. As the expected formic acid concentrations were very low, no dilution of the original reaction solution was performed. The retention time for formic acid elution was 13.3 min at a flow rate of 0.6 ml/min. The concentration of formic acid in the sample was determined by noting the formic acid peak area, and finding the concentration from the calibration plot (presented in Fig. 3-2). As the formic acid peak falls on the tail of the solvent (sodium m-periodate) peak, the

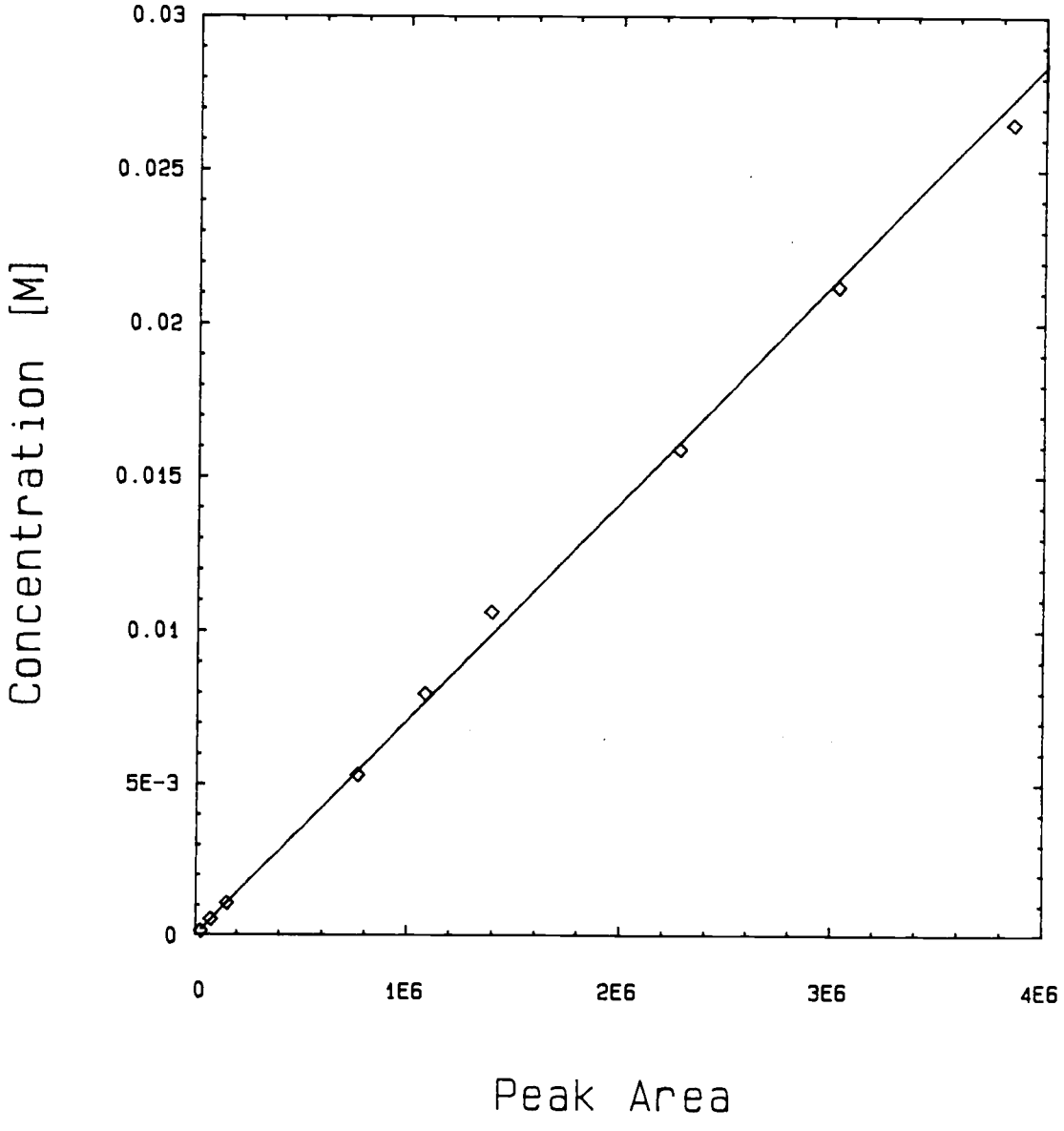


Figure 3-2: Calibration Plot for the Determination of Formic Acid

method of tangent skim was used to determine the peak area of formic acid. Sufficient time was allowed between two runs, so that all the solvent could be eluted.

3.4 Carbonyl Content of Dialdehyde Cellulose

The degree of oxidation of the α-cellulose was determined by the method of Rankin and Mehltretter [33]. A sample of the dialdehyde compound to be analyzed (about 50 mg) was reduced in a closed system using 1.5 ml of sodium borohydride solution (500 mg/50 ml 0.1 M NaOH). After 2 hr, the unreacted borohydride was decomposed by adding 1.5 ml of 2 N sulfuric acid. The volume of hydrogen evolved was measured using a 50-ml gas buret and subtracted from the volume of gas evolved by a blank to determine the hydrogen consumption of the dialdehyde sample. The degree of oxidation of the sample was then calculated by dividing the hydrogen consumption by the theoretical consumption of two molecules of hydrogen per chain residue.

3.5 Infrared Spectroscopy Studies

Infrared spectroscopy studies of dialdehyde cellulose were conducted to examine the formation of dialdehyde. Dialdehyde cellulose was dried at low temperature (30 -

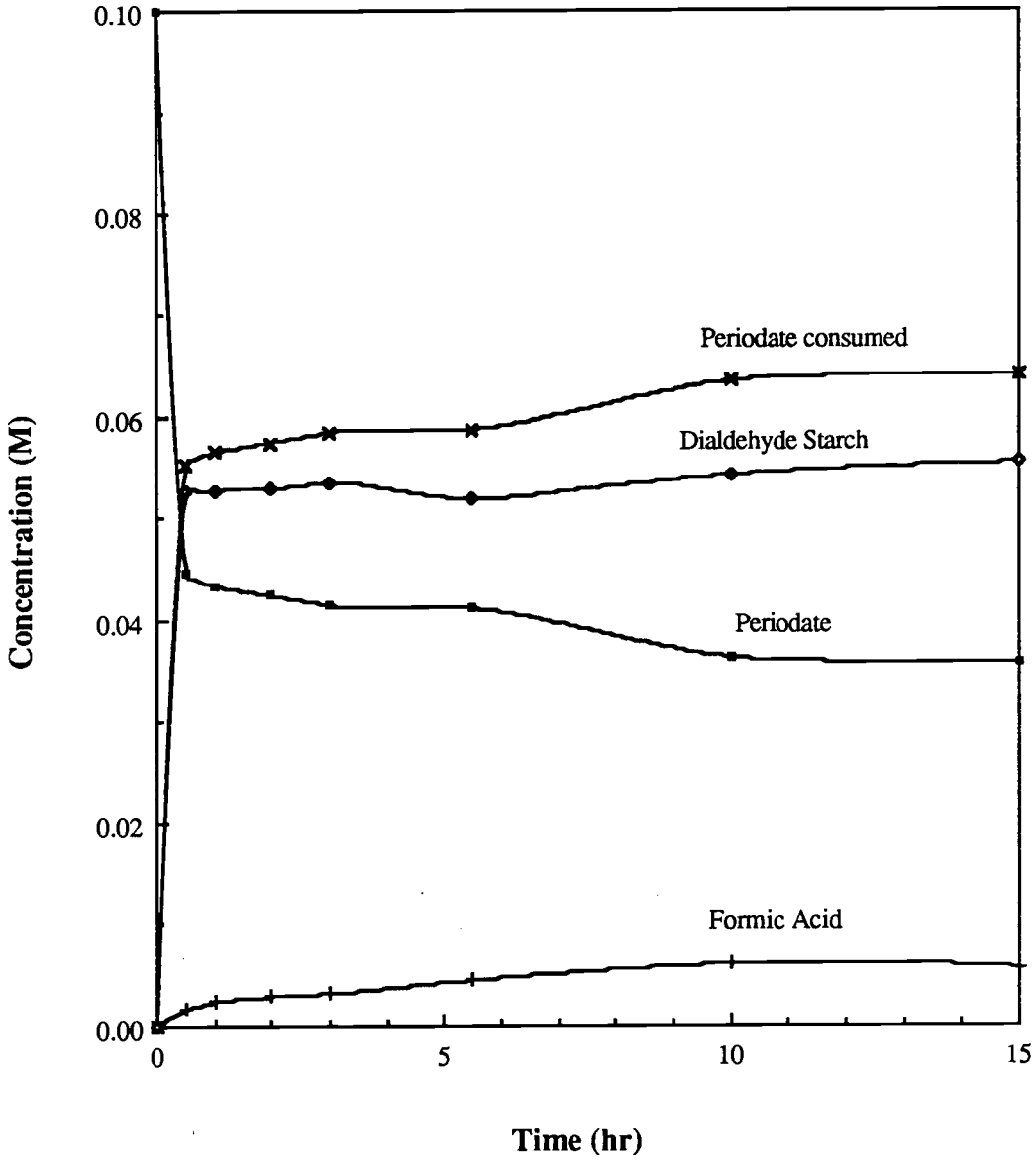
50°C). The dried sample was mixed with KBr powder. A 1% KBr disc was prepared. The disc was placed in a Nicolet IR Spectrophotometer and a IR scan on the sample was made.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Periodate Oxidation

4.1.1 Starch

Many studies have been done on the periodate oxidation of starch ([34], [35]). Most of the studies have been conducted under conditions such that the over-oxidation is negligible. Durrence [9] showed that oxidation of starch using periodic acid occurs readily at 32°C, but does not proceed to completion and levels off at approximately 80% of the theoretical. Our studies for the sodium m-periodate oxidation of starch at 50°C gave similar results, with 70% conversion achieved within ½ hr. The periodate consumption does not exactly level off at 70%, but increase very slowly after 70% conversion (see Fig. 4-1). Once 70% of the theoretical oxidation has occurred, the periodate consumption is mainly for the over-oxidation process (see Sec. 2.2.2 and Fig. 2-7), not for the formation of dialdehyde starch. The dialdehyde starch concentration remains almost constant for the reaction times shown, but it would decrease if the reaction is continued for longer times. This is indicated by the formic acid formed. Thus, if the oxidation of



Initial Starch Concentration = 0.08 M

Initial Periodate Concentration = 0.1 M

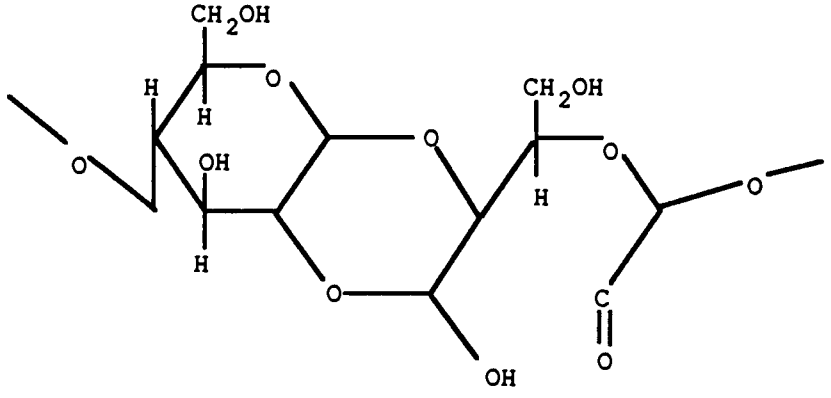
Figure 4-1: Periodate Oxidation of Starch at 50°C

starch is carried out beyond this stage, then not only would periodate be lost in the undesirable over-oxidation process, but so would dialdehyde starch. To explain the fact that oxidation of starch levels off at 80% of the theoretical Durrence [9] proposed a inter-residue hemiacetal structure for dialdehyde starch, Fig. 4-2 (A). In this structure, one of the aldehyde groups of an oxidized residue reacts with either the C-2 or C-3 hydroxyl group of an unreacted neighboring residue. Such a structure blocks the neighboring residue from reacting with periodate since the cyclic diester intermediate cannot be formed.

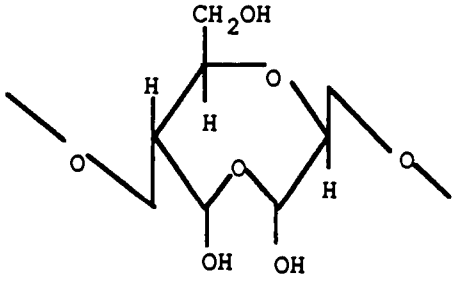
The other possible structures for the dialdehyde species are also given in Fig. 4-2. The first (B) involves hydration of both the aldehyde groups by a single water molecule to give the hemialdal, while the second (C) involves the condensation of the C-6 hydroxyl of an oxidized residue with either C-2 and C-3 aldehyde groups to give rise to a hemiacetal structure.

4.1.2 Cellulose - Studies Without Over-oxidation

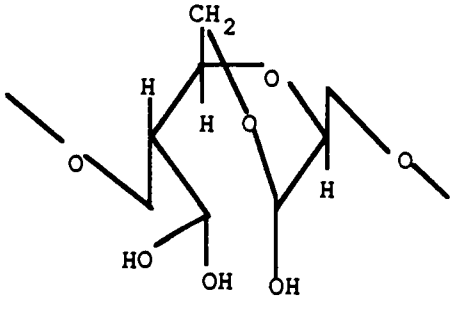
When Durrence [9] conducted studies of periodate oxidation of cellulose at 34 and 50°C he assumed no over-oxidation. He modeled the oxidation as second-order overall, first order in both periodate and cellulose.



(A) Inter-residue Hemiacetal



(B) Hemialdal



(C) Hemiacetal

Figure 4-2: Possible Structures of Dialdehyde Starch/Cellulose

We extended this study by conducting experiments at 40, 45, 51 and 60°C. Over-oxidation was neglected, so that the cellulose concentration was directly obtained from the periodate consumption, i.e.:

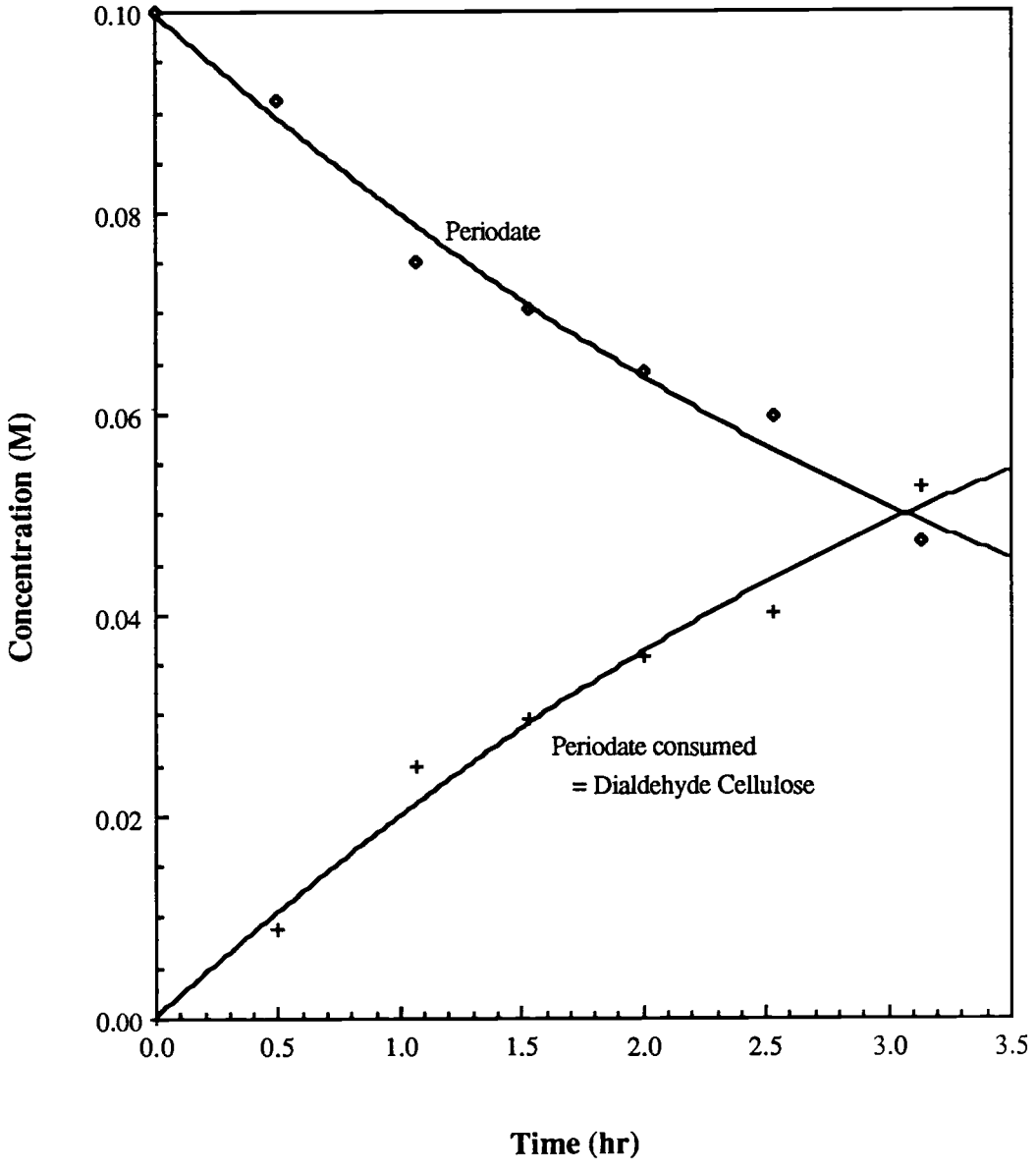
[cellulose] = [initial cellulose] - periodate consumed

..... (4.1)

All the data fits a second order rate expression as proposed by Durrence. Even at higher temperatures of 60°C (Fig. 4-3), where there is significant degree of over-oxidation (as will be shown in the next section), the fit is quite good (Fig. 4-4). The rate constants as obtained from the above runs were used to make an Arrhenius plot as shown in Fig. 4-5. The activation energy as determined from the Arrhenius plot is 12.84 kcal/gm-mol.

4.1.3 Cellulose - Studies with Over-oxidation

It would be erroneous to use the above rate expression for design purpose because, based on the quantity of formic acid formed, it is obvious that the over-oxidation reaction is significant, under the conditions employed for the experiment. Thus, the actual concentration of cellulose will be more than that predicted by the above model, while the dialdehyde cellulose concentration will be less.



Initial Cellulose Concentration = 0.09 M

Initial Priodate Concentration = 0.1 M

Figure 4-3: Periodate Oxidation of Cellulose at 60°C

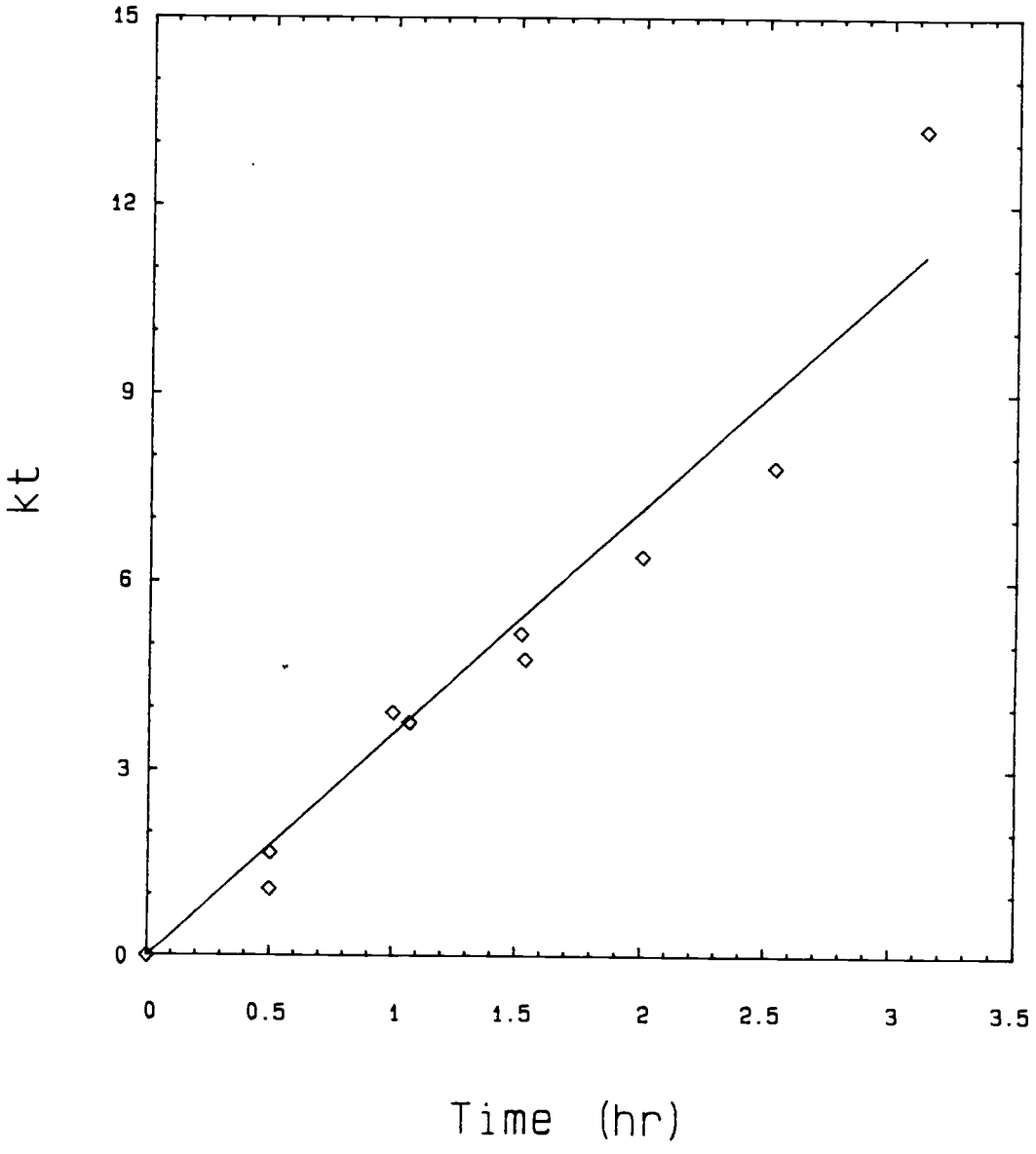


Figure 4-4: Second-Order Plot for the Run at 60°C

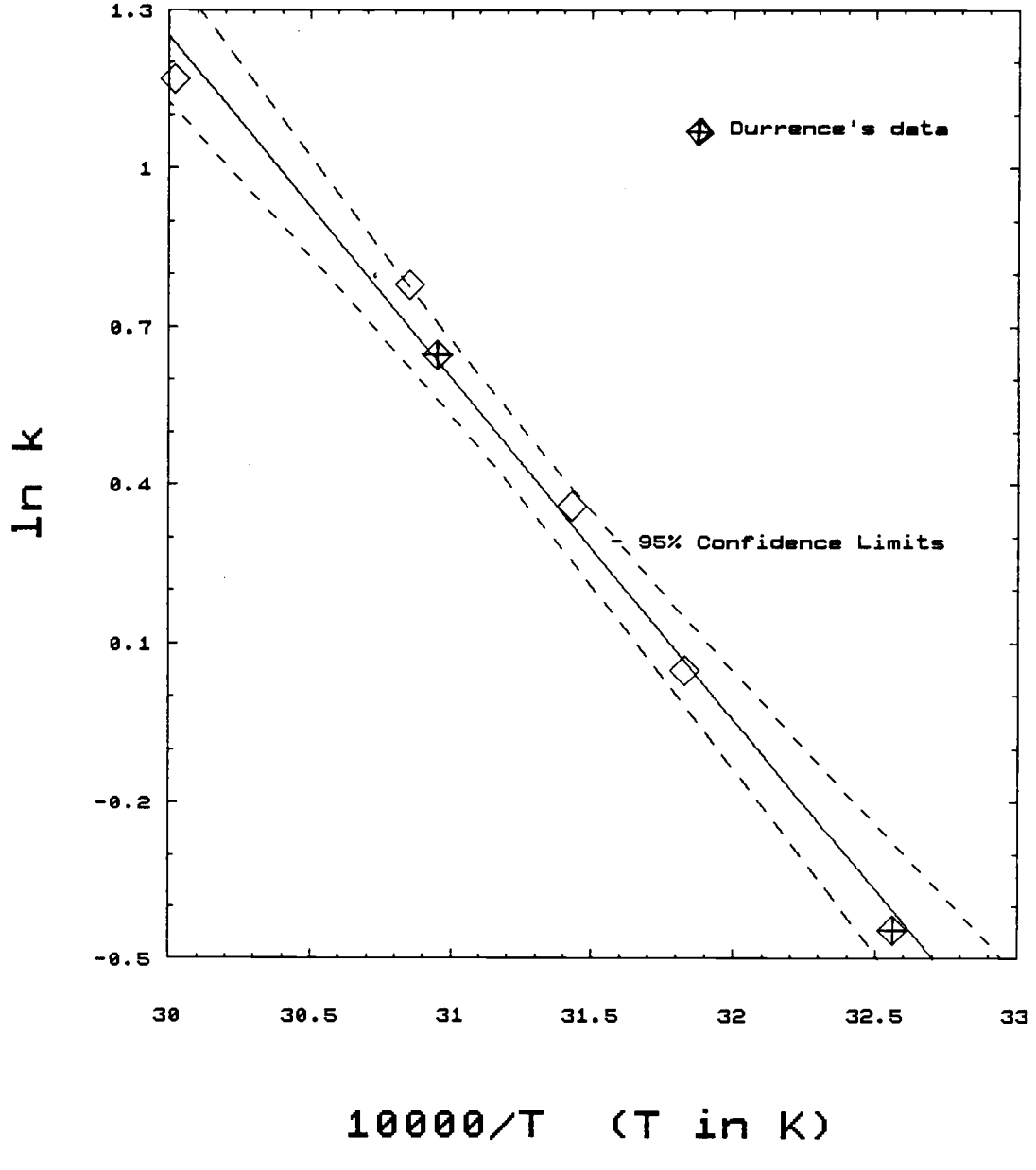
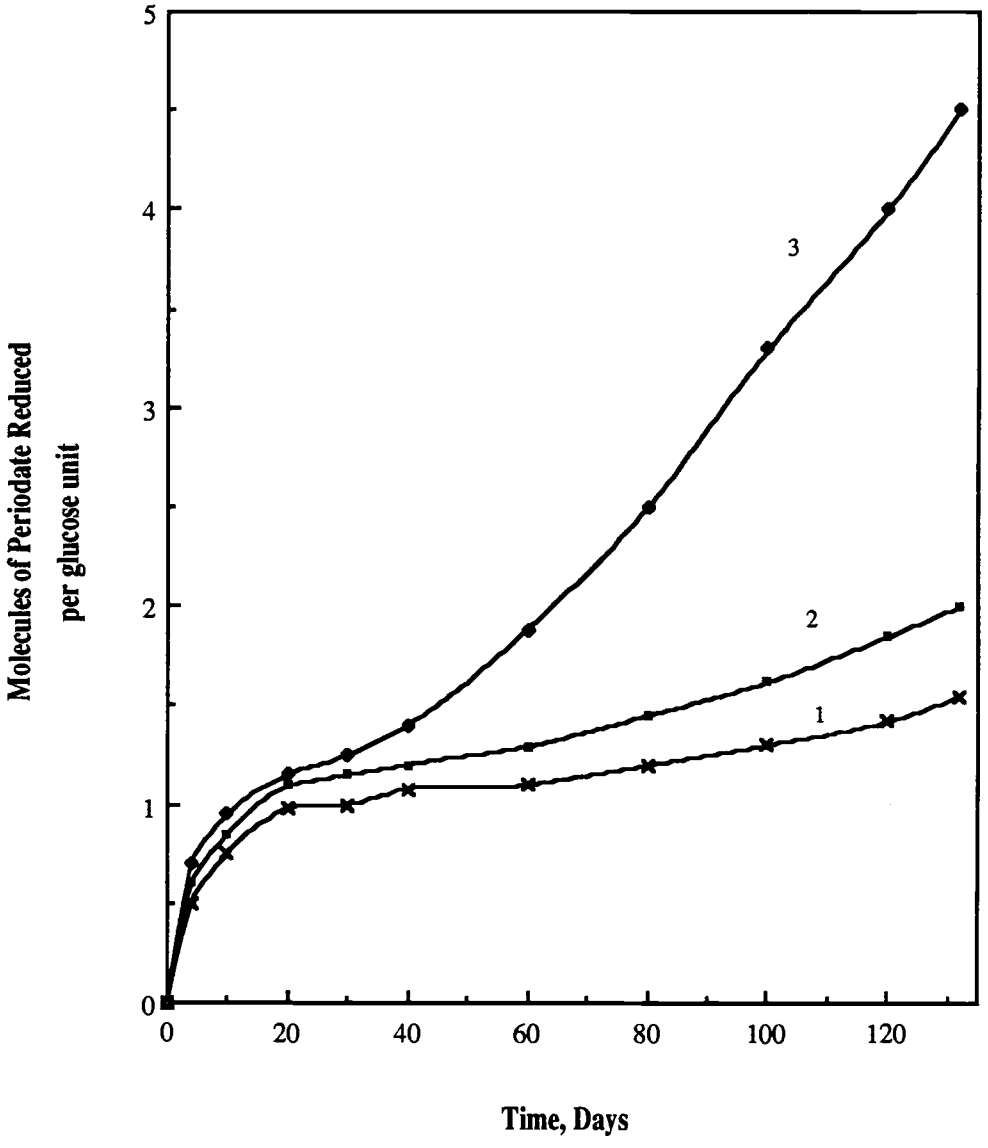


Figure 4-5: Arrhenius Plot for Periodate Oxidation of Cellulose, Assuming no Over-oxidation

Cellulose, when reacted with periodate in an unbuffered solution for a significant length of time, undergoes a marked degree of over-oxidation. This fact was first recognized by Davidson [28] and later by Head [20] who showed that light significantly accelerates the over-oxidation reaction. The results from the latter study are shown in Fig. 4-6. The general form of the rate curves shows that a relatively rapid initial reaction of the Malaprade type is followed and accompanied by slower over-oxidation reactions. During the later stages in which over-oxidation is the main reaction, the rate of reduction of periodate is at first nearly constant and then accelerates with time in spite of a falling periodate concentration. This acceleration is to be expected if the reduction of periodate is brought about to an increasing extent by a homogeneous oxidation of the water soluble products of oxidative degradation of cellulose [10].

As seen from the Fig. 4-6, the rate of both the Malaprade type of oxidation and the over-oxidation increases with an increasing ratio of periodate to cotton [20]. But the rate of over-oxidation is affected much more significantly. It is probable that for higher reaction times, when Malaprade reaction is essentially completed, the increase in the rate of periodate consumption is due to random chain scission. The dialdehyde cellulose structure is significantly more



1 - 1.6 molecules periodate per glucose unit

2 - 3.7 molecules periodate per glucose unit

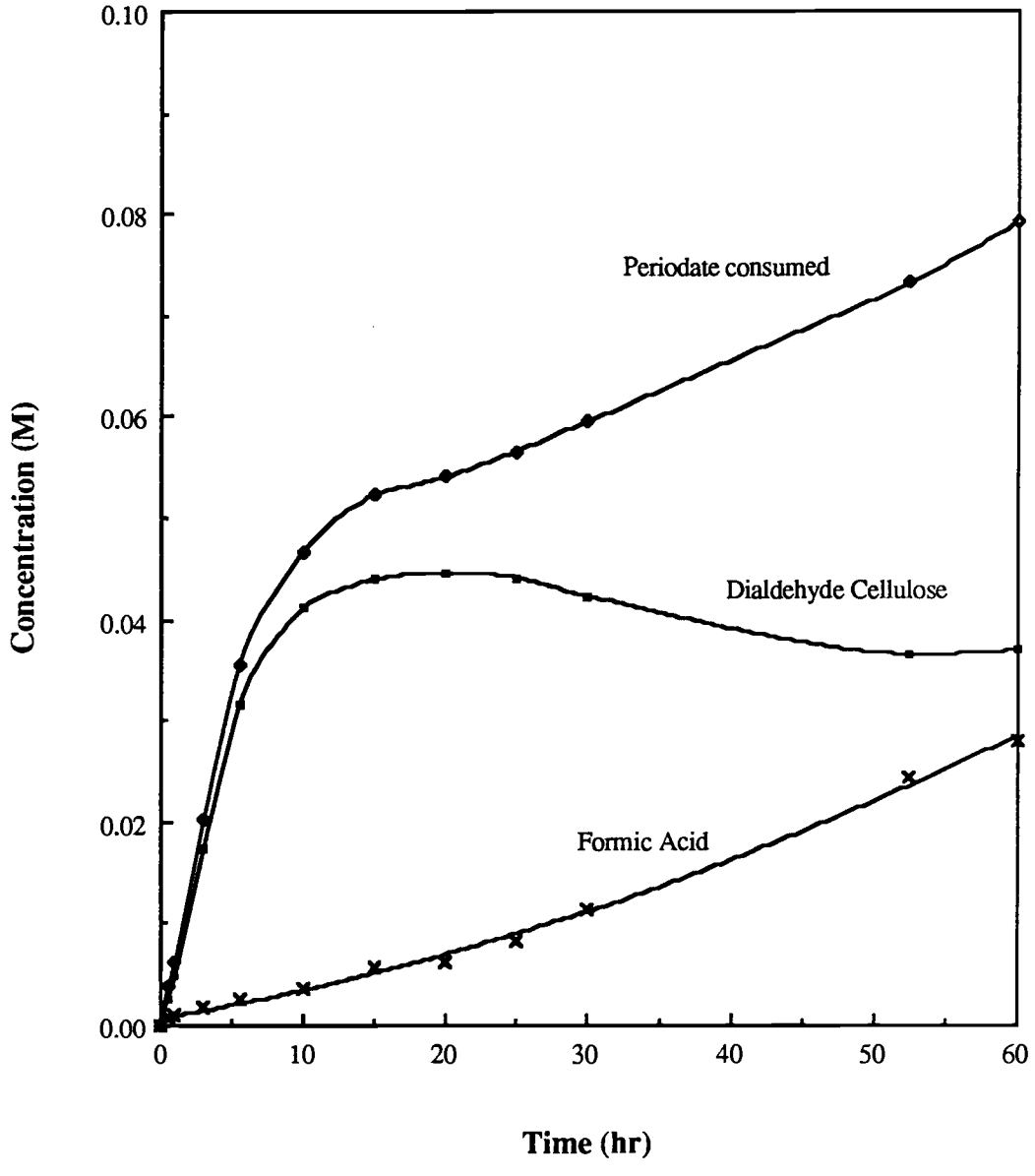
3 - 20 molecules periodate per glucose unit

Figure 4-6: Oxidation of Cotton with 0.1 M Sodium Metaperiodate in the Dark at 20°C [20]

accessible than the original cellulose, probably because of the disruption of the hydrogen bonding. This would lead to the formation of more end groups and thus an increase in rate of periodate consumption. Furthermore, the dialdehyde cellulose may partially dissolve in the periodate solution because of random chain scission. This would increase the number of end groups, and consequently, result in an increase in the rate of periodate consumption.

As is apparent from Head's study [20], higher ratios of periodate to cellulose and higher reaction times should be avoided if dialdehyde cellulose is the desired product. Thus, in this study, only slight excess of periodate was used and reaction times were kept as low as practical, so that good yields of dialdehyde cellulose are obtained. Only one run was carried on far beyond the Malaprade oxidation stage (see Fig. 4-7). The results obtained are quite similar to that obtained by Head.

This study has been conducted because of the desire to maximize the yield of dialdehyde cellulose. Therefore, the over-oxidation that occurs after the Malaprade oxidation is absolutely undesirable, and the reaction should be stopped before this stage is reached. Thus, all the experimental runs were stopped before the consumption of one mole of periodate per glucose unit. Thus, for the data of Fig. 4-7, only the data measured before 25 hr was



Initial Cellulose Concentration = 0.0617 M

Initial Periodate Concentration = 0.1 M

Figure 4-7: Extended Oxidation of α-Cellulose at 50°C

taken into consideration (see Fig. 4-8) for fitting the kinetic model. All the data are given in Appendix A.

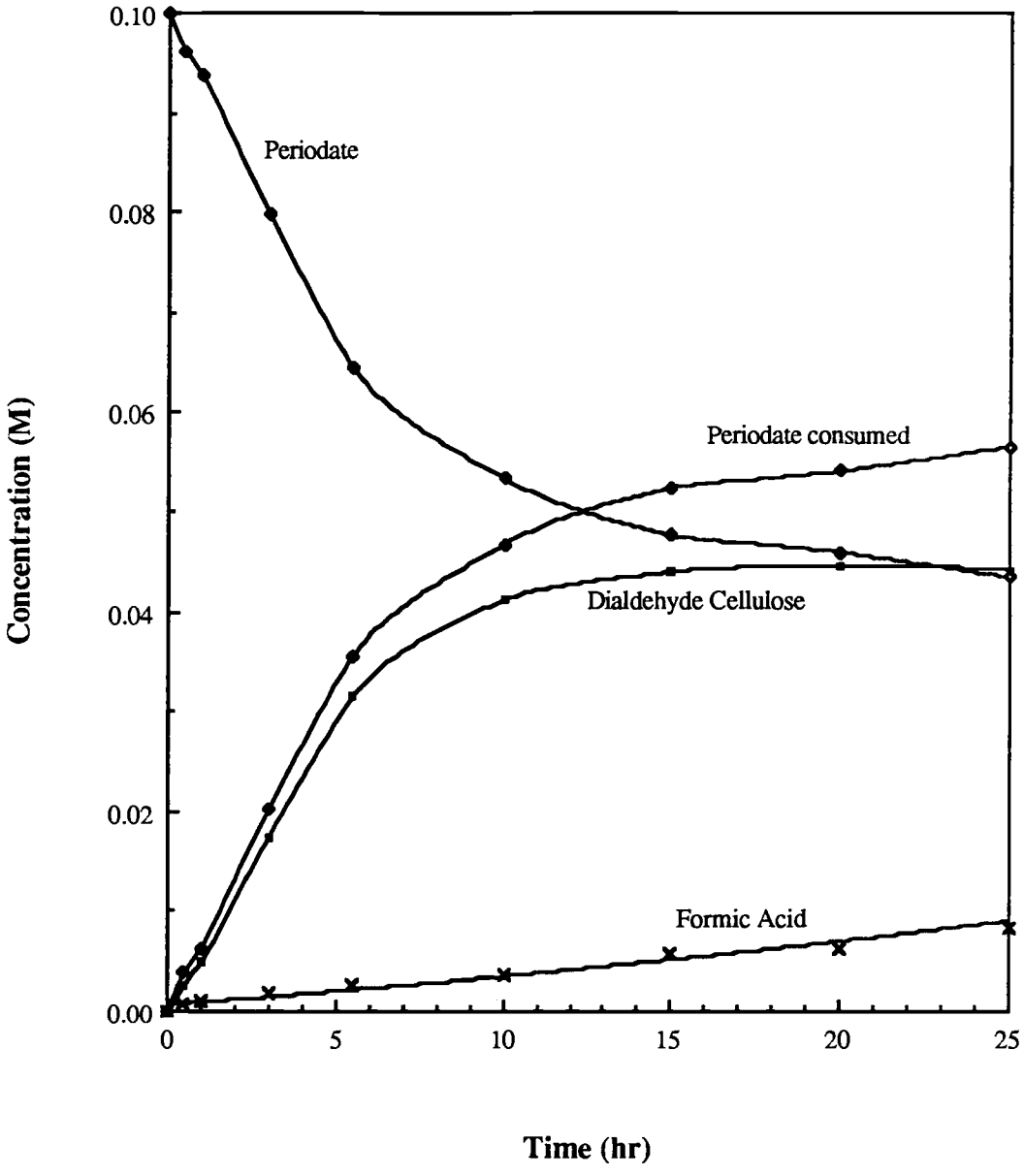
4.2 Dialdehyde Cellulose

4.2.1 IR Studies

Many workers have reported that it is difficult to obtain a good aldehyde peak for the dialdehyde cellulose. Narayan and Tsao [29] used the method of KBr disc and obtained a good IR spectrum of dialdehyde cellulose. We followed the same method, and the results are as shown in the Fig. 4-9. The presence of a peak at 1720 nm suggests the presence of aldehyde group. Also, the strength of the peak seems to indicate that the aldehyde is probably not present in the free aldehyde form. The aldehyde groups formed on periodate oxidation of cellulose are highly reactive and very little of free dialdehyde is present in solution. Of the three possible structures of the dialdehyde species discussed in Sec. 4.1.1 and Fig. 4-2, the dialdehyde cellulose exists as the hemialdal structure (Fig. 4-2 B) [9].

4.2.2 Chain Scission

For higher reaction times, the weight loss of cellulose after oxidation was more than that indicated by



Initial Cellulose Concentration = 0.0617 M

Initial Periodate Concentration = 0.1 M

Figure 4-8: Oxidation of α-Cellulose at 50°C

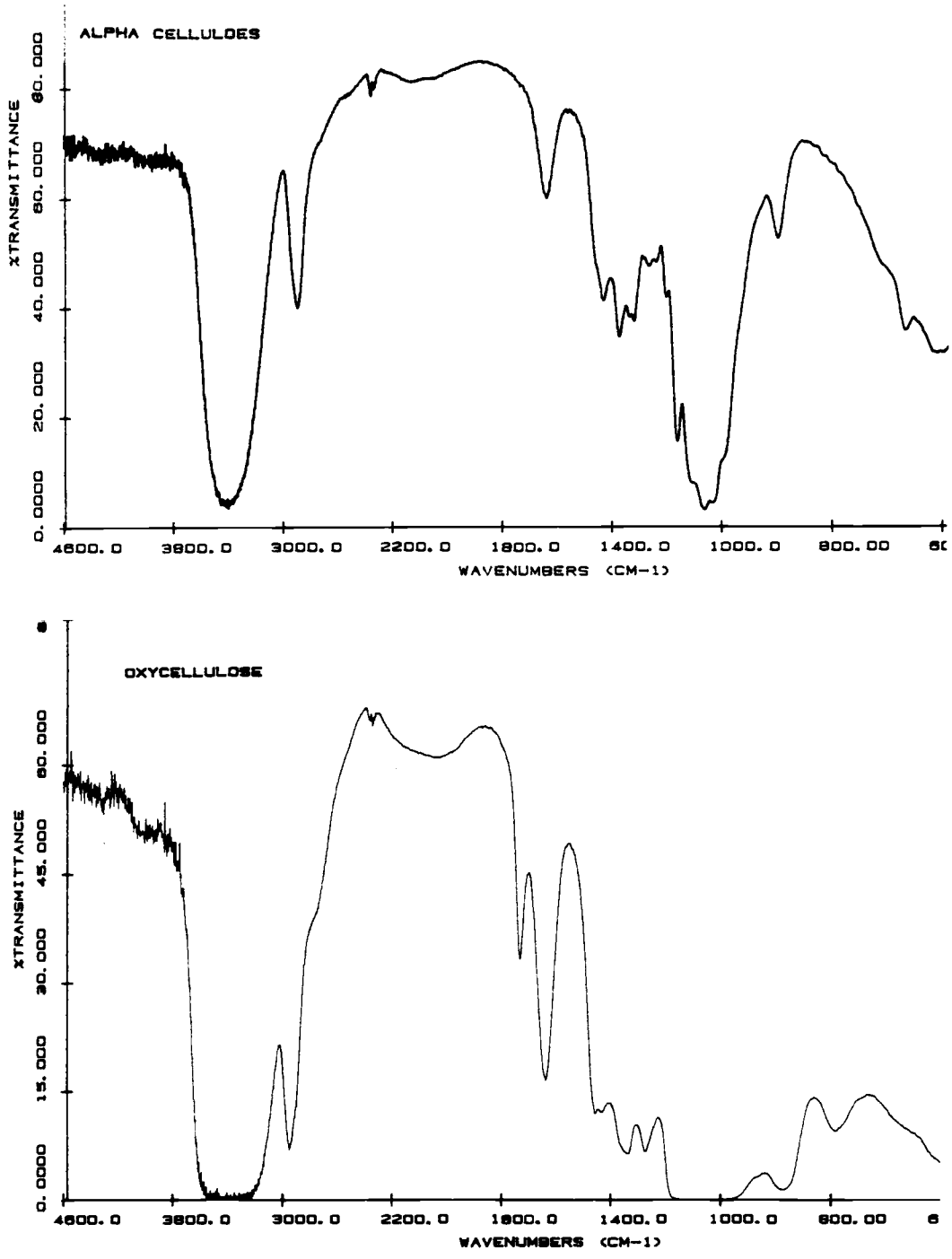


Figure 4-9: IR of Cellulose and Dialdehyde Cellulose

over-oxidation. The dialdehyde yield was lesser than that indicated by the formic acid formation. Thus, either formic acid was oxidized by periodate or dialdehyde cellulose was going into the reaction solution. Based on Head and Hughes's results [19], it is unlikely that formic acid oxidation would be significant under the employed conditions. Thus, to investigate this, the reaction mixture from the periodate oxidation of cellulose was filtered by using an Amicon ultrafiltration cell equipped with an Amicon YM5 membrane. The results obtained are as shown in Table 4-1. As seen from the table, the material balance is in better agreement when ultrafiltration system is used. The reason for this descrepancy could be that the dialdehyde cellulose partially dissolves in the reaction mixture and thus passes through the ordinary filter paper, while it is retained by the fine ultrafiltration membrane. The random chain scission of dialdehyde cellulose by periodate may produce smaller units, some of which are so small that they go into the solution. This has serious implications in the periodate consumption as it increases the number of end groups significantly.

4.2.3 Determination of Dialdehyde Cellulose

Determination of the carbonyl content of dialdehyde

Table 4-1

Material Balance After Ultrafiltration

$[Cellulose/Starch]_0 = C_0 = 15$ g/l = 0.0926 M;

$[NaIO_4]_0 = 0.1$ M

Temperature (°C)	Reaction time	[HCOOH] M	Cellulose/Starch + Dialdehyde Cellulose/Starch [M]	
			Expected = C_0-F/4	Recovered with ultra filtration
50	15	0.0066	0.09095	0.09075*
60	6.5	0.0069	0.09088	0.08606*
60	5	0.0045	0.09148	0.08525x

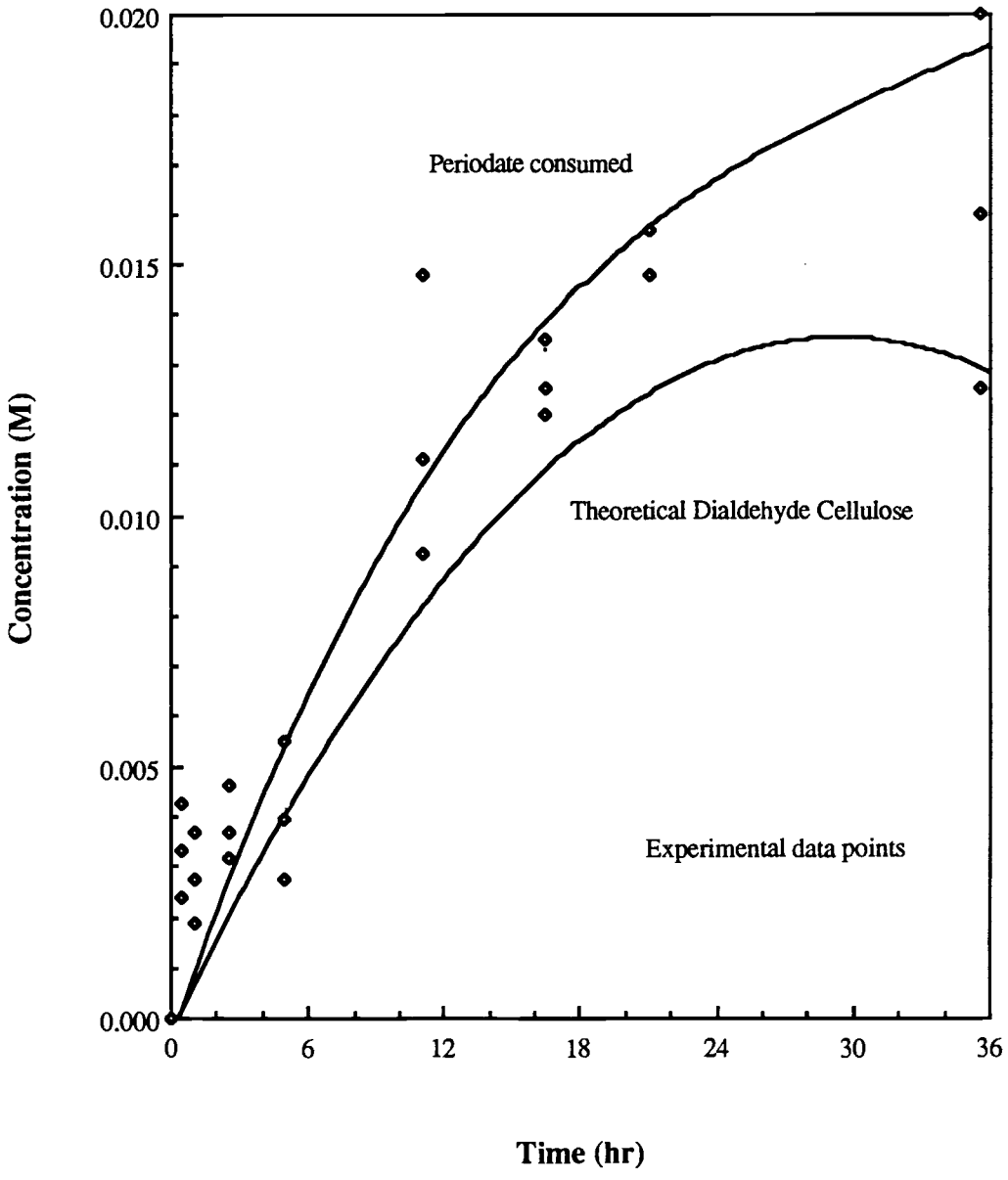
* Cellulose
x Starch

cellulose is rather a difficult and many workers have reported this problem [30]. We tried to measure the dialdehyde content of cellulose by using the method of Rankine and Mehltretter [33], which is one of the best methods reported in the literature. As this method involves measuring the gas volume, it requires very accurate measurement. In spite of all the precautions taken, we were unable to obtain consistent results. The data obtained is very scattered and thus unreliable. It is presented in Fig. 4-10. In spite of the scatter, the figure indicates that the concentration of dialdehyde cellulose is less than the periodate consumption.

4.3 Kinetic Modeling

The main objective of this project was to develop a complete kinetic model for the periodate oxidation of cellulose, which would account for both Malaprade type oxidation as well as the over-oxidation. The mechanism of periodate oxidation and over-oxidation of cellulose was explained in Sec. 2.2.2. Periodate is consumed in both the reactions and the overall reactions for the internal glucose units and the reducing end group are as follows:

$$R'\text{-}(C_6H_{10}O_5)_{n-2}\text{-}R + (n-2)\ IO_4^- \text{------>}\ R'\text{-}(C_6H_8O_5)_{n-2}\text{-}R + (n-2)\ IO_3^- + (n-2)\ H_2O \quad (2.2)$$



Initial Cellulose Concentration = 0.0185 M

Initial Periodate Concentration = 0.05 M

Figure 4-10: Dialdehyde Cellulose Measured at 50°C

$$(G)_{n-1}C_6H_{11}O_6 + 6\ IO_4^- \text{ ------> } (G)_{n-2}\text{-R} + HCHO + 4\ HCOOH + CO_2 + 6\ IO_3^- \quad (2.3)$$

where

G = moles of glucose units (including the non-reducing end groups R') per liter

R = moles of reducing end groups per liter

n = average number of glucose units (both G and R) per molecule of cellulose

4.3.1 Assumptions

The oxidation of the non-reducing end group stops after the consumption of two equivalents of periodate. Thus, this oxidation was neglected in our model.

The pH of the reaction mixture changes with the consumption of periodate. Fong [26] studied the effects of pH and diffusion on the periodate oxidation of pulps used in his experiments. He showed that at 30°C, pH has little effect on the rate of reaction and thus can be neglected. Also, he showed that for an agitation speed of 180 rpm or greater, the diffusional effects can be ignored. At higher temperatures, the diffusional effect may become significant and to investigate, we conducted runs at 180 and 320 rpm at 60°C. The results are given in Fig. 4-11. As can be seen from Fig. 4-11, this effect can also be neglected.

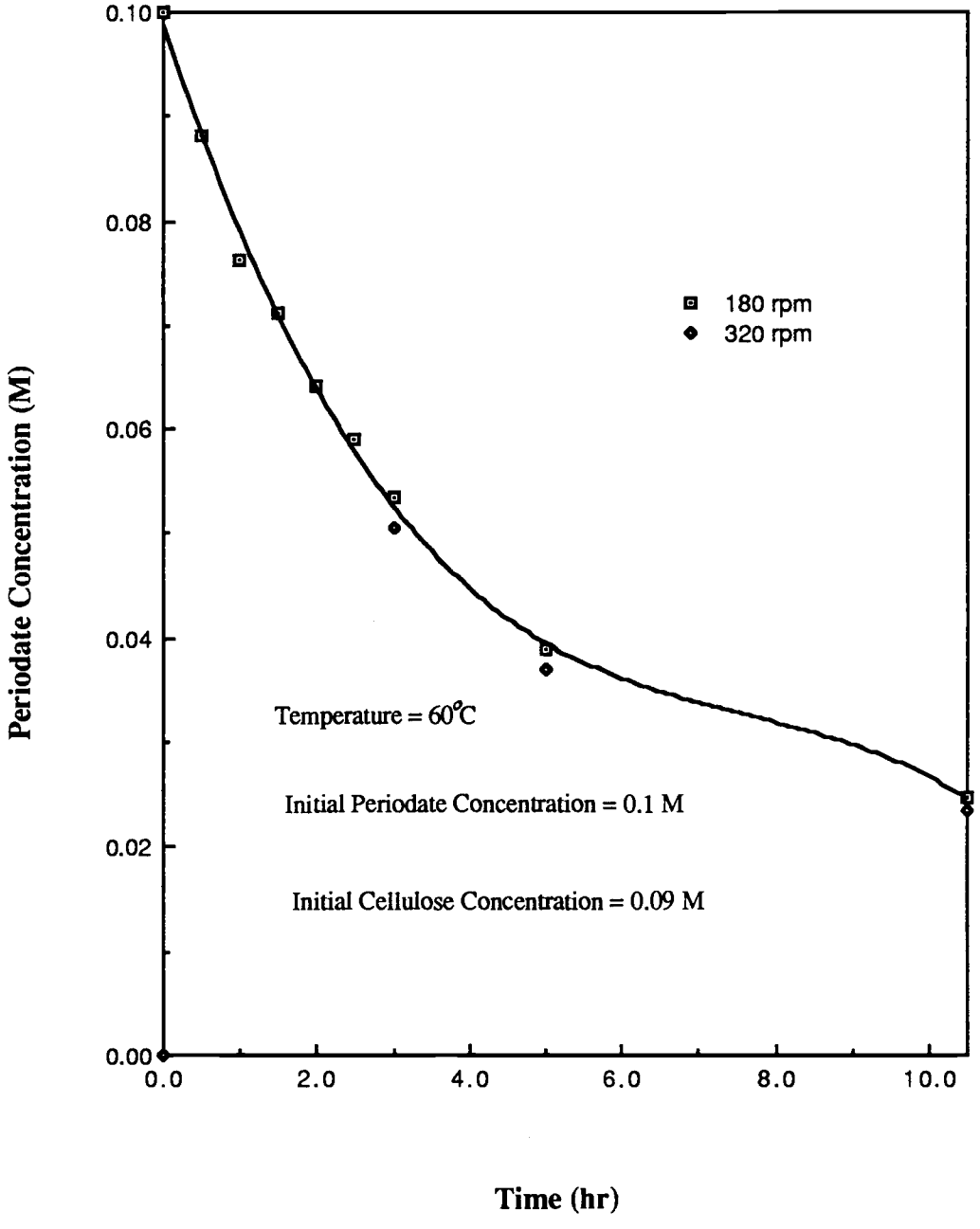


Figure 4-11: Effect of Agitation Rate on Periodate Consumption

Head and Hughes [22] have conducted a detailed study on periodate oxidation of cellobiose. They showed that initially 2 moles of periodate are consumed (per mole of cellobiose) without production of formic acid. This result suggests that the end groups in cellulose will initially consume one equivalent of periodate without production of formic acid. Then they will consume one more equivalent of periodate to form one equivalent of formic acid. Thus, it can be reasonably assumed that the end group will first form a dialdehyde species, just like the internal glucose unit, before it oxidizes to undesired products, i.e., the rates of oxidation of the internal glucose units and the reducing end groups, to form the respective dialdehydes species, are the same.

To solve the differential equations obtained, the concentration of the dialdehyde end group must be expressed in terms of the known quantities. To obtain such a relation, it is reasonable to assume that the end groups as well as the internal glucose units are equally accessible for periodate oxidation, i.e.,

$$\begin{bmatrix}\text{fraction of internal glucose}\\ \text{units attacked by periodate}\end{bmatrix} = \begin{bmatrix}\text{fraction of end groups}\\ \text{attacked by periodate}\end{bmatrix}$$

In terms of notations, this becomes,

$$[DG]/[G]_0 = [DR]/[R]_0 \qquad (4.2)$$

where [DG] and [DR] are the molar concentrations of

internal and reducing end group dialdehyde molecules, respectively; and $[G]_0$ and $[R]_0$ are the molar concentrations of glucose and reducing end groups present initially. Solving for [DR] gives

$$[DR] = [DG][R]_0/[G]_0 \qquad (4.3)$$

4.3.3 Material Balances

There is one end group per molecule of cellulose. Thus, the average number of glucose units, including both internal (G) and reducing end group (R) glucose residues, per molecule of cellulose at time zero is

$$n_0 = [C]_0/[R]_0 = ([G]_0 + [R]_0)/[R]_0$$

where $[C]_0$ represents the molar concentration of glucose units initially present in the cellulose. Thus

$$[G]_0/[R]_0 = n_0 - 1$$

Substituting in equation (4.3) gives

$$[DR] = [DG]/(n_0 - 1) \qquad (4.4)$$

The two reactions of equations 2.2 and 2.3 can be expressed as

$$G + P \xrightarrow{k_1} DG + IO_3^- + H_2O \qquad (4.5)$$

$$R + P \xrightarrow{k_1} DR + IO_3^- + H_2O \qquad (4.6)$$

$$DR + 5\ P \xrightarrow{k_2} 4\ F + HCHO + CO_2 + 5\ IO_3^- \qquad (4.7)$$

where P represents periodate and F represents formic acid.

The same rate constant, k_1, is used in equation (4.5) and (4.6) because we have assumed the probability of periodate attack on internal and reducing end group glucose residue to be the same for this reaction.

For each molecule of DR consumed in the over-oxidation process (equation 4.7), one molecule of G is converted to R and four molecules of formic acid (F) are formed. Thus, at any time

$$[R] + [DR] = [R]_0 = \text{constant}$$

Also, the amount of G lost due to over-oxidation is

$$[G]_{\text{lost}} = [F]/4$$

Thus, a overall material balance for G can be written as

$$[G] = [G]_0 - [DG] - [F]/4$$

The total concentration of glucose units available at any time for conversion to the dialdehyde species is

$$\begin{aligned} [C] &= [G] + [R] \\ &= [G]_0 + [R]_0 - [DG] - [DR] - [F]/4 \\ &= [C]_0 - [DG] - [DR] - [F]/4 \end{aligned} \quad (4.8)$$

For each molecule of R disappearing, six molecules of periodate (P) are consumed and four molecules of formic acid (F) are formed. Thus, the amount of dialdehyde species remaining at any time will be

$$[DG] + [DR] = ([P]_0 - [P]) - (6/4)\ [F] \quad (4.9)$$

Combining equations (4.8) and (4.9) gives

$$[C] = [C]_0 - [P]_0 + [P] + 1.25\ [F] \quad (4.10)$$

Also, combining equations (4.4) and (4.9) gives

$$[DR] = ([P]_0 - [P] - 1.5\ [F])/n_0 \qquad (4.11)$$

4.3.4 Model

Periodate is consumed in three separate reactions - (4.5), (4.6) and (4.7). Durrence [9] has shown the first reaction to be second order, first order with respect to both G and P. Similarly, the second reaction will also be second order, first order with respect to both R and P.

The third reaction, (4.7), is much slower in rate, and as pointed out in Sec. 2.2.2, the hydrolysis of formyl ester (Fig. 2-7 II) and glyoxyl ester (Fig. 2-7 VII) are thought to be the rate determining steps. Thus, we should expect the disappearance of periodate to be first or second order. The order of DR in unknown, but for simple chemical kinetics, it is expected to be zero or one.

The periodate rate equation for reaction (4.5) is

$$\frac{d[P]}{dt} = - k_1\ [G]\ [P] \qquad (4.12)$$

and similarly for reaction (4.6), the rate equation is

$$\frac{d[P]}{dt} = - k_1\ [R][P] \qquad (4.13)$$

If the reaction orders for DR and P in reaction (4.7) are x and y, respectively, then the periodate rate expression for this reaction is

$$\frac{d[P]}{dt} = - k_2 [DR]^x [P]^y \qquad (4.14)$$

Thus, the overall rate equation for the consumption of P is

$$\frac{d[P]}{dt} = - k_1 [G][P] - k_1 [R][P] - k_2 [DR]^x [P]^y$$

$$= - k_1 [C] [P] - k_2 [DR]^x [P]^y \qquad (4.15)$$

since [G] + [R] = [C]

The above equation does not have an analytical solution, and thus it must be solved by numerical methods. All the quantities in equation (4.15) can be written in terms of the measured quantities [P] and [F]. Thus, to solve the above equation numerically, the rate equation for F needs to be utilized. For reaction (4.7) we have

$$\frac{d[F]}{dt} = - \frac{4}{5} \frac{d[P]}{dt} = \frac{4}{5} k_2 [DR]^x [P]^y \qquad (4.16)$$

Combining equations (4.10),(4.11), (4.15) and (4.16) gives the following two differential equations, which can be used to solve for [F] and [P]

$$\frac{d[P]}{dt} = - k_1 ([C]_0 - [P]_0 + [P] + 1.25 [F]) [P]$$
$$- (k_2/n_0^x)([P]_0 - [P] - 1.5 [F])^x [P]^y \qquad (4.17)$$

$$\frac{d[F]}{dt} = \frac{4}{5} (k_2/n_0^x) ([P_0] - [P] - 1.5[F])^x [P]^y \qquad (4.18)$$

There are four unknowns in the above equations, i.e., x, y, k_1 and k_2/n_0^x. Based on the assumptions made, the first two unknowns x and y (the orders of DR and P, respectively) were varied between the value of 0 to 1 and

1 to 2, respectively. Several permutations of x and y were provided as initial input to the program. The latter two unknowns, k_1 and k_2/n_0^x, were calculated by using the optimization subroutine of Powell's conjugate method, the objective function being the sum of the squares of the difference between theoretical and experimental values. The pair of differential equations (4.17) and (4.18) were solved by using the IMSL subroutine DGEAR with the following options selected: METH=2 (stiff method of DGEAR) and MITER=2 (chord method used with Jacobian calculated internally). A flowchart and the program used for kinetic modeling are given in the Appendix B.

4.3.5 Results

The values x = 0 and y = 1 gave the best overall fit for the experimental data. Thus, the orders of DR and P are 0 and 1, respectively. Fig. 4-12 shows the overall fit of the above model for a run at 60°C, while Fig. 4-13 shows the fit for only formic acid produced. Appendix C shows the fit for all the ten successful runs made during this study. The rate constants obtained for different temperatures are given in Table 4-2.

The above rate constants were used to make Arrhenius plots (see Figs. 4-14 and 4-15). The activation energies obtained from the plot for k_1 and k_2 were 11.5 and 19.1

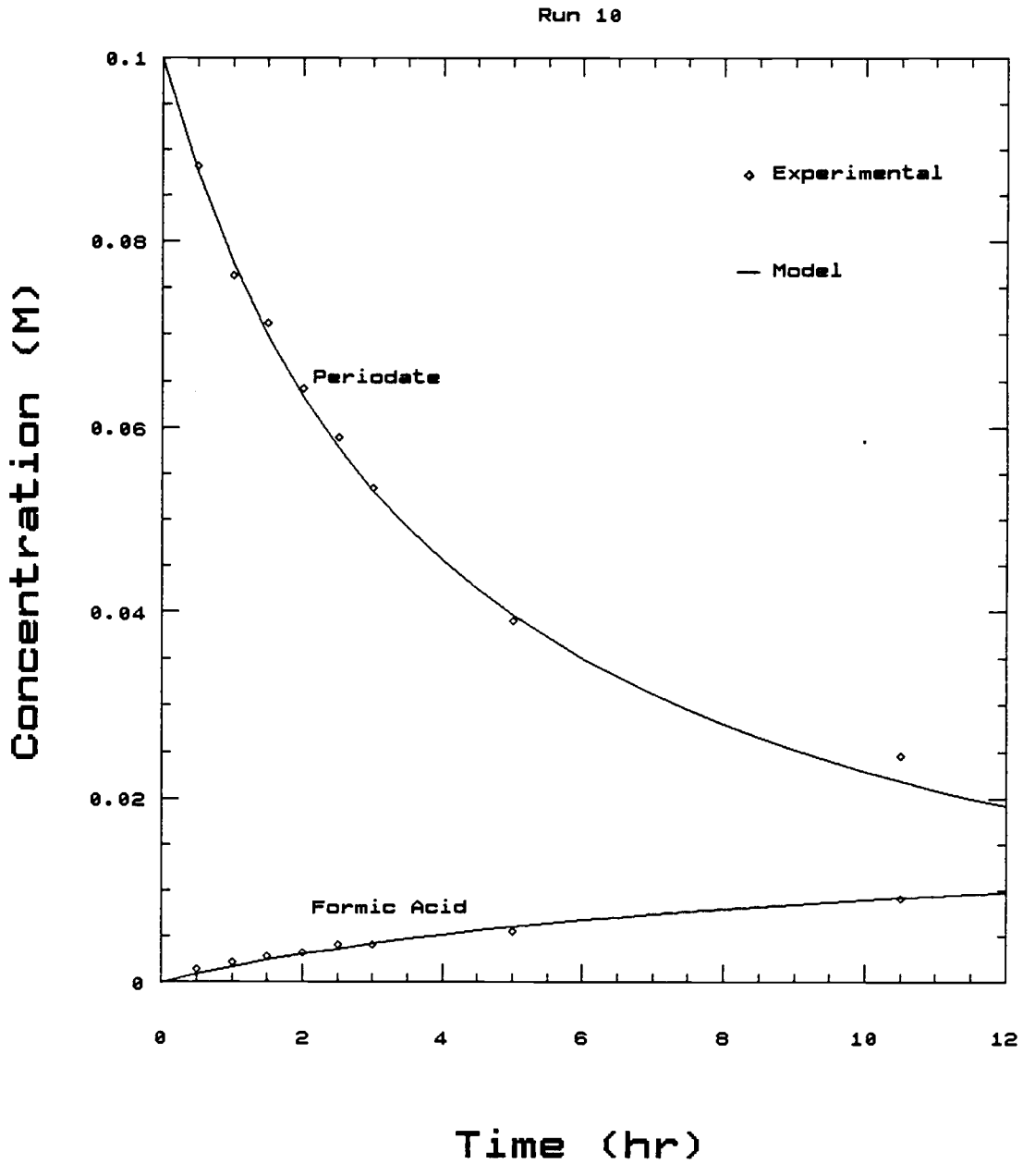


Figure 4-12: Overall Fit for the Proposed Model at 60°C.
Initial Conc.: Periodate = 0.1 M; Cellulose = 0.09 M

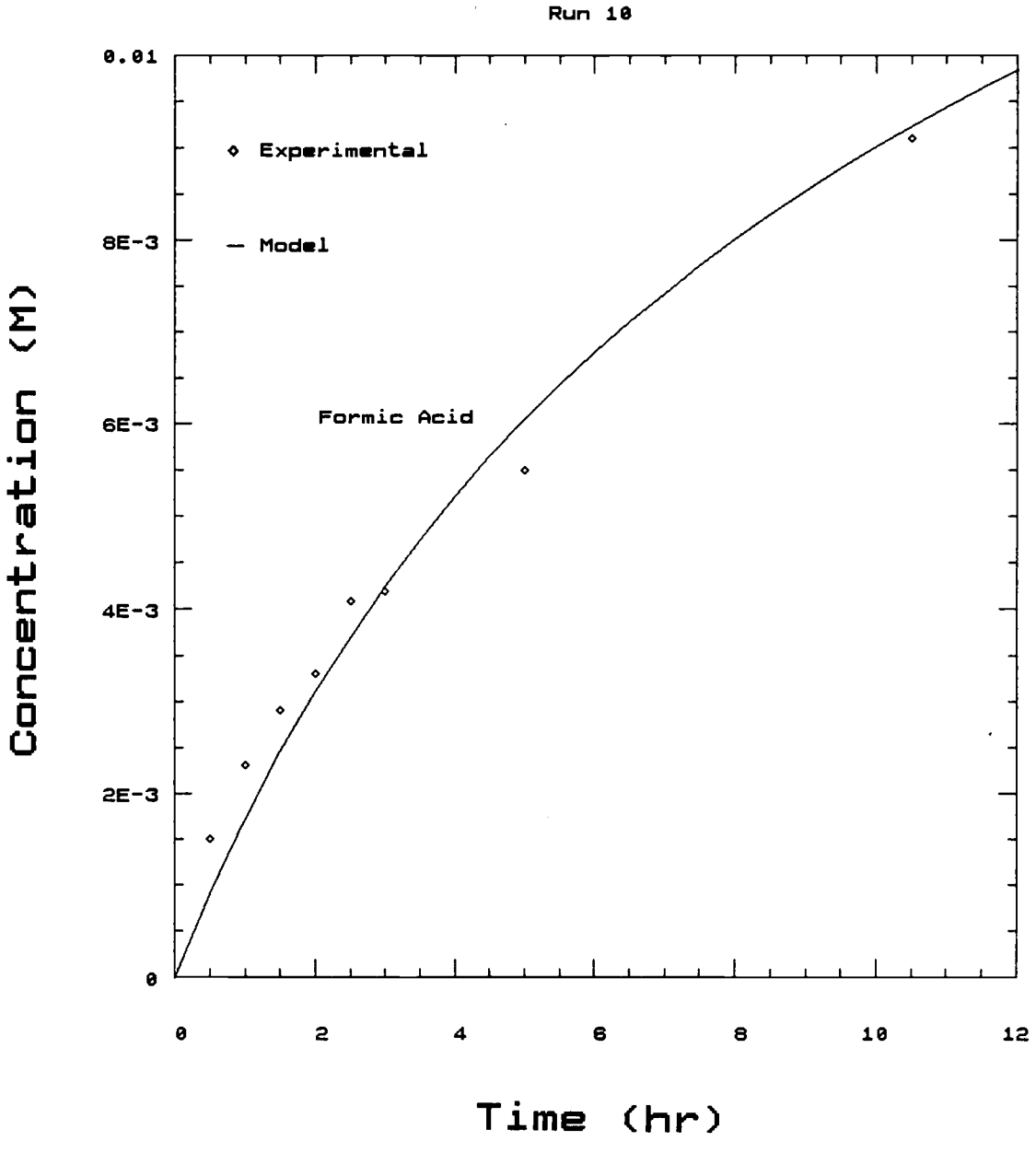


Figure 4-13: Fit for the Formic Acid Produced at 60°C.

Initial Conc.: Periodate = 0.1 M; Cellulose = 0.09 M

Table 4-2

Rate Constants for Different Runs

$[Cellulose]_0$ (M)	$[NaIO_4]_0$ (M)	Temperature (°C)	k_1 (hr^{-1})	k_2 (g-mol/hr)
0.08	0.1	32.5	0.543	0.00187
0.04	0.05	32.5	0.556	0.00101
0.08	0.1	40	0.74	0.00272
0.09	0.1	40	0.947	0.00387
0.08	0.1	45	1.166	0.00463
0.04	0.05	45	1.1397	0.00298
0.0617	0.1	50	1.44	0.00687
0.0185	0.05	50	1.256	0.0038
0.08	0.1	50	1.541	0.00962
0.09	0.1	60	2.866	0.025

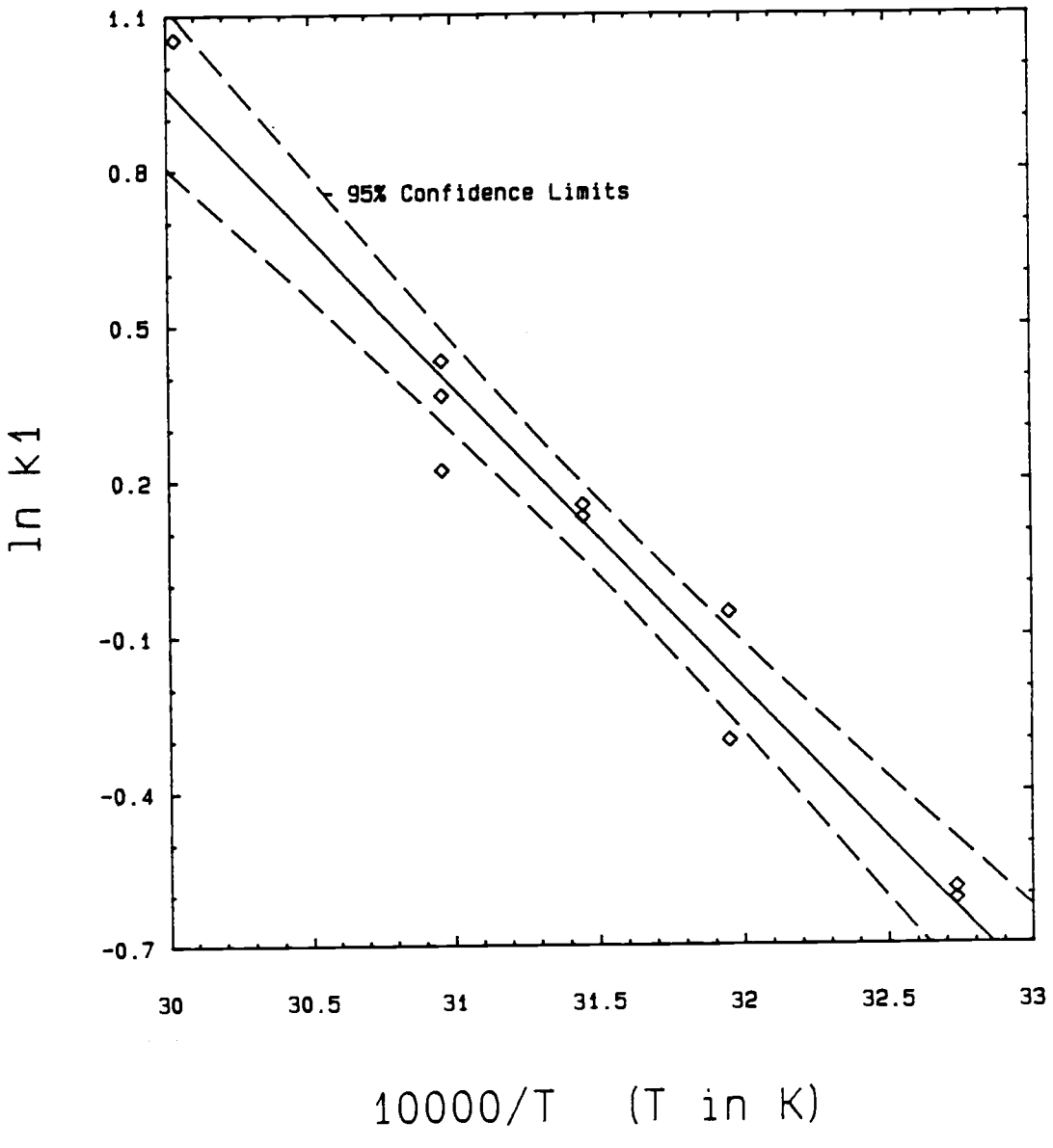


Figure 4-14: Arrhenius Plot for k_1

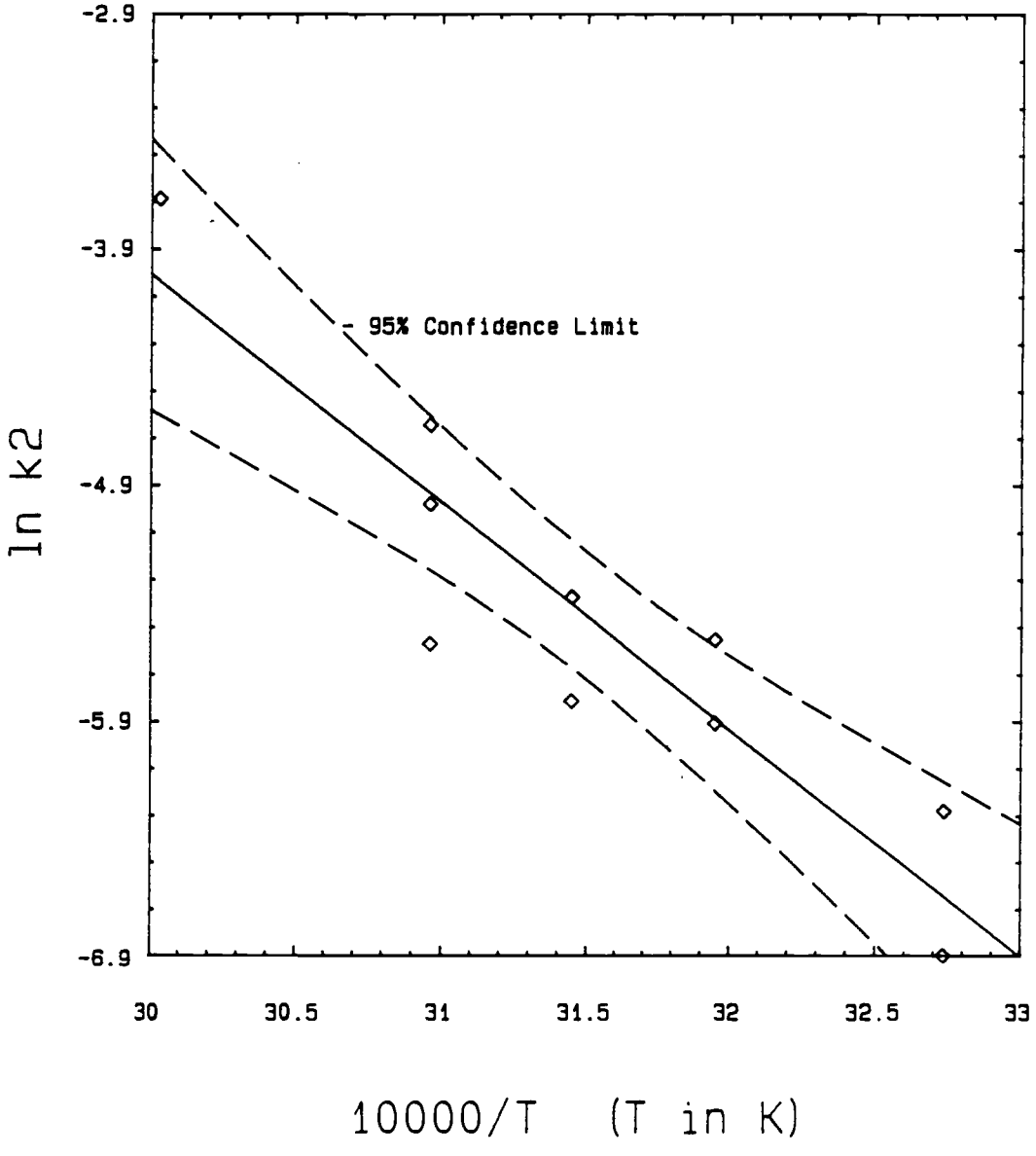


Figure 4-15: Arrhenius Plot for k_2

kcal/g-mol, respectively. The Arrhenius plot for k_2 shows a lot of scatter as compared to the same plot for k_1; this can be attributed to the greater error induced due to the measurement of very small concentrations of formic acid.

The value of x=0 in the above model signifies that the rate of reaction (4.7)

$$DR + 5\ P \xrightarrow{k_2} 4\ F + HCHO + CO_2 + IO_3^-$$

is independent of the DR concentrations. However, both k_1 and k_2 are expected to be functions of the end group concentration, and thus, they will change for different types of cellulose depending on the DP of cellulose. This argument is consistent with the fact that for cellulose with smaller DP, there will be more end groups, and hence higher rates of formic acid production, and vice versa.

Thus, the final proposed rate expression is,

$$\frac{d[P]}{dt} = - k_1 [C] [P] + k_2 [P]$$

$$\frac{d[F]}{dt} = \frac{4}{5} k_2 [P]$$

Fig. 4-16 compares the previous model proposed by Durrence with the model proposed above. The over-oxidation process has serious implications in periodate consumption. At 50°C and 60% periodate consumption, approximately 20% of the periodate consumed is used up for over-oxidation,

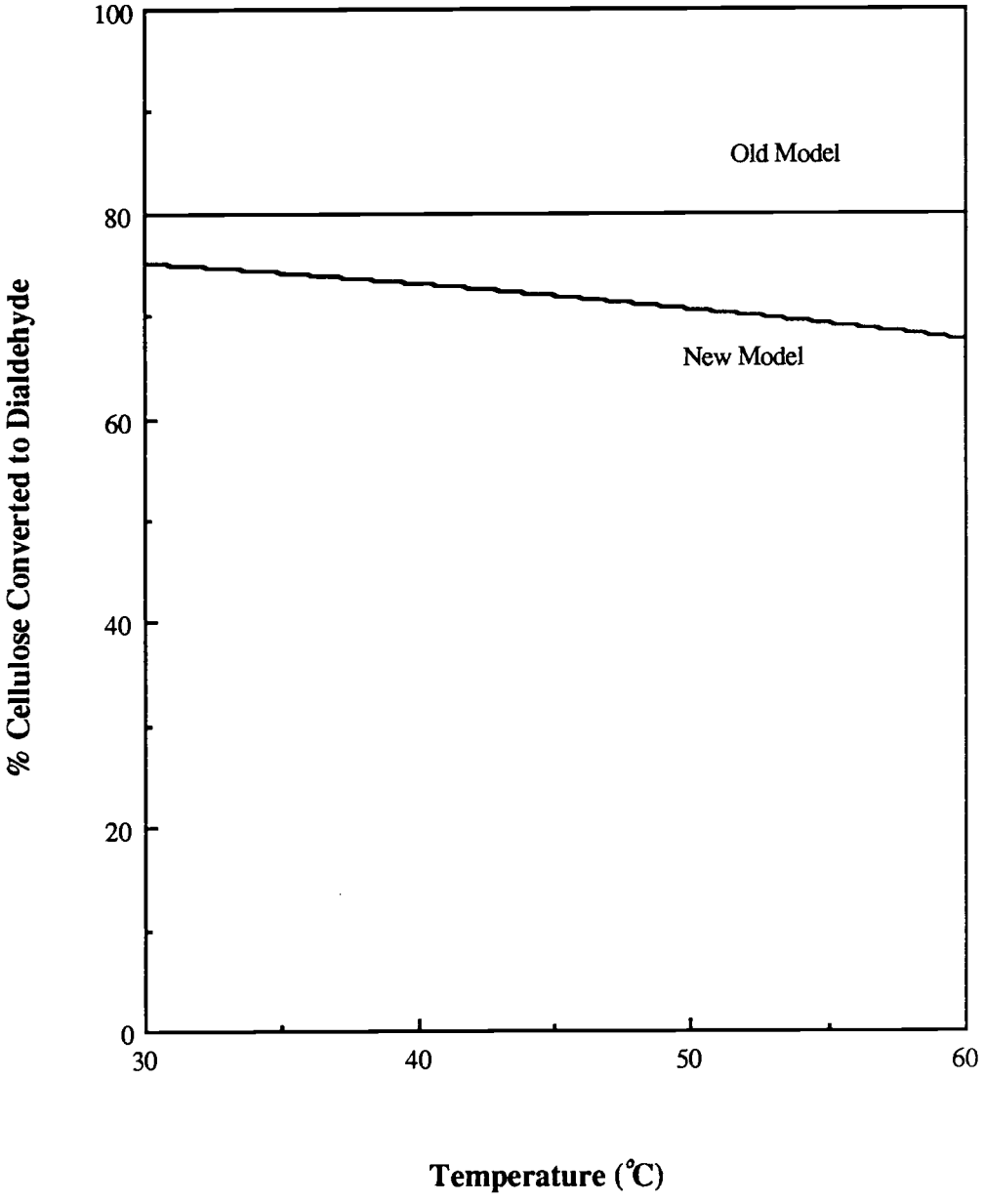


Figure 4-16: Conversion of Cellulose to Dialdehyde at 80% of Ideal Periodate Consumption (no over-oxidation)

while approximately 4% of the cellulose is lost in over-oxidation. Thus, over-oxidation must be accounted for; otherwise errors will be made in predicting the amount of dialdehyde cellulose produced based on periodate consumed.

CHAPTER 5: CONCLUSIONS

Periodate oxidation of cellulose and starch leads to a significant degree of over-oxidation at a temperatures above 40°C. Thus, any study for the periodate oxidation of cellulose and starch should include considerations for the over-oxidation process.

The sodium m-periodate oxidation of starch at 50°C gives approximately 70% yield of dialdehyde starch within ½ hr. Any further oxidation after this stage leads to an increasing degree of over-oxidation.

The periodate oxidation of cellulose involves two reaction, Malaprade type of oxidation (see Sec. 2.2.1) and over-oxidation. The former is a second order reaction, first order with respect to both periodate and cellulose concentration. The latter is first order with respect to periodate while zero order with respect to the end group concentration.

The over-oxidation process has serious implications on the periodate consumption. At 50°C and 60% periodate consumption, approximately 20% of the periodate consumed is used up for over-oxidation, while approximately 4% of the cellulose is lost in over-oxidation. Thus, it would be erroneous to neglect the over-oxidation process, as has

been done in the previous studies.

It was also found that prolonged oxidation degrades cellulose to a considerable extent, which is thought to be the direct result of random chain scission. The periodate breaks up cellulose polymer into fragments, some of which are so small that they go into the solution.

CHAPTER 6: RECOMMENDATIONS

The rate constant k_2, as obtained from the model proposed in this work, is a function of initial end groups present, i.e. it depends on DP. Further work is needed to find this dependency by investigating periodate oxidation of cellulose obtained from different sources and from different pretreatments. This study should include the measurements for the DP of all the types of cellulose used in the investigation.

Work is also needed to find the conditions (periodate concentration, temperature, pH, reaction time) under which the chain scission of the cellulose polymer becomes significant. This study could lead to the formulation of an integrated kinetic model for the periodate oxidation of cellulose, which would account for the increase in the rate of over-oxidation at higher reaction times.

Finally, a detailed study of the hydrolytic hydrogenation step in the production of ethylene glycol from cellulose is needed. The purpose of this study was to come up with a practical kinetic model for the periodate oxidation of cellulose, as applied to the production of ethylene glycol from cellulose, and a study of the above step will greatly complement this work.

REFERENCES

1. News Item, Chem. Engr. News, 56 (30), 28, 1978.

2. Goldstein, I.S., "Biomass Availability and Utility for Chemicals", Organic Chemicals from Biomass, Goldstein, I.S., Ed., CRC Press, 1981.

3. "Synthetic Organic Chemicals-US Productions and Sales", United States International Trade Commission, 1979-86.

4. Zinkel, D.F., "Turpentine, Rosin and Fatty Acids from Conifers", Organic Chemicals from Biomass, Goldstein, I.S., Ed., CRC Press, 1981.

5. Thompson, N.S., "Chemicals from Hemicellulose", Organic Chemicals from Biomass, Goldstein, I.S., Ed., CRC Press, 1981.

6. Goldstein, I.S., "Chemicals from Cellulose", Organic Chemicals from Biomass, Goldstein, I.S., Ed., CRC Press, 1981.

7. Stamm, A.J. and Harris, E.E., Chemical Processing of Wood, Chemical Publishing, 1953.

8. Otey, F.H., Sloan, J.W., Wilham, C.A. and Mehltretter, C.L., Ind. Eng. Chem., 53 (4), 267, 1961.

9. Durrence, G.M., "Ethylene Glycol and Other Oxychemicals from Cellulosic Materials", M.S. Thesis, Purdue Univ., 1984.

10. Narayan, R., Durrence, G.M. and Tsao, G.T., "Ethylene Glycol and Other Monomeric Polyols from Biomass", Biotechnol. Bioeng. Symp. Ser., 14, John Wiley & Sons, 1984.

11. Hough, L., "Periodate Oxidation of Neutral Polysaccharides: Oxidation to Formaldehyde", Meth. Carbh. Chem., Vol V, Whistler, R.L., Ed., Academic Press, 1965.

12. Hough, L. and Perry, B.M., Chem. & Ind. (London), 1421, 1957.

13. Cantley, M., Hough, L. and Pittet, A.O., Chem & Ind. (London), 1126, 1959.

14. Morrison, R.T. and Boyd, R.N., Organic Chemistry, Ch. 34-35, 3rd Ed., Allyn and Beacon, Inc., 1973.

15. Sjostrom, E., Wood Chemistry Fundamentals and Application, Appendix, Academic Press, 1981.

16. Nevell, T.P. and Zeronian, S.H., "Cellulose Chemistry Fundamentals", Cellulose Chemistry and its Applications, Nevell, T.P. and Zeronian, S.H., Ed., Halsted Press, 1985.

17. Corbett, W.M., "Determination of the Alpha-Cellulose Content of Cotton and Wood Cellulose", Meth. Carbh. Chem., Vol III, Whistler, R.L., Ed., Academic Press, 1965.

18. Anabar, M. and Guttman, S., J. Am. Chem. Soc., 83, 781, 1961.

19. Head, F.S.H. and Hughes, G., J. Chem. Soc., 2046, 1952.

20. Head, F.S.H., J. Text. Inst., 44, T209, 1953.

21. Malaprade, Bull. Soc. Chim., 43, 683, 1928.

22. Head, F.S.H. and Hughes, G., J. Chem. Soc., 603, 1954.

23. Courtois, J. and Ramer, M., Bull. Soc. Chim. Biol, 29, 240, 1947.

24. Hay, G.W., Lewis, B.A. and Smith, F., "Periodate Oxidation of Polysaccharides; General Procedures", Meth. Carbh. Chem., Vol V, Whistler, R.L., Ed., Academic Press, 1965.

25. Nevell, T.P., J. Text. Inst., 48, T484, 1957.

26. Fong, C.H., "Production of Ethylene Glycol and other Polyols from Wood", M.S. Thesis, Purdue University, 1986.

27. Goldfinger, G., Mark, H. and Siggia S., 35 (10), Ind. & Eng. Chem., 1083, 1943.

28. Davidson, G.F., J. Text. Inst., 32, T109, 1941.

29. Narayan, R and Tsao, G.T., "Annual Report to NSF, Conversion of cellulose and xylan to glycols", Grant

No. CPE 8218221, 1982.

30. Petropavlovskii, G.A., Chernova, Z.D. and Kotel'nikova, N.E., Zh. Prikl. Khim. (Leningrad), 50 (6), 1348, 1977.

31. Narkar, R.K. and Narkar, A.K., Text. Dyer Printer, 5 (1), 47, 1971.

32. Dixon, J.S. and Lipkin, D., Anal. Chem., 26, 1092, 1954.

33. Rankin, J.C. and Mehltretter, C.L., Anal. Chem., 28, 1012, 1956.

34. Mehltretter, C.L., "Production and Use of Dialdehyde Starch", Starch Chemistry and Technology, Vol II, Whistler, R.L. and Paschall, E.F., Editors, Academic Press, 1967.

35. Radley, J.A., Starch and its derivatives, 4th Ed., Chapman and Hall Ltd. (London), 1968.

APPENDICES

APPENDIX A

Data for Runs from 32.5 to 60°C

Run 1 at 32.5°C

$[Cellulose]_0$ = 0.08 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
1	0.0967	0.000574
3	0.0885	0.0008102
5	0.0817	0.0008864
7	0.0756	0.0011
12	0.06693	0.0016
19	0.05513	0.002
24	0.04999	0.0021

Run 2 at 32.5°C

$[Cellulose]_0$ = 0.04 M $[NaIO_4]_0$ = 0.05 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
1	0.04883	0.0001782
3	0.04667	0.000286
10	0.04056	0.0005168
19	0.03495	0.0006633
22	0.03346	0.0007236
24	0.03255	0.0007702
37	0.02785	0.001

Run 3 at 40°C

$[Cellulose]_0$ = 0.08 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
1	0.0962	0.0012
2	0.0898	0.0015
3	0.0864	0.0016
6	0.0708	0.0021
10	0.0654	0.0025
15	0.0512	0.0026

Run 4 at 40°C

$[Cellulose]_0$ = 0.09 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
3.0	0.0785	0.0014
5.0	0.0681	0.0018
11	0.051	0.0025
15	0.0435	0.00285
29.5	0.0294	0.0042

Run 5 at 45°C

$[Cellulose]_0$ = 0.08 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
1	0.0905	0.000711
3	0.077	0.0013
5	0.0675	0.0017
10	0.0523	0.0026
15	0.0431	0.0034
20	0.0382	0.0039
26	0.0291	0.0051

Run 6 at 45°C

$[Cellulose]_0$ = 0.04 M $[NaIO_4]_0$ = 0.05 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
1	0.04755	0.000223
3	0.0434	0.000444
5	0.04	0.000602
10	0.0341	0.000916
15	0.0287	0.0013
20	0.0267	0.0017

Run 7 at 50°C

$[Cellulose]_0$ = 0.0617 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
0	0.1	0
0.5	0.0962	0.000803
1	0.0937	0.001
3	0.0798	0.0019
5.5	0.0644	0.0027
10	0.0533	0.0037
15	0.0476	0.0056
20	0.0459	0.0063

Run 8 at 50°C

$[Cellulose]_0$ = 0.0185 M $[NaIO_4]_0$ = 0.05 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
0	0.05	0
0.5	0.05	0.00026
1	0.0484	0.000262
2.5	0.0477	0.000392
5	0.0458	0.000604
11	0.0395	0.0018
16.5	0.0337	0.002
21	0.036	0.0022
35.5	0.0306	0.0042

Run 9 at 50°C

$[Cellulose]_0$ = 0.08 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
0	0.1	0
1	0.0884	0.0013
3	0.0716	0.0022
5	0.0564	0.0032
10	0.0408	0.0042
15	0.036	0.0057
28	0.0277	0.0099

Run 10 at 60°C

$[Cellulose]_0$ = 0.09 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
0	0.1	0
0.5	0.0882	0.0015
1	0.07633	0.0023
1.5	0.0712	0.0029
2	0.0642	0.0033
2.5	0.059	0.0041
3	0.0534	0.0042
5	0.039	0.0055
10.5	0.0246	0.0091

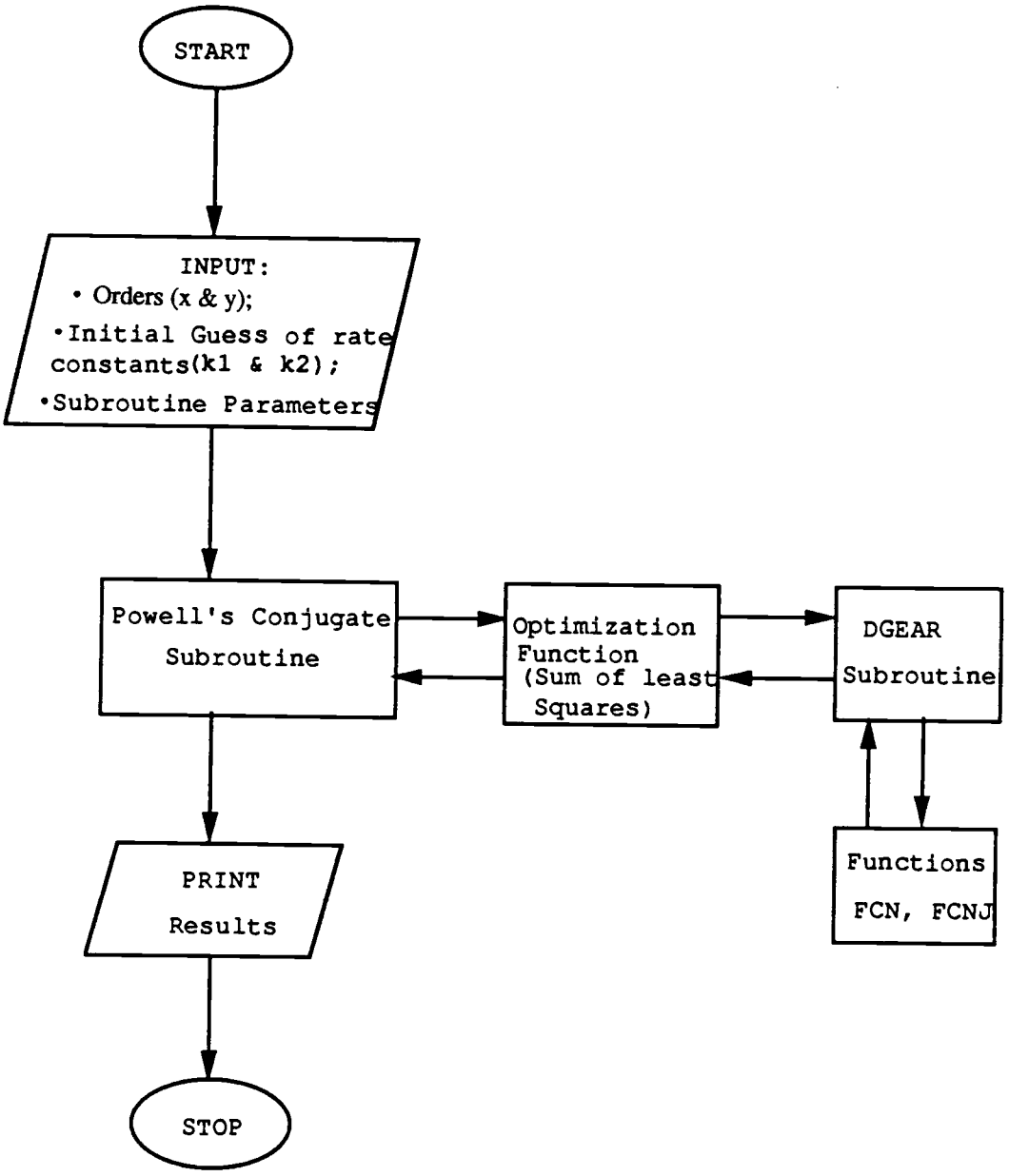
Run 11 at 50°C

$[Starch]_0$ = 0.08 M $[NaIO_4]_0$ = 0.1 M

Time (hr)	$[NaIO_4]$ M	[HCOOH] M
0	0.1	0
0.5	0.0446	0.0017
1	0.0434	0.0025
2	0.0454	0.003
3	0.0439	0.0033
5.5	0.0436	0.0046
10	0.0388	0.0062
15	0.0382	0.0058

APPENDIX B

Flow Chart and Listing of Computer Program Used in Modeling



Computer Program Used In Kinetic Modeling

```
      PROGRAM CELLULOSE
C
C THIS PROGRAM IS FOR THE KINETIC MODELING OF THE
C PERIODATE OXIDATION OF CELLULOSE.  THE ORDER OF BOTH
C (P) AND (DR) CAN BE VARIED IN THIS VERSION.
C K(2)=k3/n0,    K(1)=k1,   N & NR = ORDERS
C
      CHARACTER*20 DATA,OUT
      REAL E(2),W(10),K(2),N,ND

      COMMON/ONE/T2(10),P2(10),F2(10)
      COMMON/TWO/G0,P0
      COMMON/THREE/P1(100),F1(100)
      COMMON/FOUR/T1(100)
      COMMON/SIX/BB1,BB2,JJ
      COMMON/SEVEN/N,ND
      EXTERNAL CALCFX

      WRITE(*,*)'INPUT NAME OF DATA FILE & OUTPUT FILE'
      READ(*,*) DATA,OUT

      OPEN(UNIT=1,FILE=DATA,STATUS='OLD')
      OPEN(UNIT=2,FILE=OUT,STATUS='NEW')
      OPEN(UNIT=3,FILE='O',STATUS='NEW')

      JJ=0

      DO 5 J=1,10
           READ(1,*,END=7) T2(J),P2(J),F2(J)
           JJ=JJ+1
    5 CONTINUE

    7 WRITE(*,*) 'DOUBLE CHECK ? 1=NO , 2=YES'
      READ(*,*) M
      WRITE(*,*)'ENTER G0,IO40'
      READ(*,*) G0,P0
      WRITE(*,*) 'INPUT ORDER OF P & DR'
      READ(*,*) N,ND
    9 WRITE(*,*) 'INPUT k1 , (k2/n0)'
      READ(*,*) K(1),K(2)

      IF (K(1).LT.0) GOTO 100

      WRITE(2,*) 'DATA FILE=',DATA,'   ORDER=',N
      WRITE(2,*) 'GUESSES=',K(1),K(2)
      WRITE(*,*) 'ENTER E1,E2,ESCALE,MAXIT,IPRINT'
      READ(*,*) E(1),E(2),ESCALE,MAXIT,IP

C
C** NN IS THE NUMBER OF VARIABLES FOR THE OPTIMIZATION ***
```

```
C** METHOD***
C
      NN=2
      NSQP3N=NN**2+3*NN

      CALL BOTM(K,E,NN,NSQP3N,EF,ESCALE,IP,M,MAXIT,W)

      WRITE(*,10) K(1),K(2),EF
   10 FORMAT(1X,'OPTIMUM VALUES:'/1X,'k1=',
      # E10.5,5X,'k2/n0=',E10.5/1X,'SUM OF SQ.=',E10.5)
      WRITE(2,*)'OPTIMUM VALUES=',K(1),K(2)
      WRITE(2,*)'SUM OF SQ.=',EF
      DO 50 I=1,81
         DO 40 J=1,10
            IF(T1(I).EQ.T2(J)) THEN
              WRITE(2,20) T1(I),P1(I),P2(J),F1(I),F2(J)
              GOTO 50
            ENDIF
   40    CONTINUE
         WRITE(2,20) T1(I),P1(I),T1(I),F1(I),T1(I)
   50 CONTINUE
      WRITE(2,*)'BB1=',BB1,'   BB2=',BB2

   20 FORMAT(1X,F5.2,5X,4(F12.10,3X))

      GOTO 9

  100 CLOSE(UNIT=1)
      CLOSE(UNIT=2)

      STOP
      END
C
C***** NOTE: NOTATIONS ARE AS FOLLOWS:
C INITIAL CELLULOSE CONC. (@T=0)= G0
C INITIAL PERIODATE CONC.       = P0
C                       TIME    = T  ------- X FOR DGEAR
C                       [HCOOH] = F
C                       [IO4-]  = P
C                          Y(1) = P ! THESE ARE Y VALUES
C                          Y(2) = F ! FOR DGEAR METHOD
C                          K(1) = k1 ] X'S FOR OPTMIZATION
C                          K(2) = k2/(n0^N) ] SUBROUTINES
C
C       T1(100),P1(100),F1(100) -----> TO STORE THE
C                                      RESULTS FROM DGEAR
C                                      INTO AN ARRAY
C        T2(10),P2(10),F2(10) --------> FOR DATA FILE
C
C
      SUBROUTINE CALCFX(N,K,FUNC)
      REAL K(2),Y(2),WK(26)
```

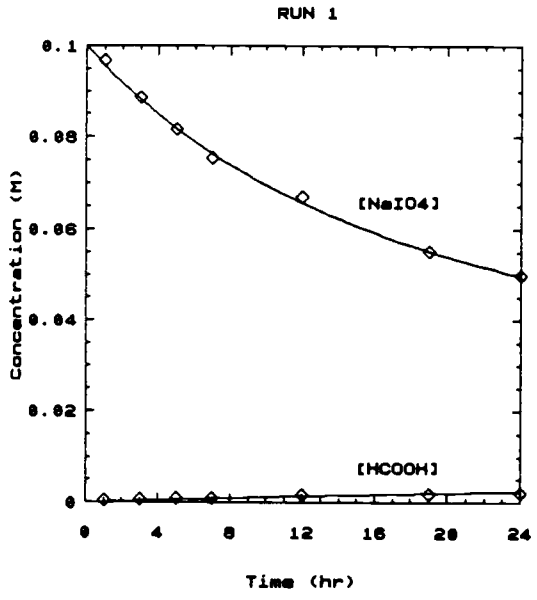
```
      INTEGER IWK(2)
      COMMON/ONE/T2(10),P2(10),F2(10)
      COMMON/THREE/P1(100),F1(100)
      COMMON/TWO/G0,P0
      COMMON/FOUR/T1(100)
      COMMON/FIVE/A,B
      EXTERNAL FCN,FCNJ

      DO 3 M2=1,100
        IF(M2.EQ.1) THEN
         P1(1)=P0
         F1(1)=0
        ELSE
         P1(M2)=0.
         F1(M2)=0.
        ENDIF
    3 CONTINUE

      Y(1)=P0
      Y(2)=0.

      IF(K(1).LT.0) THEN
        WRITE(*,*) '****** WARNING: K(1) < 0 ******'
        WRITE(2,*) '****** WARNING: K(1) < 0 ******'
        K(1)=A/10
      ELSEIF(K(2).LT.0) THEN
        WRITE(*,*) '****** WARNING: K(2) < 0 ******'
        WRITE(2,*) '****** WARNING: K(2) < 0 ******'
        K(2)=B/10
      ENDIF

      A=K(1)
      B=K(2)

C
C**** N1 IS THE NUMBER OF DIFFERENTIAL EQUATIONS.
C
      N1=2
      T=0
      H=0.00001
      TOL=0.0000005
      METH=2
      MITER=2
      INDEX=1
      J=1

      DO 20 L=5,400,5
         TEND=FLOAT(L)/10
      CALL DGEAR(N1,FCN,FCNJ,T,H,Y,TEND,TOL,METH,MITER,
     #           INDEX,IWK,WK,IER)

         J=J+1
```

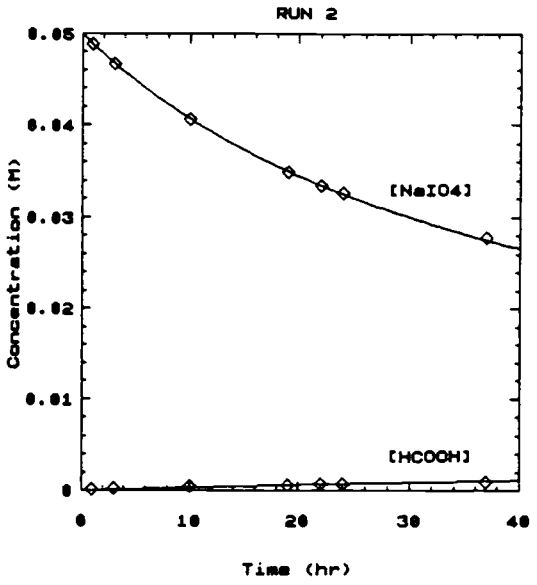
```
            T1(J)=T
            P1(J)=Y(1)
            F1(J)=Y(2)
   20    CONTINUE

         FUNC=SQ(T1,P1,F1)

         DO 50 II=1,81
            DO 40 J1=1,10
               IF(T1(II).EQ.T2(J1)) THEN
                WRITE(3,*) T1(II),P1(II),P2(J1),F1(II),F2(J1)
              ENDIF
   40       CONTINUE
   50    CONTINUE

         REWIND 3

         RETURN
         END
C
C
         FUNCTION SQ(T1,P1,F1)
         REAL T1(100),P1(100),F1(100),T2(10),P2(10),F2(10)
         COMMON/ONE/T2,P2,F2
         COMMON/SIX/BB1,BB2,JJ

         B=0
         BB1=0
         BB2=0

         DO 20 I=1,JJ
            DO 10 J=1,81
               IF(T1(J).EQ.T2(I)) THEN
C
C 100 & 1000 USED TO MAKE A LARGER OBJECTIVE FUNCTION !!!
C

                  Z1=1
                  Z2=1

                  AA1=(100*P2(I)*Z1-100*P1(J)*Z1)**2
                  AA2=(1000*F2(I)*Z2-1000*F1(J)*Z2)**2

                  BB1=AA1+BB1
                  BB2=AA2+BB2

                  B=AA1+AA2+B

               ENDIF
   10       CONTINUE
   20    CONTINUE
```

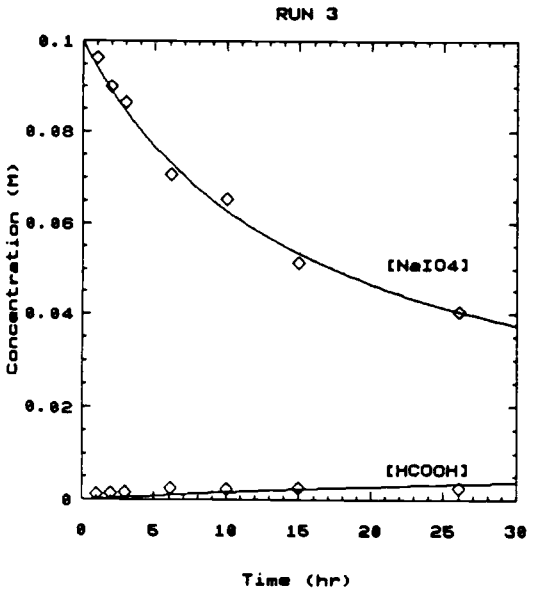
```
      SQ=B
      WRITE(*,*) 'BB1=',BB1,'    BB2=',BB2
      RETURN
      END
C
C
C
      SUBROUTINE FCN(N1,T,Y,YPRIME)
      REAL Y(N1),YPRIME(N1),T,K(2),N ,ND
      COMMON/FIVE/A,B
      COMMON/TWO/G0,P0
      COMMON/SEVEN/N,ND

      K(1)=A
      K(2)=B
      G=G0-P0+Y(1)+1.25*Y(2)
      DR=(P0-Y(1)-1.5*Y(2))
      IF(DR.LE.0) DR=0

      YPRIME(1)= -(K(1)*G*Y(1) + K(2)*(DR**ND)*Y(1)**N)

      YPRIME(2)= 0.8*K(2)*(DR**ND)*Y(1)**N

      RETURN
      END
C
C
C
      SUBROUTINE FCNJ(N1,T,Y,PD)
      REAL Y(N1),PD(N1,N1),T
      RETURN
      END
```

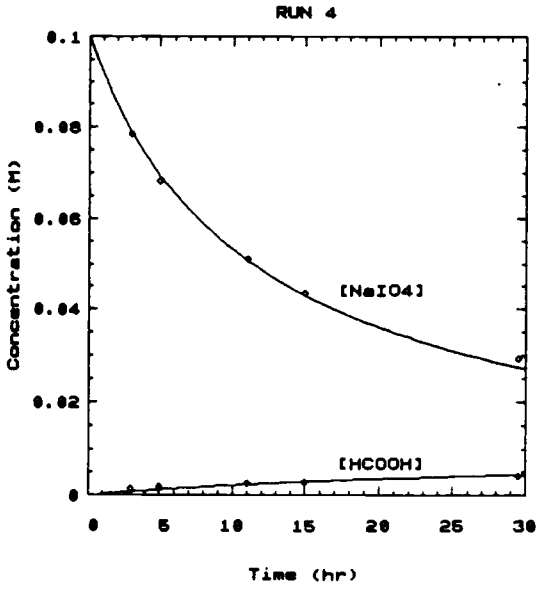
APPENDIX C

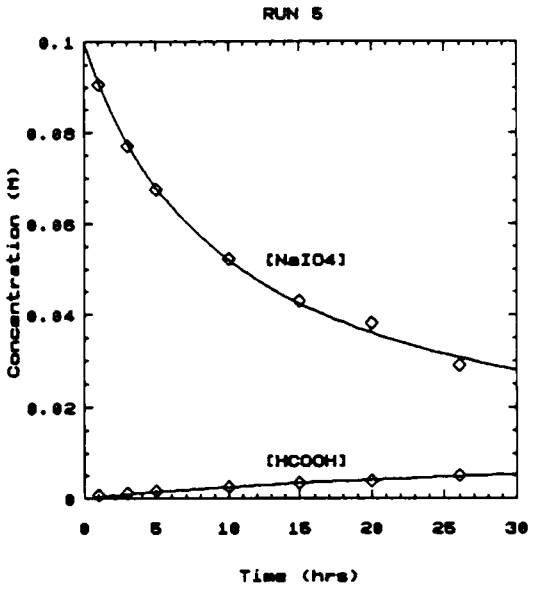
Fit of the Proposed Model for All Experimental Data

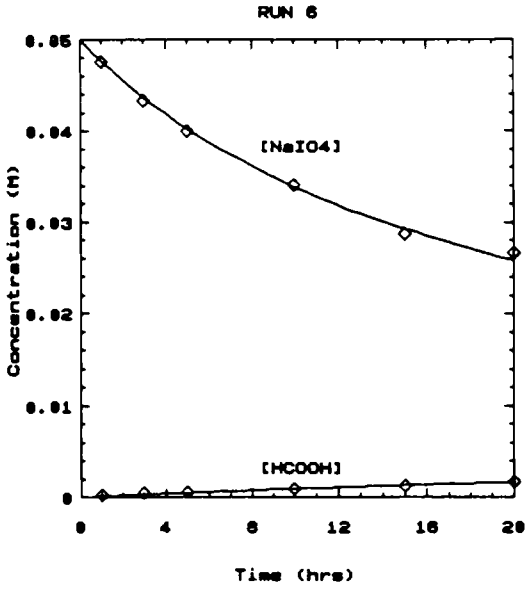


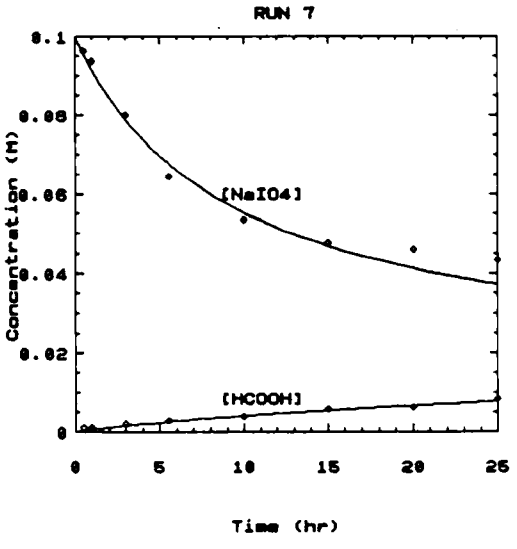


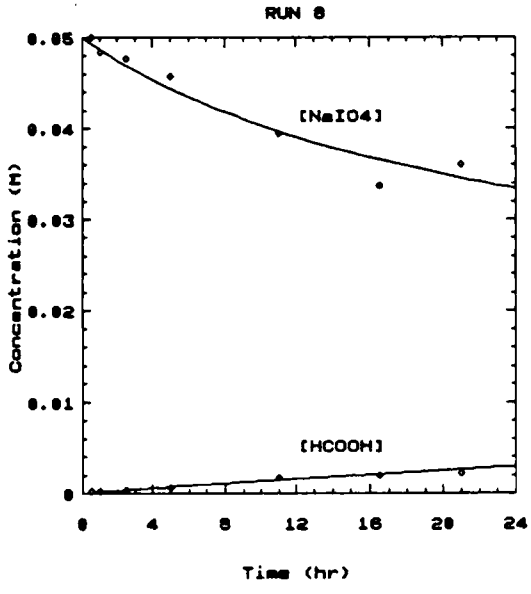


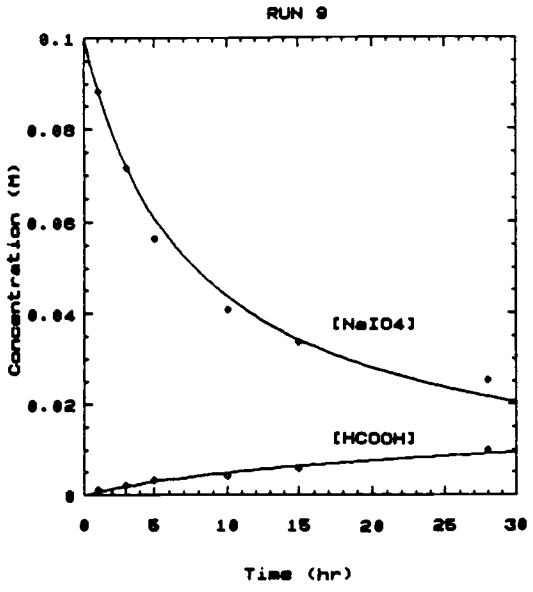


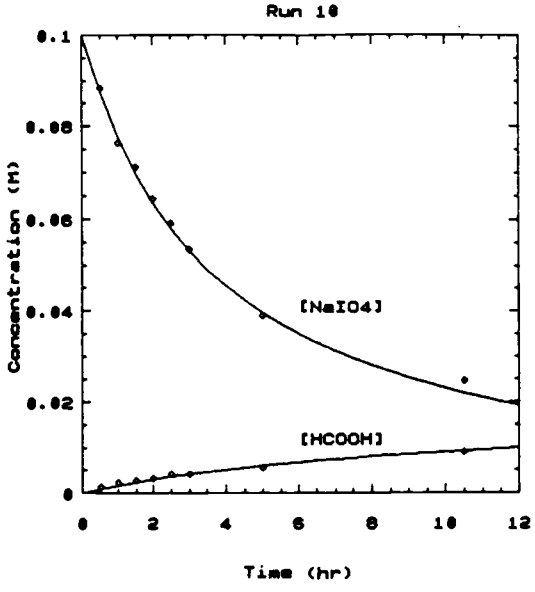

RUN 5
Concentration (M)
0.1
0.08
0.06
0.04
0.02
0
[NaIO4]
[HCOOH]
0
5
10
15
20
25
30
Time (hrs)


RUN 6
Concentration (M)
0.05
0.04
0.03
0.02
0.01
0
[NaIO4]
[HCOOH]
0
4
8
12
16
20
Time (hrs)


RUN 7
Concentration (M)
0.1
0.08
0.06
0.04
0.02
0
[NaIO4]
[HCOOH]
0
5
10
15
20
25
Time (hr)


RUN 8
Concentration (M)
0.05
0.04
0.03
0.02
0.01
0
[NaIO4]
[HCOOH]
0
4
8
12
16
20
24
Time (hr)


RUN 9
Concentration (M)
0.1
0.08
0.06
0.04
0.02
0
[NaIO4]
[HCOOH]
0
5
10
15
20
25
30
Time (hr)


Run 10
Concentration (M)
0.1
0.08
0.06
0.04
0.02
0
[NaIO4]
[HCOOH]
0
2
4
6
8
10
12
Time (hr)