AN ABSTRACT OF THE THESIS

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Cellulosic biomass materials have three principal components: cellulose, hemicellulose, and lignin. Under mild acid conditions and high temperature, the first two components yield a variety of sugars: hexoses and pentoses, which are subject to decomposition on continued exposure to hot dilute acid. In the process hexoses yield hydroxymethylfurfural (HMF) which, on continued heating, yields levulinic acid and formic acid and some uncharacterized solid products. Biomass hydrolysis research has now progressed to the point where process analysis and optimization requires a generalized kinetic correlation for hexose degradation. The kinetics for the reaction of glucose to HMF has been studied previously. However, not all of the rate constants for the dehydration of glucose and HMF had been modeled to fit the experimental data.

This research had two parts. The first was to model the kinetics for the formation of HMF from glucose in the aqueous phase using the three-constant model suggested by S. W. McKibbins et al. (1962). The other was to study the aqueous-phase reaction carried in the presence of an organic solvent, o-nitrotoluene (ONT), for the purpose of extracting HMF as it is produced; thereby minimizing subsequent degradation of HMF to levulinic acid, formic acid, and solid materials.

The HMF distribution coefficient for o-nitrotoluene was measured at different temperatures and modeled as the integrated Van't Hoff equation.

Predicted glucose, HMF, and organic acids concentration profiles were compared to the experimentally determined values. The predicted concentration profiles are in good agreement with the experimental data, indicating that the proposal three-constant model is consistent with the true reaction system. In the two-phase system case study, the process was diffusion limiting due to lack of agitation of the mixture.

MODELING THE CONVERSION OF GLUCOSE TO HYDROXYMETHYLFURFURAL

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Typed by Researcher for Daming Liu

To my wife, Lingxiu,

my mother and late father

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NOMENCLATURE

a_i	power on catalyst acid concentration in Arrhenius equation for k_i ($i = 1, 2, 3$)
acid	sulfuric acid catalyst
D	degradation products of hydroxymethylfurfural
E_i	activation energy for k_i ($i = 1, 2, 3$), cal/g-mol
f_{H+}	fugacity of hydrogen iron
F	a function of sulfuric acid concentration
G	glucose
ΔH	heat of hydroxymethylfurfural transfer
HMF	hydroxymethylfurfural
I	glucose-to-hydroxymethylfurfural intermediates
k_1, k_2	first-order rate constants, min^{-1}
k_3	second-order rate constant, liters/g-mol min
m	equilibrium distribution coefficient for hydroxymethlfurfural
m_0	hydroxymethylfurfural equilibrium distribution coefficient extrapolated to infinite temperature
ONT	o-nitrotoluene
P	condensation products formed by the combination of hydroxymethylfurfural with its precursors
R	gas law constant = 1.987 cal/g-mol K
SSE	sum of squares error
t	batch reaction time, min

T	temperature, °C or K
V_a, V_s	volume of aqueous and solvent phases respectively, liters
yield	moles of HMF produced per mole of glucose fed to a batch reactor
[ ]	concentration, g-mol/liter or M

Greek Symbols

α_G	activity coefficient for glucose
α_{H+}	activity of hydrogen ion
α_{HMF}	activity coefficient for hydroxymethylfurfural
Φ	volume ratio of solvent to aqueous phase in a two-phase system, (V_s/V_a)

Subscripts

a	aqueous phase
e	equilibrium conditions
s	solvent phase
0	initial or reference condition

MODELING THE CONVERSION OF GLUCOSE TO HYDROXYMETHYLFURFURAL

CHAPTER 1

INTRODUCTION

Attempts to utilize the carbohydrate fraction of agricultural residues have been directed toward the development of processes for the production of simple sugars. During the hydrolysis of the cellulosic material, there is heavy destruction of monosaccharides resulting in low yields of sugar that is contaminated with large quantities of hydroxymethylfurfural (HMF), furfural, levulinic acid, formic acid and uncharacterized humic materials. A thorough understanding of the competitive reactions which take place during the production of glucose from cellulose is needed for the optimum design of a cellulose hydrolysis plant.

The kinetics for the acid catalysis of glucose to HMF and then levulinic and formic acids has been studied extensively (Saeman, 1945; McKibbins et al., 1962; Taylor et al., 1971; Smith et al., 1981; Bienkowski et al., 1986). However, some of the researchers' models did not fit the experimental data well. After analyzing their experimental data, Mckibbins et al. (1962) proposed a three-constant model to explain the experimental phenomena, but did not determine all of the parameters in the kinetic expression.

Solvent extraction has been suggested for increasing the yield of intermediate products during the conversion of biomass to the degradation products in a well agitated reaction system (Sproull, 1986).

This research project deals with the production of HMF from glucose using a kinetic model suggested by S. W. McKibbins et al. in the Forest Products Journal of January, 1962. The first portion of the research determined the validity of McKibbins aqueous phase model for predicting HMF formation from glucose, which entailed the determination of kinetic constants by performing a computer optimization on the sum of squares of differences between McKibbins' HMF concentration data and concentration profiles predicted by the model. McKibbins' HMF yield data were used to evaluate kinetic constants in the proposed model as a function of temperature and sulfuric acid concentration. Several aqueous phase experiments were conducted here at Oregon State University to verify glucose disappearance and HMF formation rates predicted by McKibbins' model. Predicted glucose, HMF, and total organic acids concentration profiles, based on the proposed model, were compared to the experimental data.

The second part of the research evaluated the potential of using o-nitrotoluene (ONT) as a solvent for recovering

HMF from reacting aqueous solutions. The HMF distribution coefficient for o-nitrotoluene was measured as a function of temperature. Two-phase experiments were conducted at 180 and 200°C with glucose being converted to HMF in the presence of o-nitrotoluene. McKibbins' kinetic model was used to predict the two-phase production of HMF from glucose in a batch reactor assuming (1) a diffusion-controlled process and (2) a process with instantaneous mass transfer.

CHAPTER 2

THEORY

2.1 Conversion of Glucose to Hydroxymethylfurfural

Hydroxymethylfurfural is produced in an acidified aqueous glucose solution and also decomposes under these same conditions. Kinetic treatment of the decomposition has been described by the reaction mechanism represented by

$$\text{Glucose} \dashrightarrow \text{HMF} \dashrightarrow \text{Levulinic acid} + \text{Formic acid}$$

(Singh et al., 1948; Wing, 1960; Mckibbins et al., 1962) and by

$$\text{Glucose} \dashrightarrow \text{Intermediate} \dashrightarrow \text{HMF} \dashrightarrow \begin{array}{c}\text{Levulinic acid}\\ + \\ \text{Formic acid}\end{array}$$

(Wolform et al., 1948; Taylor et al., 1971).

The dehydration of glucose in dilute solutions of mineral acid has been shown to follow a first-order rate law (Saeman, 1945; McKibbins et al., 1962; Heimlich and Martin, 1960; Bienkowski et al. 1984).

$$\frac{d[G]}{dt} = - k_1[G] \qquad (2\text{-}1)$$

where [G] is the concentration of glucose, t the time of the batch reaction, and k_1 the first-order rate constant for glucose dehydration.

The disappearance of HMF in dilute mineral acids has also been investigated and shown to be a first-order reaction (Teunissen, 1931; Singh et al., 1948; McKibbins et al. 1962).

$$\frac{d[HMF]}{dt} = - k_2[HMF] \qquad (2\text{-}2)$$

where [HMF] is the concentration of hydroxymethylfurfural and k_2 is the first-order rate constant for HMF degradation.

Singh et al. (1948) have shown that levulinic acid displays no marked tendency to decompose at these reaction conditions. Formic acid is also a very stable product; therefore, further decomposition reaction need not be considered. However, an overall experimental study of this series of reactions showed that the yield of HMF increases as the initial glucose concentration is decreased (McKibbins, 1962). This indicates that HMF disappears by a higher order reaction (Levenspiel, 1972). Since the HMF disappearance study indicated a first-order decay for HMF it appears likely that the HMF reacts with one of its precursors rather than with itself or with one of its reaction products. This notion is supported by the fact that McKibbins observed that approximately 25% of the initial glucose in glucose-to-HMF experiments was converted to solid materials.

A possible model suggested by McKibbins et al. that would account for the observed behavior is:

$$G \xrightarrow{k_1} I \xrightarrow{k_1'} \text{HMF} \xrightarrow{k_2} D$$

$$I + \text{HMF} \xrightarrow{k_3'} P$$

where

G = glucose

I = glucose-to-HMF intermediates

HMF = hydroxymethylfurfural

D = degradation products

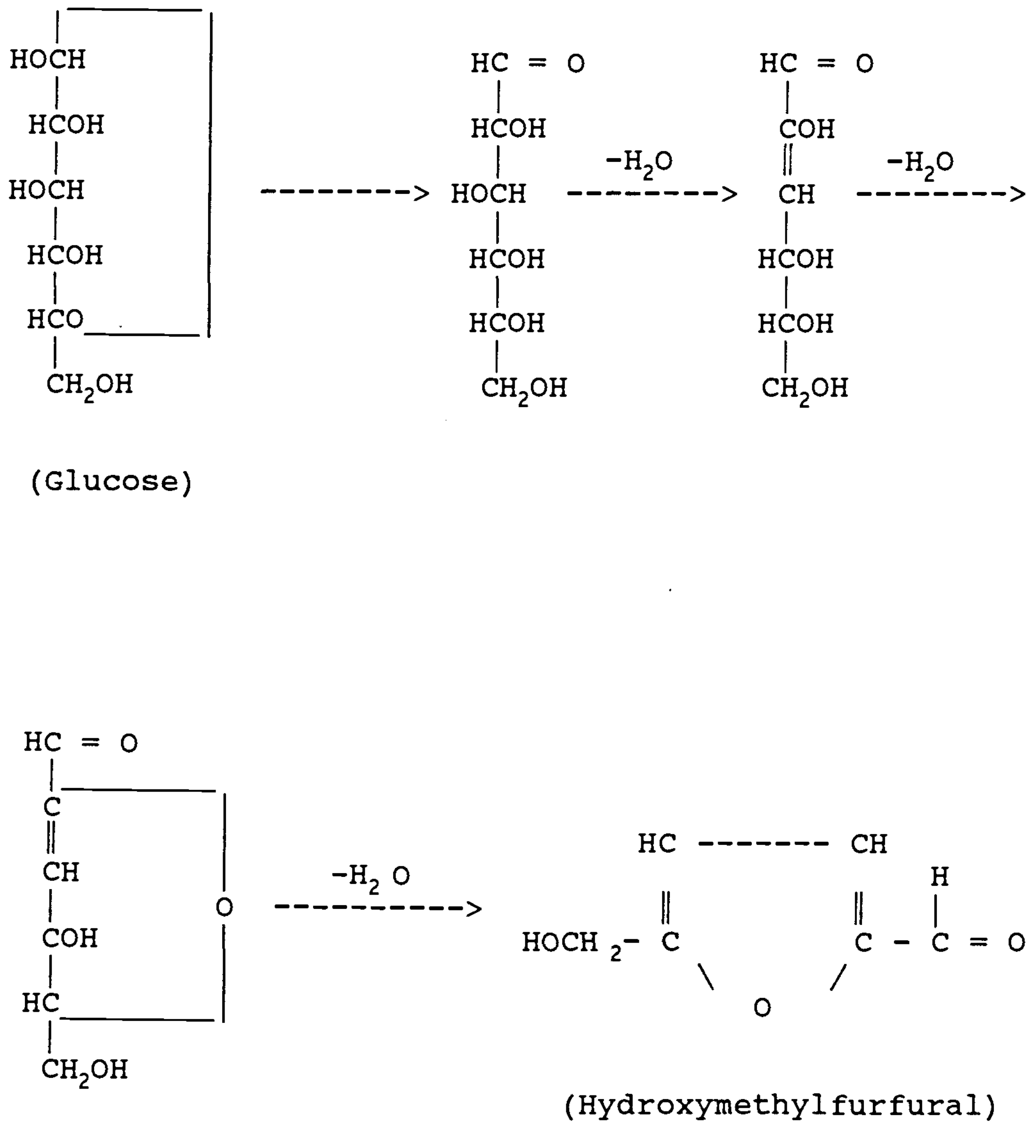
P = solid materials

and k_1, k_1', k_2, and k_3' are the corresponding rate constants for this model.

The exact mechanism for the acid catalyzed conversion of glucose to HMF has not yet been fully deduced; however, Ulbricht et al. (1984) have suggested the multi-intermediate step reaction sequence illustrated in Figure (2-1).

FIGURE 2-1

Proposed Mechanism for the Dehydration of Glucose to Hydroxymethylfurfural (Ulbricht et al. 1984)



The kinetic rate equation for glucose conversion in the McKibbins model is given by Equation (2-1). The rate expressions for the glucose-to-HMF intermediates, lumped together as I, and HMF are:

$$\frac{d[I]}{dt} = k_1[G] - k_1'[I] - k_3'[I][HMF] \qquad (2\text{-}3)$$

and

$$\frac{d[HMF]}{dt} = k_1'[I] - k_2[HMF] - k_3'[I][HMF] \qquad (2\text{-}4)$$

where [I] is the concentration of intermediates and all of the rate constants are from McKibbins model.

According to the steady-state approximation, the intermediates are present in very small quantities; thus, their rates of change in the system after a short time can never be great. Therefore, with negligible error, the rate of change of the concentration of intermediates can be set to zero:

$$\frac{d[I]}{dt} = 0 \qquad (2\text{-}5)$$

By making use of this steady-state approximation, Equation (2-3) can be solved for [I] to obtain:

$$[I] = \frac{k_1[G]}{k_1' + k_3'[HMF]} \qquad (2\text{-}6)$$

Since the presence of HMF is observed, the destruction of HMF must be considerably slower than its formation, thus, one can make the approximation that:

$$k_1' \gg k_3' [HMF] \qquad (2\text{-}7)$$

Therefore, the expression for [I] in Equation (2-6) reduces to:

$$[I] = \frac{k_1[G]}{k_1'} \tag{2-8}$$

Substituting Equation (2-8) into Equation (2-4) gives the simplified kinetic rate equation for HMF:

$$\frac{d[HMF]}{dt} = k_1[G] - k_2[HMF] - k_3[G][HMF] \tag{2-9}$$

where the kinetic constant k_3 is defined as:

$$k_3 = \frac{k_1 k_3'}{k_1'} \tag{2-10}$$

All of the kinetic constants can be modeled by the Arrhenius expression with a proportionality factor for the sulfuric acid concentration:

$$k_i = k_{i0} \exp(-E_i/RT)\ F([H_2SO_4]) \qquad (2\text{-}11)$$

where for i = 1, 2, 3

k_{i0} = the pre-exponential factor

E_i = activation energy for the reaction (cal/g-mol K)

R = gas constant (1.987 cal/g-mol K)

T = temperature (K)

$[H_2SO_4]$ = catalyst concentration (M)

F = a function of $[H_2SO_4]$

2.2 Two-Phase Kinetics

The dehydration of glucose in acidic aqueous media includes several side reactions which reduce the yield of HMF (Scallet and Gardner, 1945; Heimlich and Martin, 1960; McKibbins et al.,1962; Taylor et al.,1971). In the hydrolysis reaction that converts hexosans to hexoses, a considerable amount of the monosaccharide reacts to form HMF and then levulinic acid and formic acid, which appear in the product as undesirable contaminants (Saeman, 1945; Garves, 1981). In both processes high yields of the desired product can only be achieved by the removal of HMF from the reaction zone.

There are three choices for the removal of HMF from the acidified aqueous phase; solvent extraction, adsorption on solids and steam distillation. The first method is probably the most economically feasible choice.

Extraction of the HMF into a solvent phase can be modeled as a two-phase system with the assumption that both liquids are totally immiscible. The distribution coefficient for any given component is a measure of how the component distributes between two immiscible phases. In this project the distribution of HMF between an organic solvent phase and an acidic aqueous phase is of interest. Accordingly, the distribution coefficient for HMF is defined as the equilibrium ratio of the concentration of HMF in the solvent phase to the concentration of HMF in the aqueous phase:

$$m = \frac{[HMF]_{se}}{[HMF]_{ae}} \tag{2-12}$$

where

$[HMF]_{se}$ = hydroxymethylfurfural concentration in solvent phase at equilibrium (M)

$[HMF]_{ae}$ = hydroxymethylfurfural concentration in aqueous phase at equilibrium (M)

Since the HMF distribution coefficient is an equilibrium constant, its temperature dependence is expected to follow the Van't Hoff equation:

$$m = m_0 \exp(-\Delta H/RT) \tag{2-13}$$

where

m_0 = the extrapolated value for m at infinite temperature.

ΔH = the enthalpy change (cal/g-mol) for the transfer of HMF from water to the solvent.

In the two-phase system, two processes are taking place, the formation and degradation of HMF in the aqueous phase plus the mass transfer of HMF from the aqueous phase to the solvent phase. If the rate of formation of HMF is much bigger than the rate of interphase mass transfer, the simplifying assumption of diffusion-controlled can be applied. In the limit, the rate of formation of HMF can be predicted by the aqueous phase reaction rate expression, Equation (2-9).

The other extreme is when the process is reaction-controlled. In this case the slow step is the rate of formation of HMF in the aqueous phase. For this extreme of instantaneous mass transfer, Sproull (1986) has shown that

$$\frac{d[HMF]}{dt} = \frac{k_1[G] - k_2[HMF] - k_3[G][HMF]}{1 + m\Phi} \qquad (2\text{-}14)$$

where

$$\Phi = \frac{\text{Volume of Solvent Phase } (V_s)}{\text{Volume of Aqueous Phase } (V_a)} \qquad (2\text{-}15)$$

The third possibility is when the process is neither reaction nor diffusion-controlled, in which both effects are significant. In this situation, the rate of formation of HMF will be between the extremes given by Equations (2-9) and (2-14). Accurate computation of HMF yields under such condition requires HMF mass transfer coefficient data.

CHAPTER 3

LITERATURE REVIEW

3.1 Glucose Dehydration

Glucose is an intermediate product in the conversion of biomass to liquid fuels and chemicals via acid hydrolysis and subsequent fermentation. The general scheme of glucose dehydration in acid solution has been given by Wolfram, Schuetz, and Cavalieri (1948). The acid-catalyzed decomposition of glucose has been described as a first order reaction.

Many studies have been conducted to estimate the kinetic parameters for glucose dehydration. Five possible models for correlating the first-order rate constant for glucose dehydration as a function of acid concentration and reaction temperature have been compared by Bienkowski et al. (1987). This comparison is given in Table (3-1). Bienkowski's criteria for model discrimination is the comparison of root mean square residuals, i.e., the square root of the sum of the squares of the residuals divided by the degrees of freedom, where the degrees of freedom is the number of data points minus the number of adjustable parameters. Bienkowski showed that Models 1 and 2 have considerably smaller residuals than the other models. Since this project focuses on the model and data presented by Saeman, McKibbins and their coworkers, only Model 1 (with k_1 directly proportional to acid concentration raised to the power a_1) will be given further consideration.

The ranges of experimental conditions used by various investigators and their kinetic parameters for k_1 are given for Model 1 in Table (3-2). Note that the k_1 data has been fitted to a three-parameter expression based on Model 1 in Table (3-1).

$$k_1 = k_{10} \, [H_2SO_4]^{a1} \exp(-E_1/RT) \qquad (3\text{-}1)$$

as well as to a two-parameter expression based on the acid exponent of Model 1 forced to be 1.00.

$$k_1 = k_{10} \, [H_2SO_4] \exp(-E_1/RT) \qquad (3\text{-}2)$$

According to the root mean square residual values calculated by Bienkowski et al. (1987), each set of k1 data from various investigators fits Equation (3-2) well, but a slight improvement can be obtained when the acid exponent a is allowed to float as in Equation (3-1). Therefore, a three-parameter expression, including k_{10}, a_1, and E_1, based on Model 1 was chosen in the over-all kinetic study.

TABLE 3-1

Proposed Models for the First-Order Glucose Dehydration Kinetic Constant

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MODEL 1 (Saeman, 1945; later Mckibbins, 1962; modified by McCarty et al.*)

$$\ln k_1 = \ln k_{10} + a_1 \ln [H^+] - E_1/RT$$

MODEL 2 (rapid protonation; Liler*)

$$\ln k_1 = \ln k_{10} + \ln [H^+] + \ln f_{H+} - E_1/RT$$

MODEL 3 (same as MODEL 2, except f_{H+} temperature dependence added)

$$\ln k_1 = \ln k_{10} + \ln [H^+] + \ln f_{H+}(T) - E_1/RT$$

MODEL 4 (MODEL 1 modified for slow proton transfer)

$$\ln k_1 = \ln k_{10} + a \ln [H^+] - E_1/RT - E_{11}[H^+]/RT$$

MODEL 5 (same as MODEL 4, except $[H^+]$ replaced by activity, α_{H+})

$$\ln k_1 = \ln k_{10} + a_1 \ln [\alpha_{H+}] - E_1/RT - E_{11}[\alpha_{H+}]f_{H+}/RT$$

where f_{H+} and α_{H+} are the fugacity and activity for hydrogen ions in the aqueous solution; the activation energy is a linear function of the hydrogen iron concentration in Models 4 and 5.

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* These articles were referenced by Bienkowski et al. (1987) as follows:

Liler, M., Reaction Mechanisms in Sulfuric Acid, Academic Press, London (1971).

McCarty, P.C., and Baugh,K., Proceedings 4th Annual Solar and Biomass Energy Workshop, USDA, Holiday Inn, Atlanta, GA, April 17-19 (1984).

TABLE 3-2

Evaluation of Kinetic Model Parameters for First-Order Disappearance of Glucose Fit to Model 1 in Table 3-1

$$k_1 = k_{10}\ [H_2SO_4]^{a1}\ \exp(-E_1/RT),\ \text{min}^{-1}$$

Date set	Temp. (°C)	Acid conc. (wt%)	a_1	k_{10} x10^{15} (min^{-1})	E_1 (cal/g-mol)	Root mean square residual
Bienkowski (1987)	100-144	4-20	1.00	0.214	31,050	0.2683
			1.33	0.213	31,060	0.1621
Saeman (1945)	160-190	0.4-1.6	1.00	5.86	33,800	0.1133
			1.19	10.18	33,890	0.0464
Kobayashi*	90-150	0.4-1.6	1.00	1.295	32,290	0.1406
			0.93	0.439	31,480	0.1405

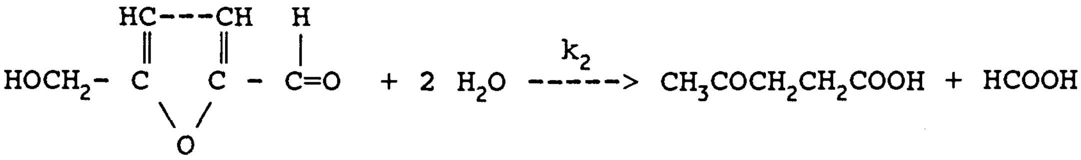
* Referenced by Bienkowski et al. (1987):

Kobayashi, T., Hakko Kyokai, 337-341 (1950).

3.2 Hydroxymethylfurfural Degradation

Hydroxymethylfurfural (HMF) is an intermediate breakdown product of hexose decomposition. It is a reactive, colorless substance that can be participated in numerous chemical reactions (Ulbricht et al., 1984).

The disappearance of HMF follows a first-order mechanism (McKibbins et al., 1962). In this decomposition, the furane ring in HMF is opened with the production of levulinic and formic acids according to the following reaction:



$$\begin{array}{l} \qquad\quad HC{-}{-}{-}CH \quad\; H \\ \qquad\quad \| \qquad\;\; \| \qquad | \\ HOCH_2-\; C \qquad C - C{=}O \;\; + \; 2\; H_2O \; \xrightarrow{k_2} \; CH_3COCH_2CH_2COOH \; + \; HCOOH \\ \qquad\qquad \backslash\;/ \\ \qquad\qquad\; O \end{array}$$

The HMF disappearance rate constant has been determined and correlated with temperature by means of the Arrhenius expression times some function of the acid catalyst concentration (Teunissen, 1931; McKibbins et al., 1962; Heimlich et al., 1960 and Taylor et al., 1971):

$$k_2 = k_{20}\ \exp(-E_2/RT)\ F([\text{acid}]) \qquad (3\text{-}3)$$

where F is a function of the acid catalyst concentration.

The ranges of experimental conditions used by various investigators and their kinetic parameters for k_2 are given in Table (3-3). Under 0.06-1.8 M sulfuric acid concentration and 180-220°C temperature, the reaction conditions in which we are interested, the activation energy of 23110 cal/g-mol was determined by McKibbins et al., (1962).

The potential of levulinic acid as an organic intermediate was emphasized by Leonard (1956). Its formation from glucose via HMF displays a plateau value due to the stability of levulinic acid to the reaction conditions. The plateau value of levulinic acid yield increases with decreased temperature and decreased initial glucose concentration and is independent of catalyst concentration except at low concentrations where it decreases with decreased amounts of catalyst (McKibbins et al., 1962).

The formation of levulinic acid from HMF as a starting material also displays a plateau value as a function of time. The plateau yield displays the same general trends with temperature and catalyst concentration indicated above (McKibbins et al., 1962).

TABLE 3-3

Evaluation of Kinetic Model Parameters for First-Order Disappearance of HMF

$$k_2 = k_{20} \exp(-E_2/RT)\ F([\text{acid}]),\ \text{min}^{-1}$$

Date set	Temp (°C)	[acid]	k_{20}	E_2 (cal/g-mol)	F([acid])
McKibbins (1962)	180-260	0.06-1.8 M H_2SO_4	2.4×10^{11}	23110	α_{HMF}x[acid]
Heimlich (1960)	100-130	0.35 M HCl	3.8×10^{9}	22700	[acid]
Taylor (1971)	106-127	-	6.03×10^{11}	25700	-

where α_{HMF} is the activity coefficient for HMF.

CHAPTER 4

EXPERIMENTAL APPARATUS AND PROCEDURE

4.1 Aqueous Phase Kinetics

Kinetic studies were performed in batch reactors which are stainless steel bombs constructed from 3/4" ID by 1.6" long Swagelok weld fittings capped on one end and plugged and welded at the other and the interior was bored out to a constant diameter with approximately 11 ml of internal volume.

The reaction bombs were charged with 9.3 ml of a solution of 0.556 or 0.278 M glucose and 0.1 M sulfuric acid, made up with distilled and deionized water. This volume was selected to allow for the volume expansion of the liquid at reaction temperatures (160 - 200°C). A volumetric pipet was used to measure the appropriate volume. A thread lubricant was applied to the threads of the swagelok fitting to prevent heat damage. The Swagelok caps were then screwed onto the bombs using a torque wrench to apply a maximum torque of 60 ft-lb, which was high enough to prevent vapor from escaping and yet not strip the threads.

The reaction vessels, spaced 1 to 2.5" apart from each other, were placed inside a stainless steel basket which ensured uniform heating. The basket was then placed in a

Lauda model KS20D high temperature oil bath with a digital thermometer. The temperature of the bath can be controlled to within ± 0.1°C when the bath is covered. The high temperature oil used in the bath is a high boiling point (390°C) aromatic hydrocarbon oil, dibenzyl toluene, able to withstand temperatures up to 220°C without creating a fire hazard. The entire heating unit was placed under a ventilated hood since the odor of oil vapor is noticeable at temperatures greater than 160°C.

The reaction bombs were heated for specific time intervals and were then quenched in a tub of ice water. After reaching room temperature, the reaction mixture was removed from the bombs and filtered through a Gelman filter apparatus twice using 0.45-μm cellulose acetate filters and collected in clean HPLC autosampler vials for future analysis. It took approximately 1 ml to fill each vial. High performance liquid chromatography (HPLC) was chosen because of the presence of non-volatile sugars, sugar derivatives, and resins in the solution.

4.2 Measuring the Hydroxymethylfurfural Distribution Coefficient

To measure the distribution coefficient of HMF between o-nitrotoluene (ONT) and an aqueous solution, equal volumes of ONT and water, containing a known concentration of HMF, were added to 3/4" OD by 3.0" long glass vials. After capping, the test vials were immersed in an water bath maintained at a constant temperature. The vials were shaken by hand every hour. After allowing at least 24 hr to establish equilibrium, the samples were remove from the bath and the organic and aqueous phases were separated immediately. The aqueous phase was then analyzed by HPLC. Equilibrium distribution coefficients are measured at 25, 45, 65, and 85°C.

4.3 Two-Phase Kinetics

For the two-phase reaction experiments, 3.1 ml of a solution of known glucose and sulfuric acid concentration were added to 6.2 ml of o-nitrotoluene in the reaction bombs. The volumetric pipets again were used to measure the correct volume of each liquid phase. The reaction mixtures were heated for various times at a specified temperature, quenched, removed, and filtered in the same manner discussed in Section 4.1. The two-phase mixtures were added into 3/4" OD by 3.0" long glass vials and allowed to equilibrate at room temperature for at least 24 hr. Then the two phases were separated using disposable pipets, filtered a second time, and stored in separate glass vials for future analysis. Analysis for glucose and HMF in the aqueous phase was performed by HPLC while analysis for HMF in the solvent phase was performed by gas chromatography (GC).

4.4 Analytical Methods

4.4.1 Chromatographic Methods

Chromatography is a general technique for separating or concentrating one or more components from a physical mixture. All chromatographic systems consist of three components: a solute (sample), a mobile phase (solvent system), and a stationary phase (adsorbent). As each individual sample component or solute moves through the stationary phase, individual molecules are alternately held in the moving phase (sample plus added solvent or gas) or sorbed in the stationary phase. In this manner, a separation is effected. Solute molecules, which are preferentially held in the stationary phase, will be in the moving phase a smaller fraction of the time than molecules which prefer the moving phase, and these more strongly sorbing solutes will not be carried along the column as far or as fast as less strongly sorbing sample components.

4.4.2 Analysis of Aqueous Phase by High Performance Liquid Chromatography

The analytical method of high performance liquid chromatography was used in this project to analyze nonvolatile carbohydrates without the preparation of derivatives. The particular carbohydrate column used is composed of a Ca^{+2} based resin. Carbohydrate and aromatic compounds are separated on the basis of the hydrophilic interactions between the bound Ca^{+2} ions and the polar side groups of the mobil phase and sample molecules. For hexoses the most strongly retained compounds are those with adjacent axial-equatorial-axial OH groups (Angyal, 1980). The mobile phase to be used is distilled, deionized and degassed water; it is to be pumped through the column at a flow rate of 0.5 to 0.6 ml/min. The use of a refractive index detector allows accurate efficient analysis of the sugar solutions with complete recovery of the sample.

The equipment for this experimental work involved a spectra physics model SP8780 XR autosampler, a Beckman model 110B solvent delivery module, a Biorad HPLC column heater, an Altex Spherogel Ca^{+2} resin, 6.5 mm ID by 300 mm long, column, an Altex model 156 Refractive Index Detector, and a Beckman model 427 integrator.

The sensitivity of the RI detector for glucose and HMF is high; glucose and HMF concentrations as low as 1.0 mM can be detected. The high sensitivity and linearity are provided by the use of a light source of particularly stable output and an electronic radiometer circuit which compensates for small light losses due to the intrinsic coloring of the dissolved substance. An in-line filter apparatus, which utilizes disposable 0.45-μm filters, is installed in front of the carbohydrate column to remove any solid particles and prevent damage to the column packing. The disposable filters are replaced when the solvent pump gauge reads a pressure greater than 1150 psig; this corresponds to changing the filters every week when the system is under daily use.

The mobil phase used for sample analysis in this project was distilled, deionized, and degassed water flowing at a constant rate of 0.6 ml/min. The carbohydrate column was heated to 90°C and the RI detector was allowed to warm up for 45 min. During this time water was flowing through the entire system. After the column had reached both thermal and chemical equilibrium, the pressure drop over the column was, on the average, 800 psig as displayed by the solvent pump gauge. This value is acceptable because the maximum pressure that the column can withstand is 1000 psig.

The filtered reaction samples were loaded into the autosampler carousel. The model SP8780 XR autosampler was programmed to inject 20-μl samples at 35-min intervals until all of the samples were analyzed. The respective absorbance readings were recorded by the Beckman 427 integrator on heat sensitive paper. A helium gas line was connected to autosampler which pressurized the vials prior to injection and purged the sample lines after each injection.

The attenuation of the integrator was set at either 512 or 1024 and the chart speed was set at 0.25 cm/min. The average retention times for glucose and HMF are 8 and 19 min, respectively.

External standards for glucose and HMF were analyzed before and after the reaction samples. These standards provide a relationship between the absorbance readings of the glucose and HMF and their respective concentrations. Standards were prepared every three weeks and stored in a refrigerator to minimize microbial growth.

The Spherogel resin can be regenerated several times before replacement. This was accomplished by running a 5 mM solution of $Ca(NO_3)_2$ through the column overnight at a flow rate of 0.1 ml/min. By adding up to 10% acetonitrile to the mobile phase, one can alter selectivity between sugars, organic acids, and other organic components, thereby optimizing the separation of many organic mixtures.

4.4.3 Analysis of Solvent Phase by Gas Chromatography

A Hewlett Packard 5840A Gas Chromatography System (GC) was used to analyze the HMF in the solvent (o-nitrotoluene) phase. Two stainless steel 1/8" OD and 6 ft long columns, packed with 80/100 mesh material on Hayesep Q support, were used in the GC. The oven temperature was set at 270°C. The mobile phase, helium, flow rate was set at 25 ml/min. A thermal conductivity detector was used as the detection unit in the GC. Samples (3 μl) were manually injected into the column port.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Aqueous Phase Dehydration of Glucose

Various researchers found that the glucose disappearance follows a first-order mechanism (Saeman, 1945; McKibbins et al., 1962; Heimlich and Martin, 1960; Bienkowski et al., 1984):

$$\frac{d[G]}{dt} = - k_1[G] \qquad (5\text{-}1)$$

The integrated form of Equation (5-1) is

$$[G] = [G]_0 \exp[-k_1 t] \qquad (5\text{-}2)$$

where

$[G]_0$ = initial glucose concentration (M)

k_1 = rate constant (min^{-1})

t = time (min)

Experimental values of $\ln\{[G]/[G]_0\}$ from this lab plotted against time resulted in straight lines from which the values of k_1 were determined. Data collected at a sulfuric acid concentration of 0.1 M and temperatures of 160, 180, and 200°C are plotted in Figures (5-1), (5-2), and (5-3), respectively. The solid line in each figure represents the equation of the line calculated from the linear regression analysis, i.e., it is based on the best fit of all the data for both initial concentrations. All three figures indicate that there is no effect of initial glucose concentration on the value of k_1. This result was anticipated since glucose disappears by a first-order reaction.

The resulting rate constants as functions of temperature were correlated to the Arrhenius equation from which an activation energy of 32,400 cal/g-mol was obtained. See Figure (5-4).

The glucose dehydration experiments performed in this project is in the same range as McKibbins' experiments (1962) except this study included a temperature of 160°C. Hence, measured values of k_1 should compare well with values predicted using the parameters of McKibbins. The anticipated results are confirmed in Figure (5-5), where the predicted k_1 values are calculated from Mckibbins' k_1 expression.

The resulting Arrhenius parameters from this work and that from McKibbins are reported in Table (5-1). The values of k_{10} and E_1 are very close to the values obtained by McKibbins. These results support the assertion that glucose decomposition follows a first-order reaction model under the conditions studied, and that the kinetic parameters estimated here are consistent with those found by McKibbins.

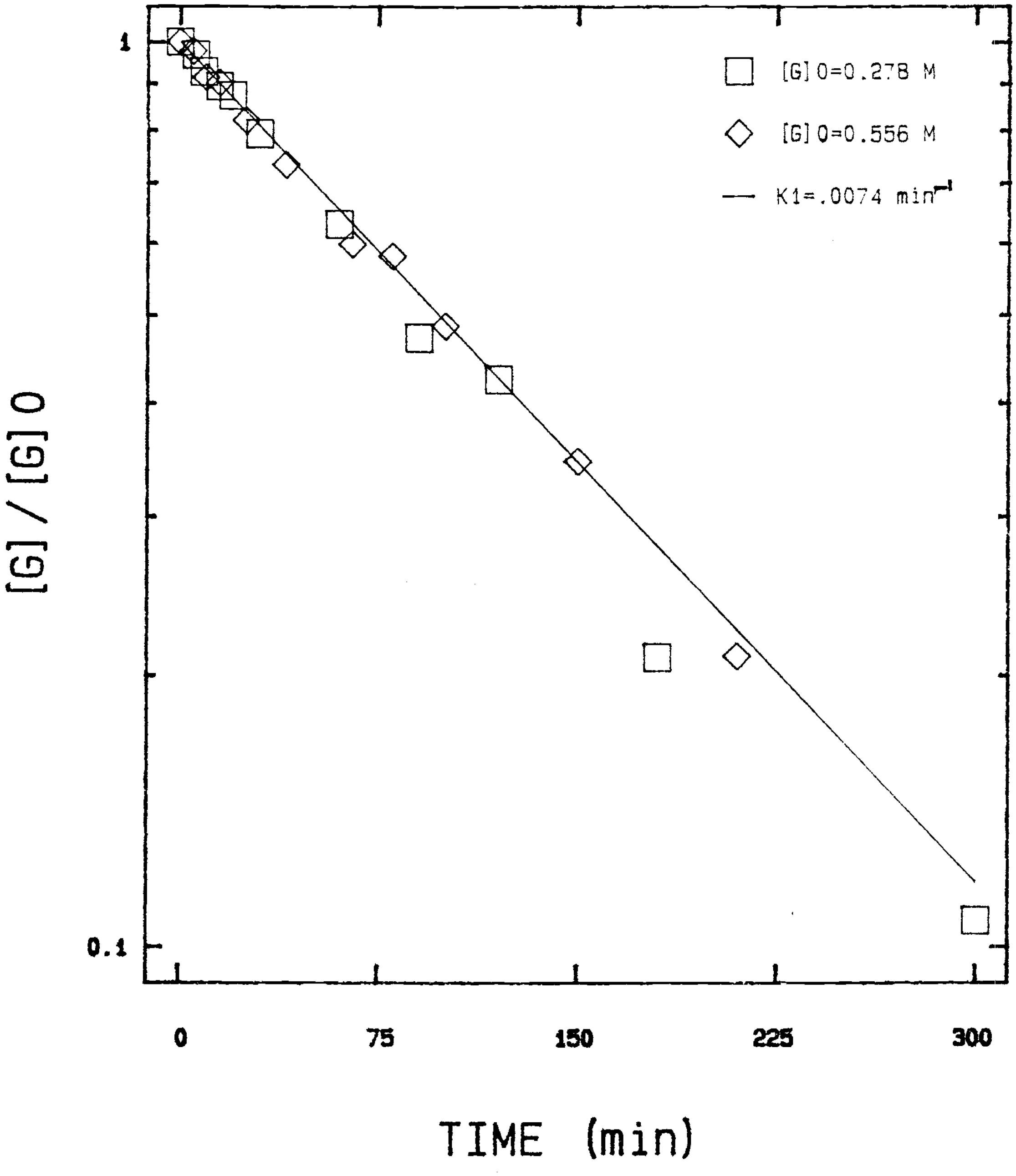


Figure 5-1

Kinetic Data for the Dehydration of Glucose
in Dilute Sulfuric Acid
T = 160°C, $[H_2SO_4]$ = 0.1 M

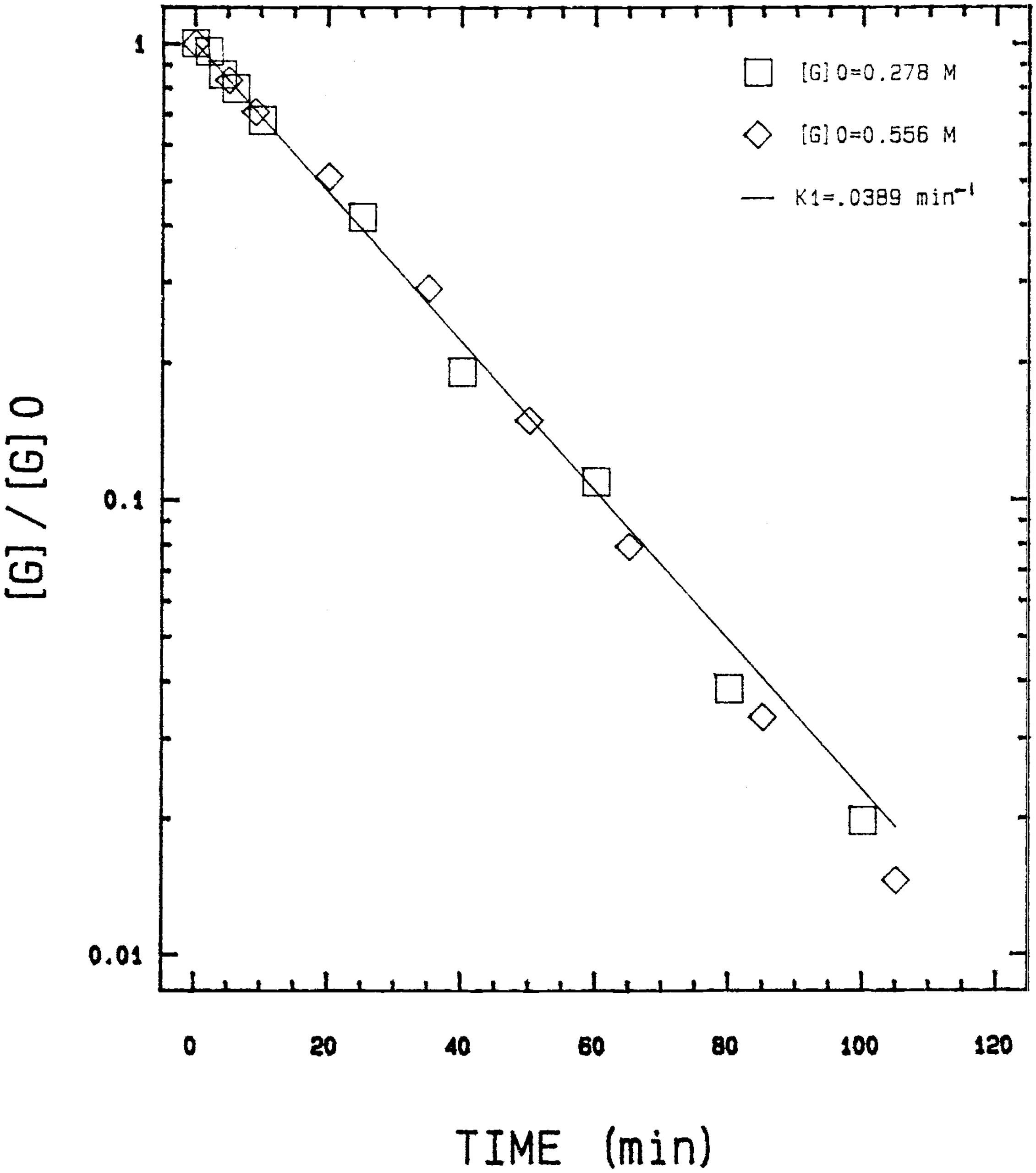


Figure 5-2

Kinetic Data for the Dehydration of Glucose
in Dilute Sulfuric Acid
T = 180°C, [H_2SO_4] = 0.1 M

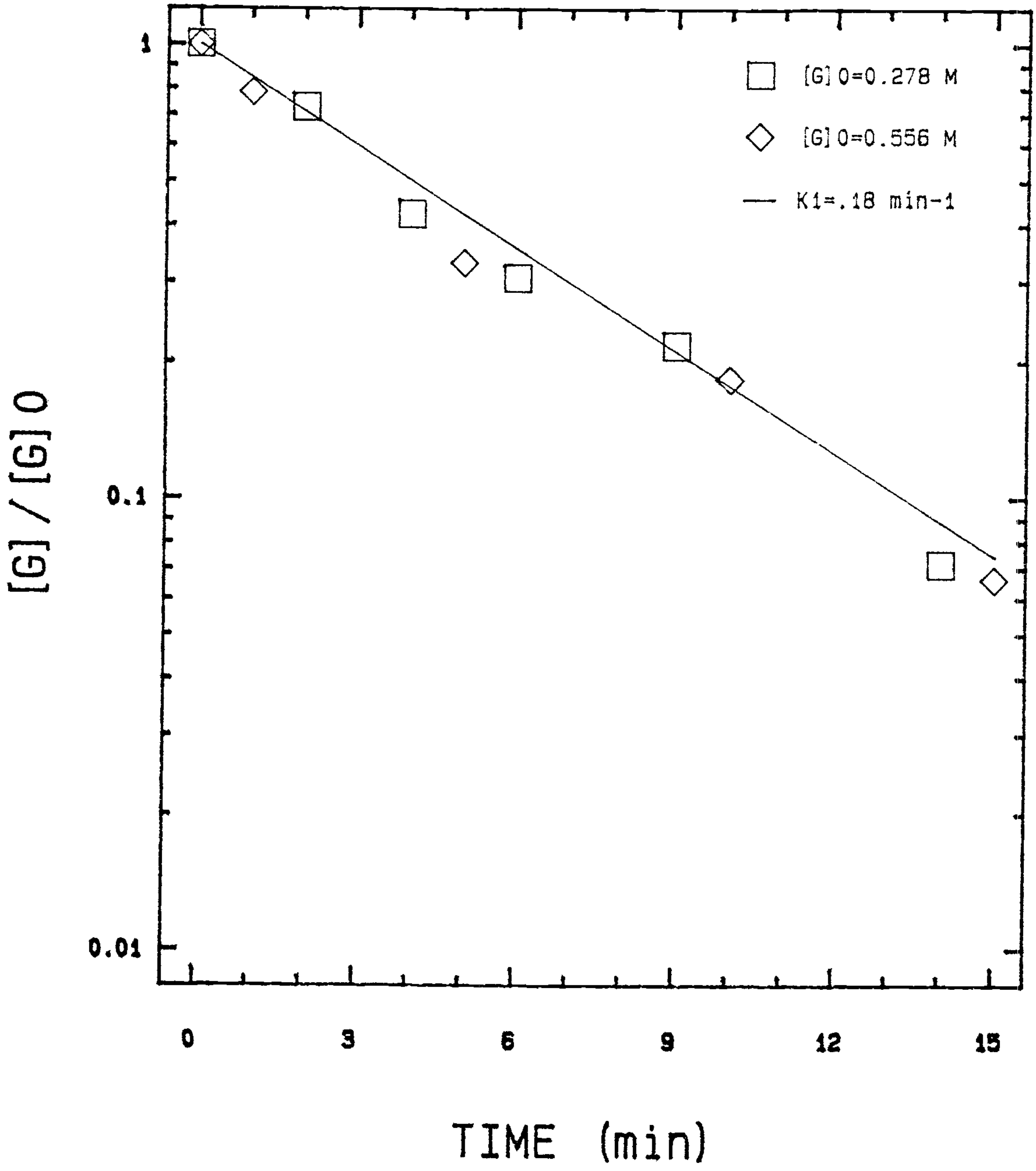


Figure 5-3

Kinetic Data for the Dehydration of Glucose
in Dilute Sulfuric Acid
T = 200°C, $[H_2SO_4]$ = 0.1 M

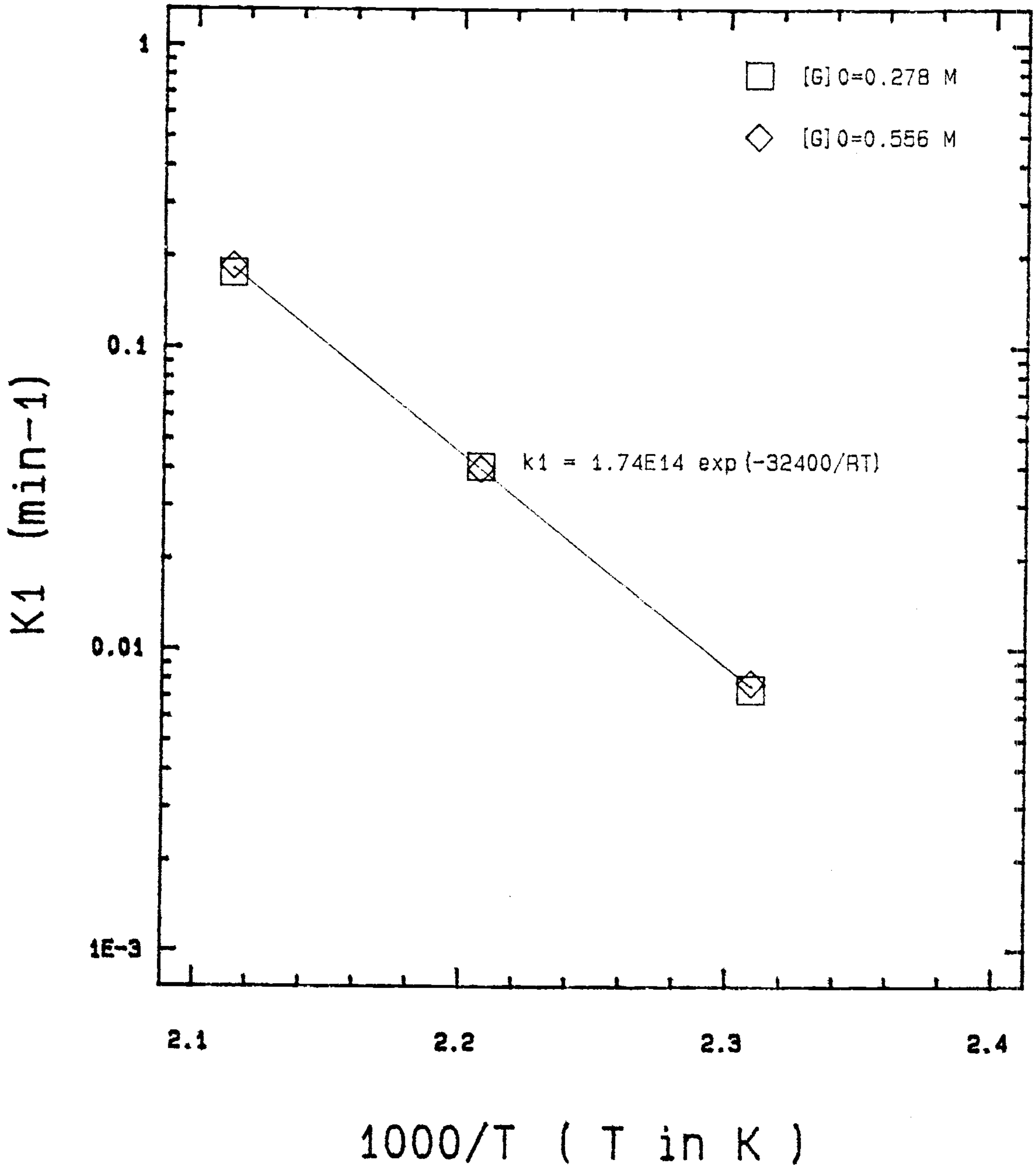


Figure 5-4

Arrhenius Plot for the k_1 Data
160°C ≤ T ≤ 200°C, $[H_2SO_4]$ = 0.1 M

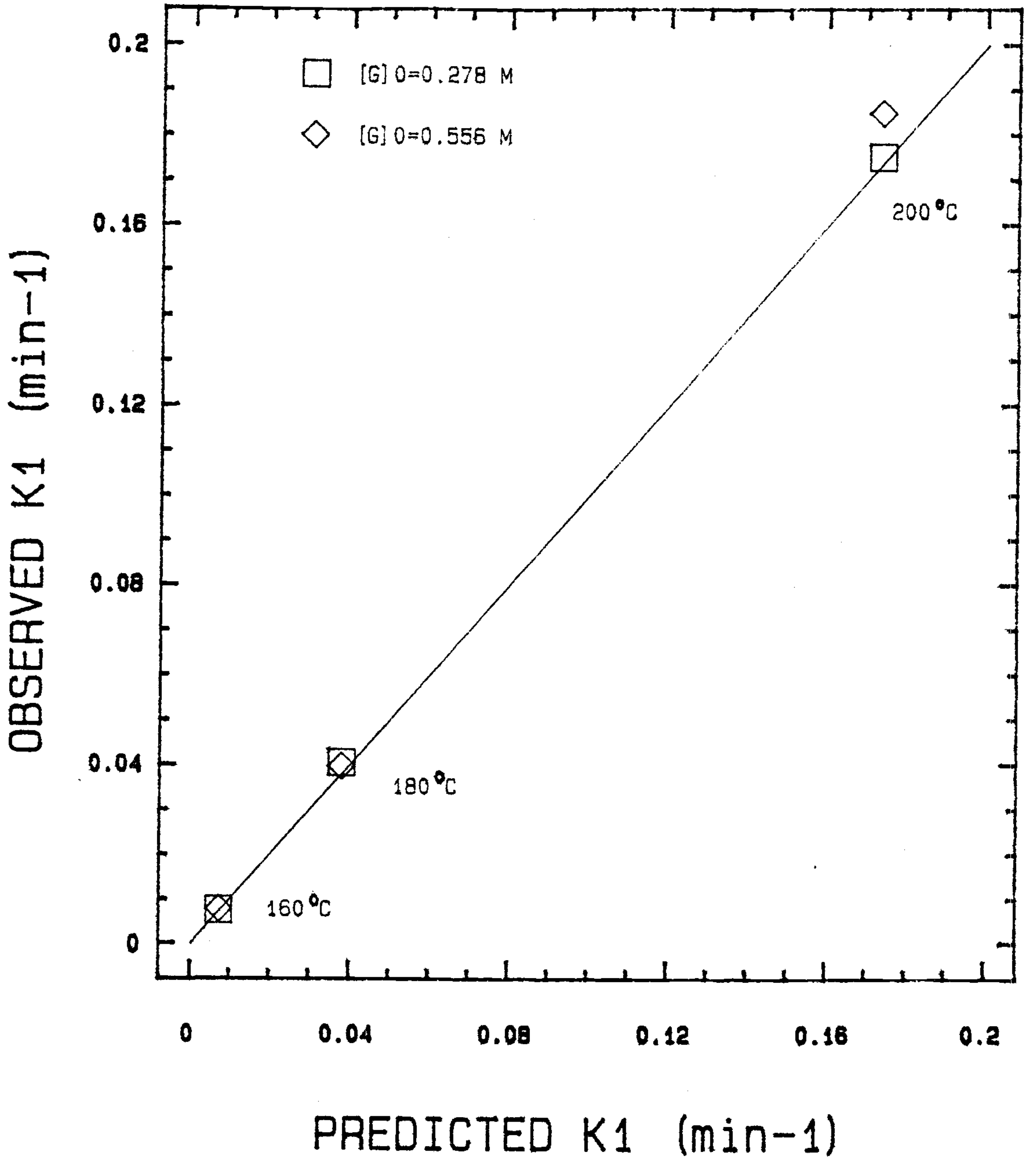


Figure 5-5

Agreement of Observed and Predicted
Glucose-Dehydration Rate Constants
160°C ≤ T ≤ 200°C, $[H_2SO_4]$ = 0.1 M

TABLE 5-1

Range of Experimental Conditions Used and Estimated Glucose-Dehydration Kinetic Parameters

Conditions of Experiments

	Temperature ($^\circ$C)	Sulfuric Acid Concentration (M)	Initial Glucose Concentration (M)
This Work	160 - 200	0.1	0.278 - 0.556
McKibbins	180 - 260	0.025 - 0.4	0.278 - 1.112

Comparison of Parameter Values at 0.1 M H_2SO_4

	Pre-exponential Factor k_{10} (min^{-1})	Activation Energy E_1 (cal/g-mol)	k_1 (min^{-1})	
			180°C	200°C
This Work	1.74×10^{14}	32,450	0.0389	0.180
McKibbins	1.83×10^{14}	32,510	0.0377	0.175

5.2 Aqueous Phase Conversion of Glucose to Hydroxymethylfurfural

5.2.1 Aqueous Phase Kinetic Model

The reaction mechanism for the formation of HMF from glucose can be represented by the proposed three-constant aqueous phase kinetic model given in Section 2.1.

$$G \xrightarrow{k_1} I \xrightarrow{k_1'} HMF \xrightarrow{k_2} D$$

$$I + HMF \xrightarrow{k_3'} P$$

The resulting reaction rate expressions for glucose and HMF are:

$$\frac{d[G]}{dt} = - k_1[G] \qquad (5\text{-}3)$$

$$\frac{d[HMF]}{dt} = k_1[G] - k_2[HMF] - k_3[G][HMF] \qquad (5\text{-}4)$$

where

$$k_3 = \frac{k_1 k_3'}{k_1'} \qquad (5\text{-}5)$$

McKibbins (1962) evaluated the first-order rate constants, k_1 and k_2, as a function of the Arrhenius equation, acid concentration and activity coefficient (α) for the respective reactant:

$$k_1 = 1.85\text{x}10^{16} \ \alpha_G \ [H_2SO_4] \ \exp(-32510/RT) \qquad (5\text{-}6)$$

and:

$$k_2 = 4.8\text{x}10^{11} \ \alpha_{HMF} \ [H_2SO_4] \ \exp(-23110/RT) \qquad (5\text{-}7)$$

where k_1 and k_2 have the units of $\min^{-1}$, the sulfuric acid concentration is in units of M, T is in degrees Kelvin, R = 1.987 cal/g-mol K, and values of the glucose and HMF activity coefficients as a function of sulfuric acid concentration can be obtained from the McKibbins article (1962).

Instead of referring to McKibbins' activity plots to determine values of k_1 and k_2 at given sulfuric acid concentration, it would be better to model these first-order kinetic constants as a function of $[H_2SO_4]$. The model most frequently used for these purpose has the sulfuric acid concentration raised to a power (Bienkowski et al., 1987):

$$k_i = k_{i0}\ [H_2SO_4]^{ai}\ \exp(-E_i/RT) \qquad (5\text{-}8)$$

Hence, all that needs to be done is to evaluate a_1 and a_2. This was done by plotting values of log k_1 and log k_2 values from McKibbins et al., (McKibbins et al. 1962), versus log $[H_2SO_4]$. The resulting values obtained are: $a_1 = 0.86$ and $a_2 = 1.06$.

5.2.2 Evaluation of k_3 Parameters

The second-order rate constant k_3 can also be modeled by Equation (5-8). Values of the rate constant parameters for k_1 and k_2 can be utilized along with McKibbins' HMF concentration-time data to evaluate the k_3 parameters k_{30}, E_3 and a_3.

A computer program was written which varied the value of k_3 and integrated the HMF rate expression, Equation (5-4), over the total reaction time. A fourth-order Runge-Kutta routine was employed to perform the numerical integration (Appendix A). The sum of squares differences were then calculated in the optimization routine.

$$SSE = ([HMF]_{ob} - [HMF]_t)^2 \tag{5-9}$$

where:

$[HMF]_{ob}$ = observed hydroxymethylfurfural concentration (from McKibbins, 1962)

$[HMF]_t$ = predicted hydroxymethylfurfural concentration (from proposed model based on current guess of k_3)

Each of the observed HMF concentration profiles from McKibbins et al. is based on a smooth curve drawn through large set of data points collected for a particular set of conditions. The smooth curves were drawn by McKibbins et al. (McKibbins et al. 1962). The optimum value of k_3 was determined for each data set which minimized the sum of squares of error terms for observed and predicted HMF concentrations. Plots illustrating McKibbins' data points and the best possible curves that the McKibbins' model can produce are shown in Figure (5-6) and Figure (5-7) for sulfuric acid concentrations of 0.025 and 0.1 M, respectively. The temperature range in each is 180 to 220°C. Twenty different values of k_3 as determined by the computer program at various temperatures and sulfuric acid concentrations conditions are given in Table (5-2).

These values of k_3 were then used to evaluate the k_3 parameters in the following expression.

$$k_3 = k_{30}\ [H_2SO_4]^{a3}\ \exp(-E_3/RT) \tag{5-10}$$

Taking the logarithm of both sides of Equation (5-10) allows one to calculate the Arrhenius parameters by linear regression for a given sulfuric acid concentration.

$$\ln k_3 = \ln k_{30} + a_3 \ln [H_2SO_4] - E_3/RT \qquad (5\text{-}11)$$

The five different values of E_3 as calculated by applying Equation (5-11) to the five constant-$[H_2SO_4]$ columns in Table (5-2) ranged from 19,800 to 20,800 cal/g-mol. An overall average value for the exponential factor a_3, was calculated by plotting log $k_3/\exp(-E_3/RT)$ for all of the data given in Table (5-2) to obtain $a_3 = 0.71$. Next, an Arrhenius plot for $k_3/[H_2SO_4]^{a3}$ was constructed to obtain best estimates of the Arrhenius parameters based on all twenty data points. The results which are illustrated in Figure (5-8) are:

$a_3 = 0.71$

$k_{30} = 2.4\text{x}10^{10}$ min^{-1} M^{-1}

$E_3 = 20{,}300$ cal/g-mol

TABLE 5-2

Values of k_3 (min^{-1} M^{-1}) at Various Temperatures and Acid Concentrations Evaluated from McKibbins' Data

$[G]_0 = 0.556$ M

T (°C)	$[H_2SO_4]$ (M)				
	0.025	0.05	0.10	0.20	0.40
180	0.32	0.45	0.70	1.30	2.37
190	0.50	0.70	1.08	1.99	3.57
200	0.82	1.15	1.76	3.22	5.74
220	2.08	2.87	4.30	7.78	13.64

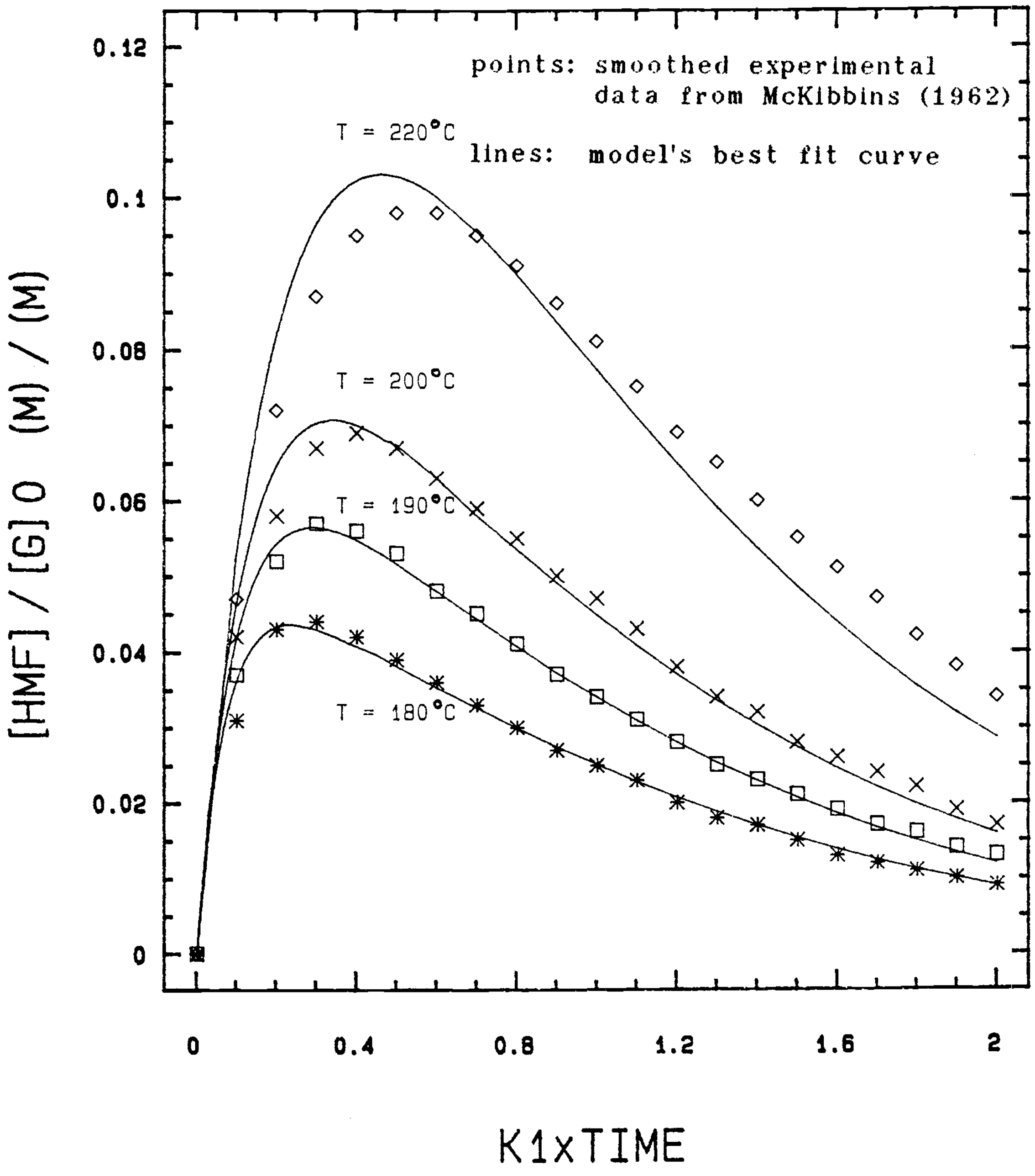


Figure 5-6

Comparison of HMF Concentration profiles Predicted by the Proposed Model to those from McKibbins' Experiments
$[G]_0$ = 0.556 M, $[H_2SO_4]$ = 0.025 M

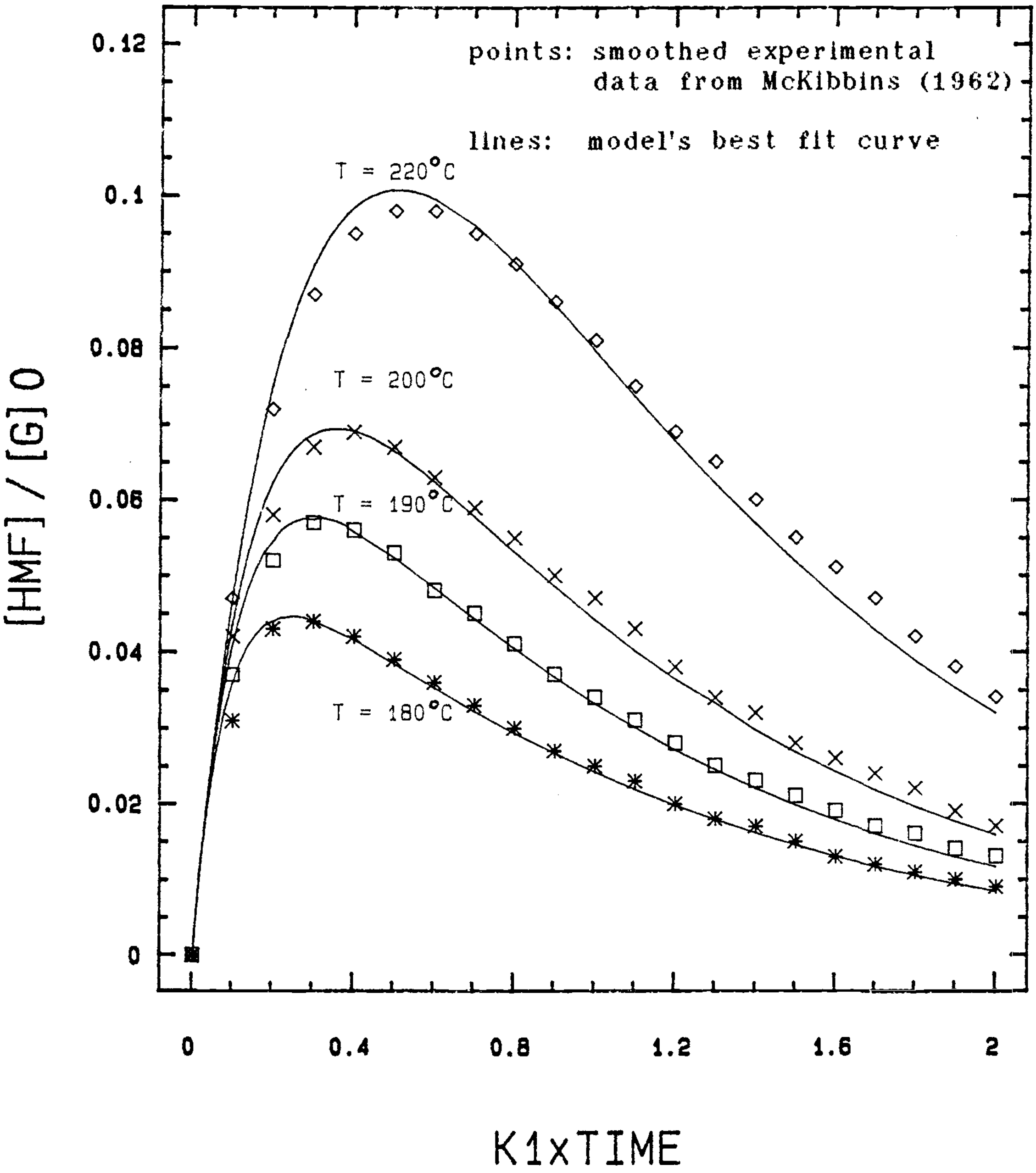


Figure 5-7

Comparison of HMF Concentration profiles Predicted by the Proposed Model to those from McKibbins' Experiments
$[G]_0 = 0.556$ M, $[H_2SO_4] = 0.1$ M

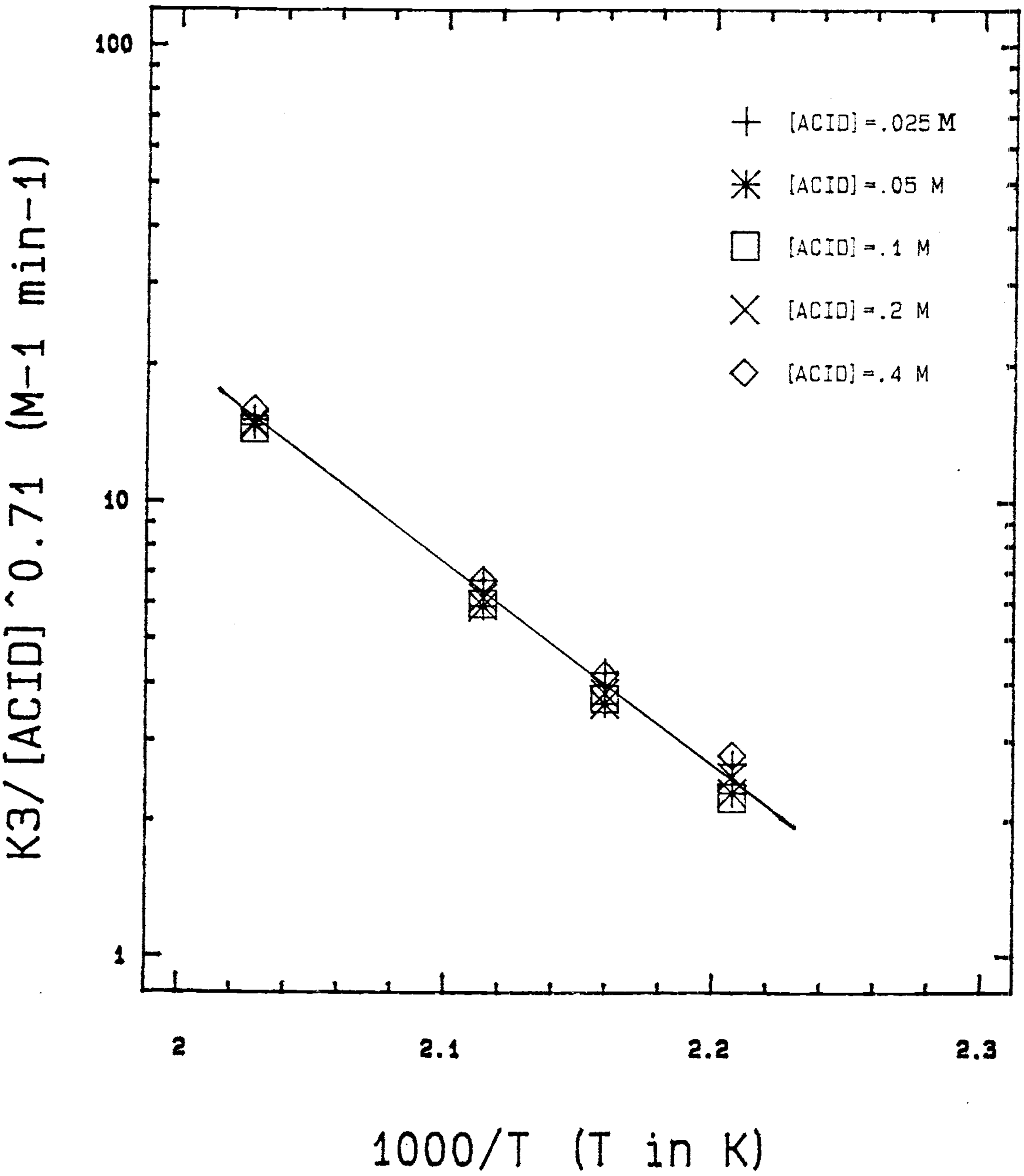


Figure 5-8

Arrhenius Plot for k_3 at Various
Sulfuric Acid Concentration
(180 to 220°C)

5.2.3 Agreement of the Proposed Kinetic Model with Aqueous Phase Experimental Data

Experimentally measured (at Oregon State University) HMF concentration profiles at 160, 180 and 200°C are compared to the model prediction in Figures (5-9) and (5-10) while the McKibbins' experimental data points and the best possible curve that the model can produce are shown in Figures (5-6) and (5-7). These results show that the model fits the experimental data very well, especially at the lower temperatures. At higher temperatures the model overestimates the HMF concentration before the maximum is reached and at longer times the theoretical HMF concentrations are lower than the experimental HMF concentrations. Errors are probably attributed to the simplified reaction mechanism for the conversion of glucose to HMF, since all reaction intermediates are treated as a single species.

The primary conclusion of this work is that the proposed three-constant model can be used to predict the formation of hydroxymethylfurfural from glucose for temperatures between 160 and 220°C and sulfuric acid concentrations between 0.025 and 0.4 M. A secondary conclusion is that experimental data collected at OSU is consistent with experimental data collected by McKibbins.

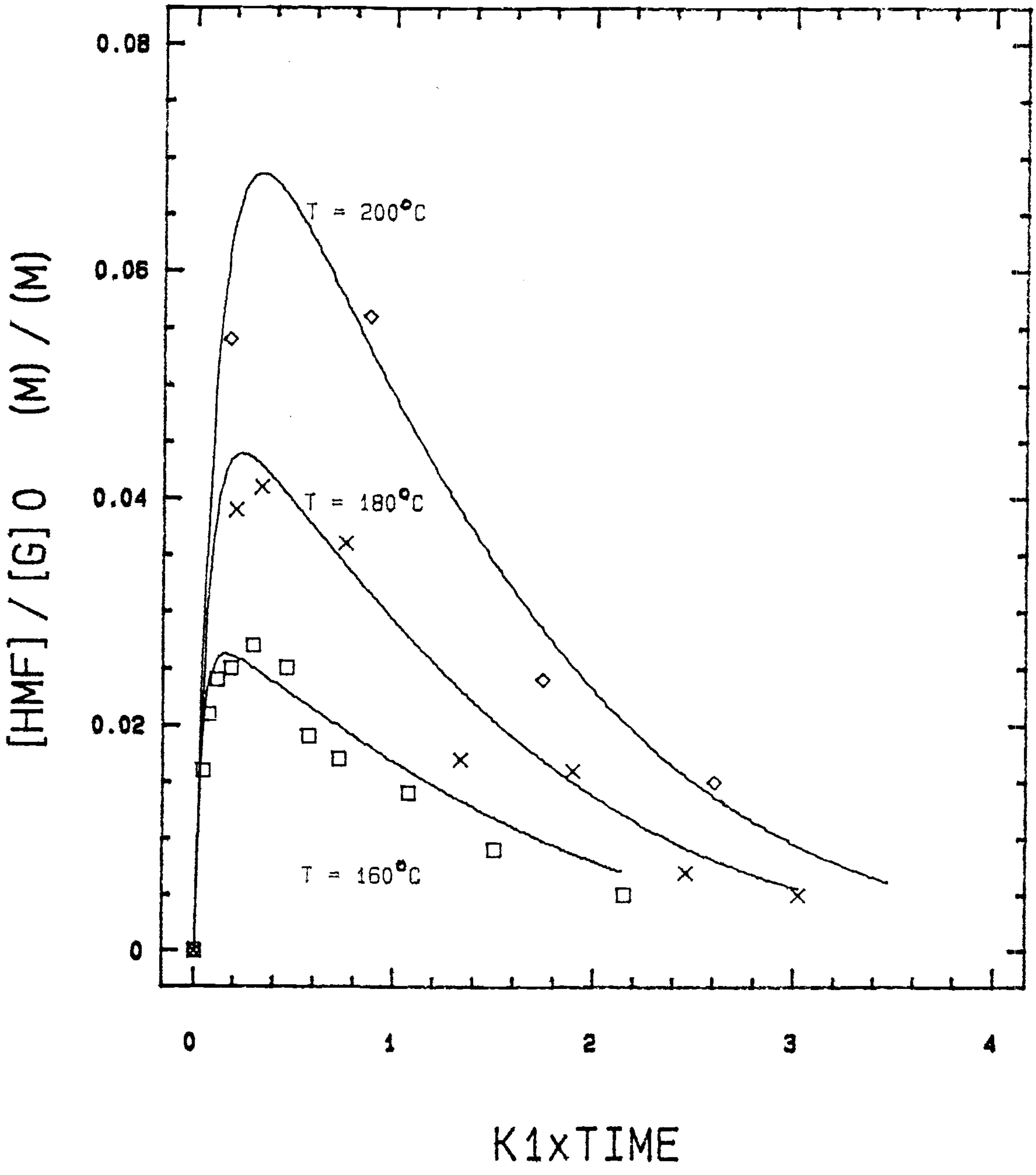


Figure 5-9

Comparison of Experimentally Measured HMF Concentration Profiles to Model Prediction
$[G]_0$ = 0.556 M, $[H_2SO_4]$ = 0.1 M

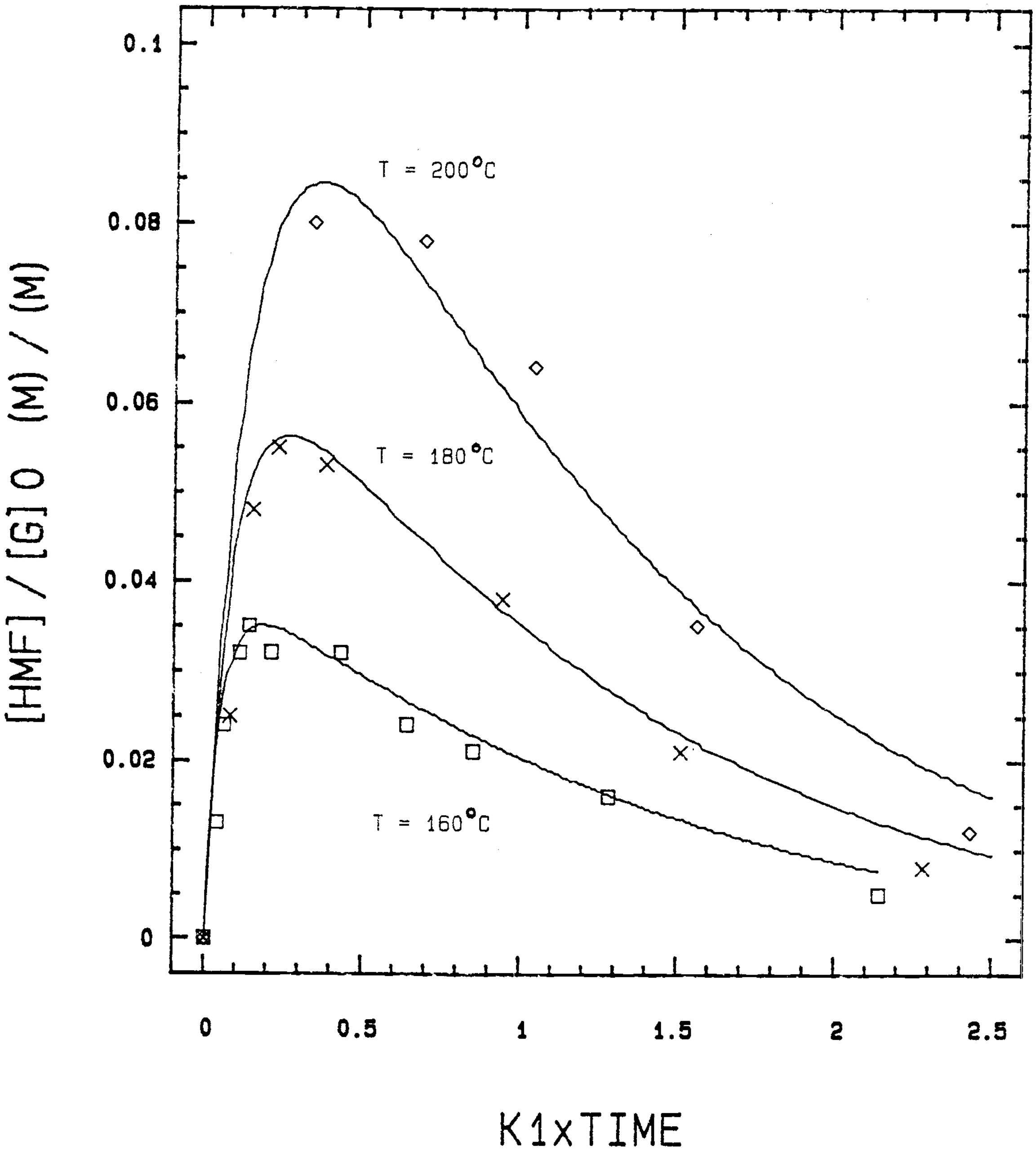


Figure 5-10

Comparison of Experimentally Measured HMF Concentration Profiles to Model Prediction
$[G]_0 = 0.278$ M, $[H_2SO_4] = 0.1$ M

5.2.4 Discussion of Kinetic Parameters

Variation of the kinetic constants (k_1, k_2, k_3) with acid concentration is shown in Figure (5-11) and a corresponding Arrhenius plot is given in Figure (5-12). The first plot can be used to obtain values of the kinetic constants as a function of temperature for a given acid concentration; whereas, the latter gives values of k_1, k_2, and k_3 for a given temperature. Final estimates of the kinetic parameters for all three kinetic constants are given in Table (5-3).

Since unreacted glucose will, in general, be unrecoverable, HMF yield in an aqueous-phase system can be defined as the ratio of HMF formed to the initial glucose present:

$$\text{Yield of HMF} = \frac{\text{HMF Formed}}{\text{Glucose Present Initially}} = \frac{[\text{HMF}]}{[\text{G}]_0} \qquad (5\text{-}12)$$

As can be seen from Equation (5-4) the maximum theoretical yield of HMF from glucose increases as the ratios of k_1 to k_2 and k_1 to k_3 increase. Since the activation energy for HMF formation, E_1, is greater than the activation energies for HMF degradation, E_2 and E_3 (see Figure (5-12) and Table (5-3)), the maximum theoretical HMF yield increases with temperature. This point is confirmed in Figures (5-6), (5-7), (5-9) and (5-10).

No comparisons can be made between the relative values of the fist-order constants, k_1 and k_2, and the second-order constant k_3 because the units between rate constants of different orders are different. But, the change of catalyst acid concentration will have an effect on all three rate constants, and hence effect the HMF yield. Therefore, although the data in Figure (5-11) shows that k_1 increases relative to k_2 when the acid concentration is decreased, one can not necessarily conclude that the HMF yield increases as sulfuric acid concentration is decreased.

TABLE 5-3

Final Estimates of the Parameters for the Proposed Aqueous Phase Kinetic Model

$$k_i = k_{i0}\ [H_2SO_4]^{ai}\ \exp(-E_i/RT)$$

i	units of k_i	k_{i0}	a_i	E_i (cal/g-mol)
1	min^{-1}	1.3×10^{15}	0.86	32,500
2	min^{-1}	4.7×10^{11}	1.06	23,100
3	$M^{-1}\ min^{-1}$	2.4×10^{10}	0.71	20,300

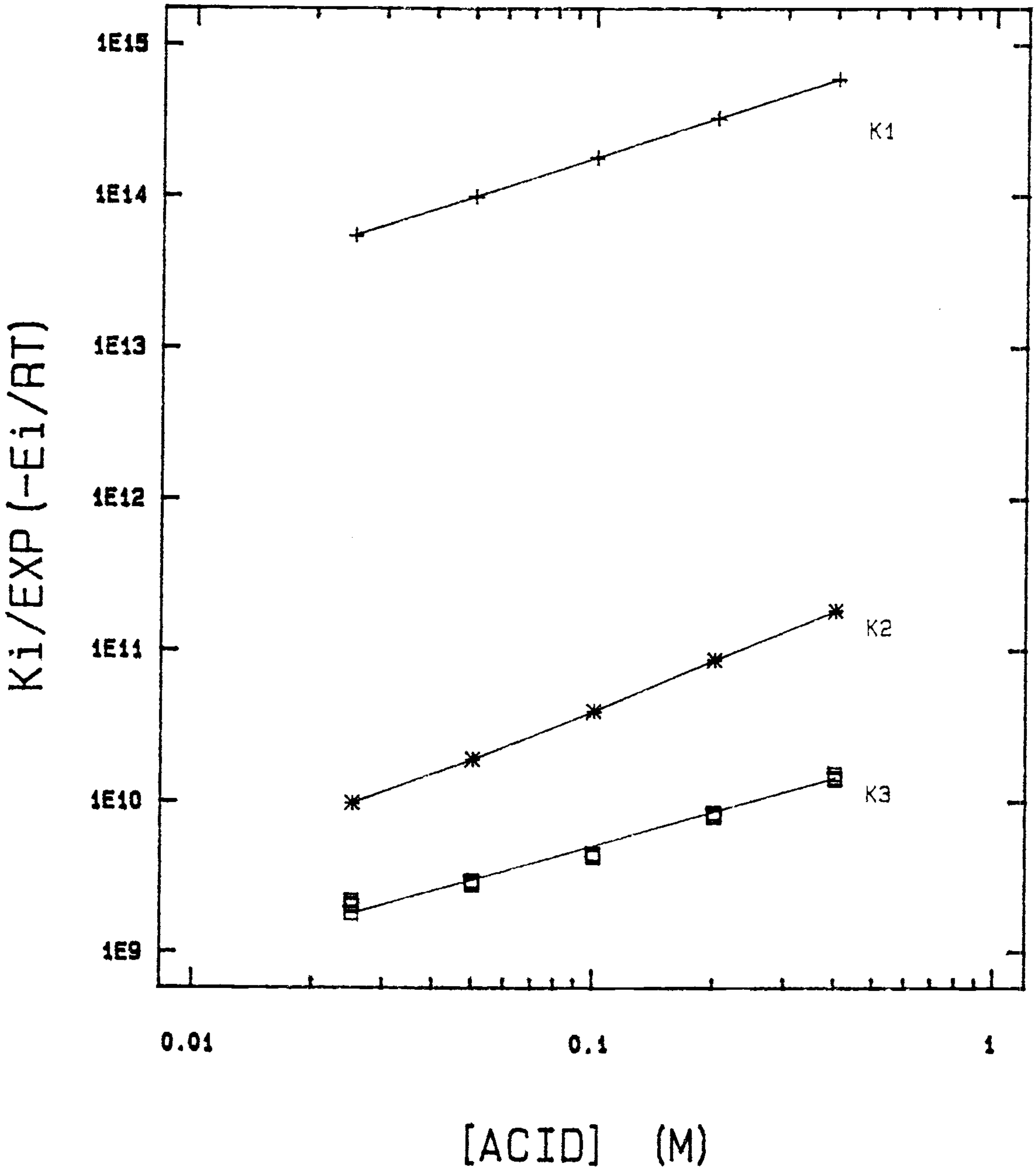


Figure 5-11

Effect of Sulfuric Acid Concentration
on the Kinetic Rate Constants

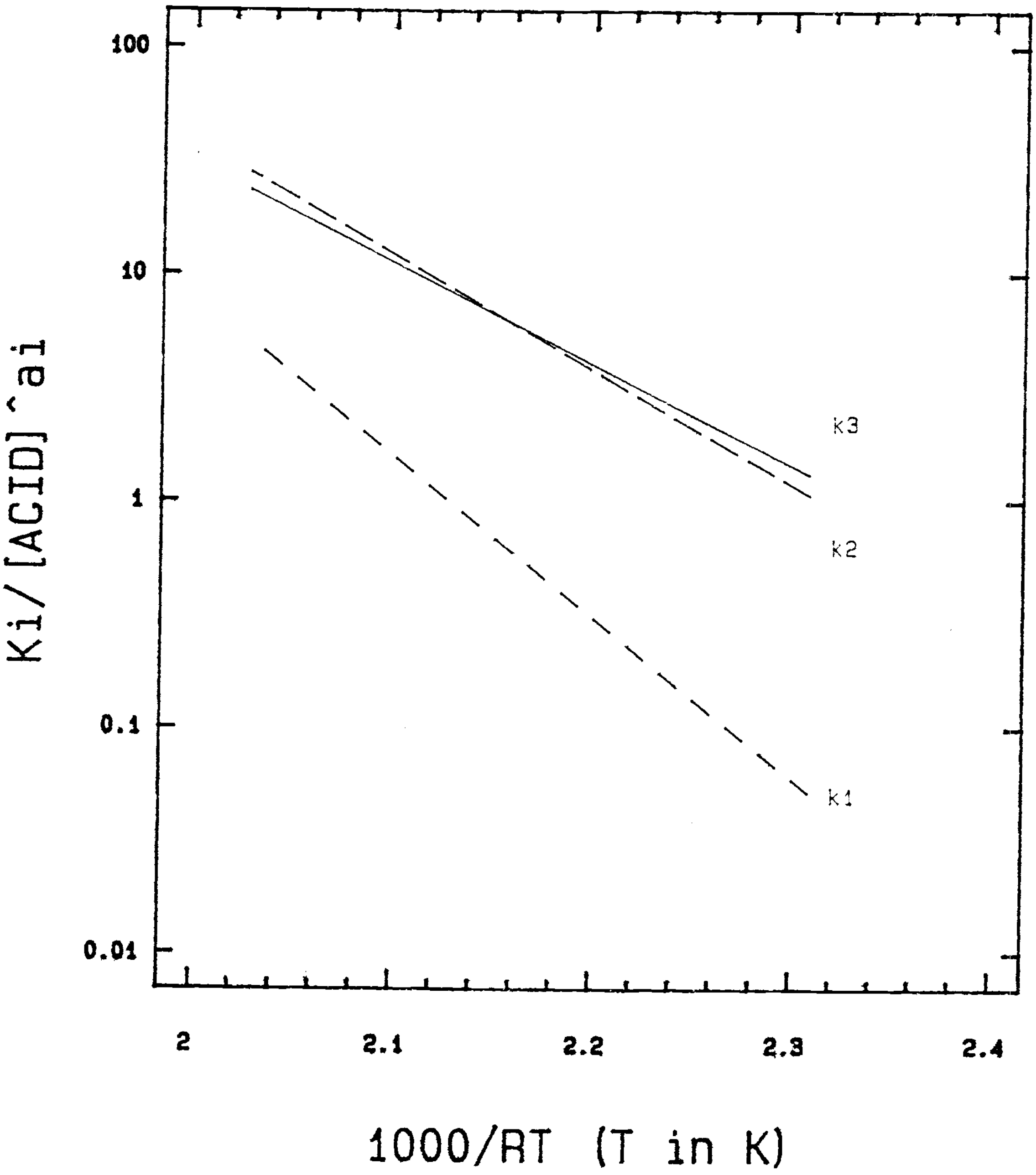


Figure 5-12

Arrhenius Plot for the Three Kinetic Rate Constants (160 to 220°C)

5.2.5 Yield of Total Organic Acids

Data on the formation of organic acids from glucose have been collected to provide further confirmation of the proposed model. According to the HMF degradation mechanism described in Section 3.2, HMF reacts with two molecules of water to form levulinic acid plus formic acid:

$$C_6H_6O_3 + 2H_2O \xrightarrow{k_2} C_5H_8O_3 + CH_2O_2$$

HMF degradation by this reaction should be first-order with respect to [HMF] in aqueous solutions. The rate of formation of organic acids (lumped together as D) is given by:

$$\frac{d[D]}{dt} = k_2[HMF] \qquad (5-13)$$

where k_2 is the first-order HMF degradation constant.

A computer program (Appendix B) was written to calculate the yield of total organic acids according to the suggested three-constant model by the simultaneous numerical integration of Equations (5-3), (5-4), and (5-13). Figures (5-13) and (5-14) give the comparison of experimental and predicted profiles for the formation of organic acids from glucose via HMF. The predicted profiles are in good agreement with the experimental data, which provides further support for the proposed three-constant model.

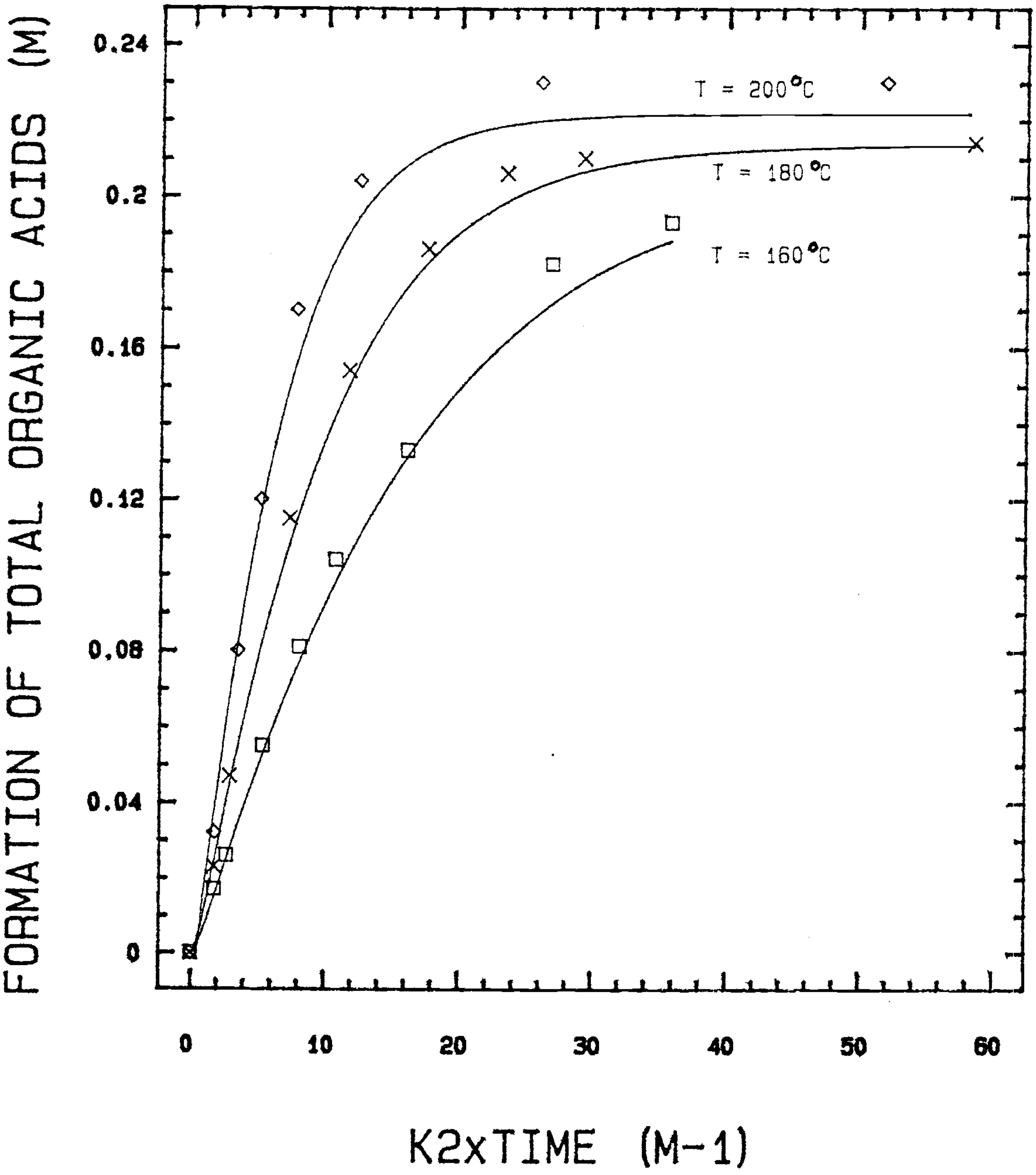


Figure 5-13

Predicted and Observed Yield of Total Organic Acids
Concentration-Time Profiles
$[H_2SO_4]$ = 0.1 M, $[G]_0$ = 0.278 M

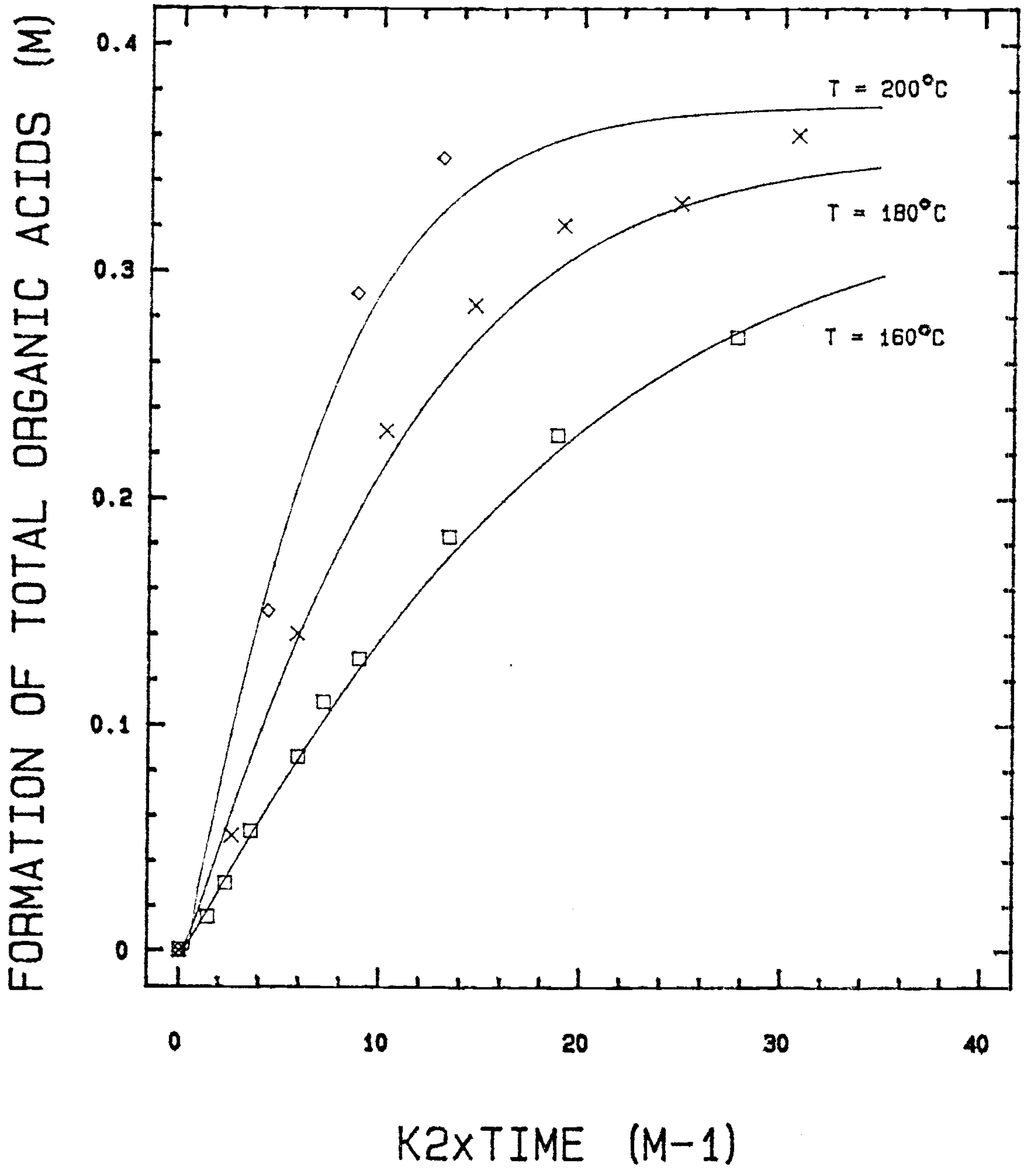


Figure 5-14

Predicted and Observed Yield of Total Organic Acids
Concentration-Time Profiles
$[H_2SO_4] = 0.1$ M, $[G]_0 = 0.556$ M

5.3 Hydroxymethylfurfural Distribution Coefficient

o-Nitrotoluene is an excellent solvent for furfural (Sproull, 1986). Since furfural and HMF are similar, we originally expected o-nitrotoluene also be a good solvent for HMF. Furthermore, when using biomass for the production of chemicals, the cellulose portion of the biomass is converted to glucose and then HMF, while the hemicellulose portion is converted to xylose and arabinose and then furfural. For process simplicity, we would prefer to use the same solvent for the recovery of both furfural and HMF.

THe HMF distribution coefficient has been defined in Equation (2-12) as the equilibrium ratio of HMF concentration in the solvent phase (i.e., o-nitrotoluene) to the HMF concentration in the aqueous phase:

$$m = \frac{[\mathrm{HMF}]_{se}}{[\mathrm{HMF}]_{ae}} \qquad (5\text{-}14)$$

Since the HMF distribution coefficient as an equilibrium constant, its temperature dependence is expected to follow the integrated Van't Hoff equation (see Section 2.2). The results given in Figure (5-15) confirm this expectation.

$$m = 9.93 \exp(-2240/RT) \qquad (5\text{-}15)$$

Initially , we planned to evaluate the HMF distribution coefficient by ratioing measured solvent-phase and aqueous-phase HMF concentrations; however, HMF could not be separated from o-nitrotoluene with the gas chromatograph in our laboratory. Therefore, in our experiments which used equal volumes of solvent and water with all of the HMF initially in the aqueous phase, m was computed from $[HMF]_a$ as follows:

$$m = \frac{[HMF]_{a0} - [HMF]_{ae}}{[HMF]_{ae}} \qquad (5\text{-}16)$$

where $[HMF]_{a0}$ is the initial aqueous phase HMF concentration and $[HMF]_{ae}$ is the aqueous phase HMF concentration at equilibrium.

The value of ΔH, the enthalpy change for the mass transfer of HMF from water to o-nitrotoluene, is positive; which means that energy is required to transfer HMF from water to o-nitrotoluene. Because the value of ΔH is relatively large, m increases fairly rapidly with temperature. For example, m almost doubles in going from 25 to 85°C.

A good HMF solvent should have a high distribution coefficient for HMF and very low distribution coefficient for all other components present in the reaction system. At reaction (e.g., 180°C), the o-nitrotoluene distribution coefficient for furfural is 8.5 (Sproull, 1986), indicating that o-nitrotoluene is a very good solvent for furfural. However, extrapolation of the o-nitrotoluene distribution coefficient for HMF to 180°C gives $m = 0.83$, which is less than 1.0 and an order of magnitude lower than the corresponding value obtained for furfural at the same temperature. Therefore, pending an economic analysis, we can conclude that o-nitrotoluene is not likely to be a very good solvent for HMF.

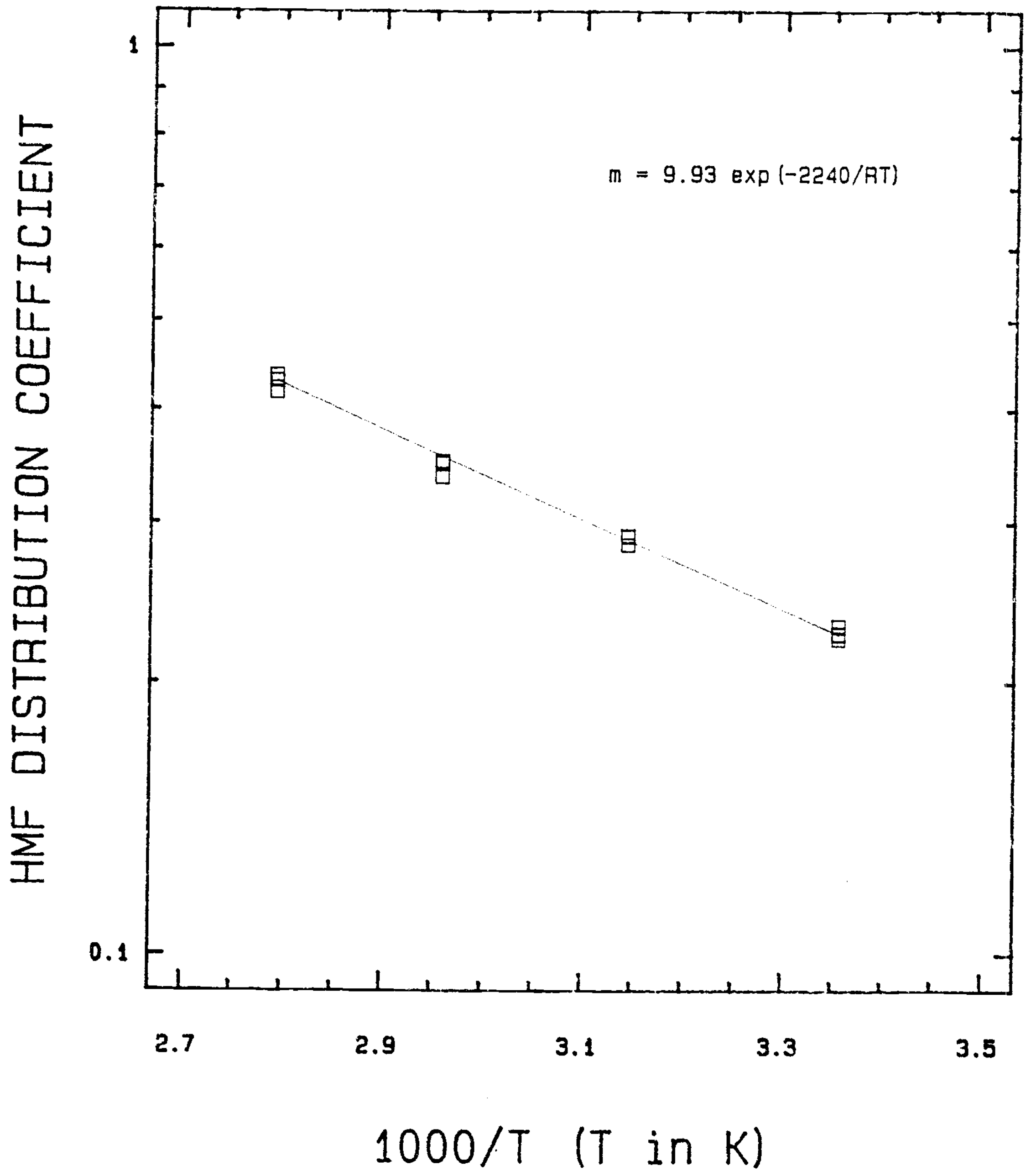


Figure 5-15

Temperature Dependence of the HMF Distribution Coefficient for o-Nitrotoluene

5.4 Two-Phase Kinetics

To increase its yield, the HMF should be extracted into the solvent phase as soon as it is formed. An acceptable solvent must not interact with the aqueous phase except to facilitate the transfer of HMF. In particular, it must not react with glucose, the primary reactant.

Figure (5-16) compares the glucose degradation data in the aqueous phase of both one-phase and two-phase reaction experiments at 180°C. The concentration time profiles were corrected for the heat up times by omitting data taken at reaction times less than 5 min. The data for the two reaction systems are in good agreement, which confirms that the presence of o-nitrotoluene phase does not affect the degradation of glucose.

In a two-phase system the yield of HMF can be defined as the sum of HMF formed in both liquid phases divided by the initial glucose present:

$$\text{HMF Yield} = \frac{\text{HMF in aqueous phase} + \text{HMF in solvent phase}}{\text{glucose present initially}}$$

$$= \frac{V_a[\mathrm{HMF}]_a + V_s[\mathrm{HMF}]_s}{V_a[G]_0} = \frac{[\mathrm{HMF}]_a + \Phi[\mathrm{HMF}]_s}{[G]_0} \qquad (5\text{-}17)$$

where Φ is the ratio of the volume of the solvent phase to the volume of the aqueous phase (V_s/V_a).

Experimentally-measured HMF yields were calculated from aqueous-phase HMF concentration data, where the aqueous phase had come to equilibrium with the solvent after the two-phase reaction sample had been quenched.

$$\text{HMF Yield} = \frac{(1 + m_{25^\circ C}\Phi)\ [\mathrm{HMF}]_a}{[G]_0} \qquad (5\text{-}18)$$

where $m_{25^\circ C} = 0.23$ is the HMF distribution coefficient at room temperature.

Predicted HMF formation profiles have been computed for both diffusion-controlled and reaction-controlled conditions. If the two-phase system is diffusion controlled, i.e., the aqueous phase reaction rates are much greater than the rate of HMF interphase mass transfer, then HMF formation is simply based on the amount of HMF produced in the aqueous phase according to Equation (2-9). On the other hand, if the two-phase system is reaction rate controlled, i.e., the rate of interphase mass transfer is much greater than the rate of chemical reaction, then HMF formation can be computed on the basis of instantaneous mass transfer, Equation (2-14).

Predicted HMF yield profiles have been computed at 180 and 200°C for both diffusion-controlled and reaction-controlled conditions, and are compared to experimental data in Figures (5-17) and (5-18), respectively. All of the experimentally-determined HMF yield data are quite close to the predicted diffusion-controlled profiles, which suggests that the rate of reaction in our experiments was much faster than the rate of interphase mass transfer. This observation is not surprising since the cross-sectional area of the reaction bombs was small and the two-phase reaction mixtures were not agitated. In addition, a resinous material collected at the water-solvent interface, which undoubtedly retarded the diffusion of HMF from the aqueous phase to the solvent phase.

As was discussed earlier, higher yields of HMF in an aqueous phase system are obtained at higher temperatures because E_1 is greater than both E_2 and E_3. A comparison of HMF experimental data and model predictions in Figures (5-17) and (5-18) shows that this is also true for a two-phase system. Note that the experimental data at 200°C (Figure

(5-18)) is closer to the predicted diffusion-controlled yield profile than the corresponding 180°C data (Figure (5-17)). This is not surprising because reaction rates tend to increase much faster with temperature than diffusion rates. (Sproull (1986) has reported activation energy for furfural diffusion to be less than 1 kcal/g-mol versus activation energies for reaction above 20 kcal/g-mol.)

In a two-phase reaction system with an acidic aqueous phase containing glucose, in the aqueous phase, HMF is produced. Under the condition of instantaneous mass transfer, a portion of HMF diffuses into the solvent phase. Thus, the degradation of HMF in the aqueous phase for reaction-controlled system is slower than for diffusion-controlled system. This results in higher HMF yields for reaction-controlled systems as compared to diffusion-controlled systems. Figures (5-17) and (5-18) show that HMF yield is nearly double for the reaction-controlled system versus to the diffusion-controlled system. This information can be used to design a two-phase reactor for HMF production.

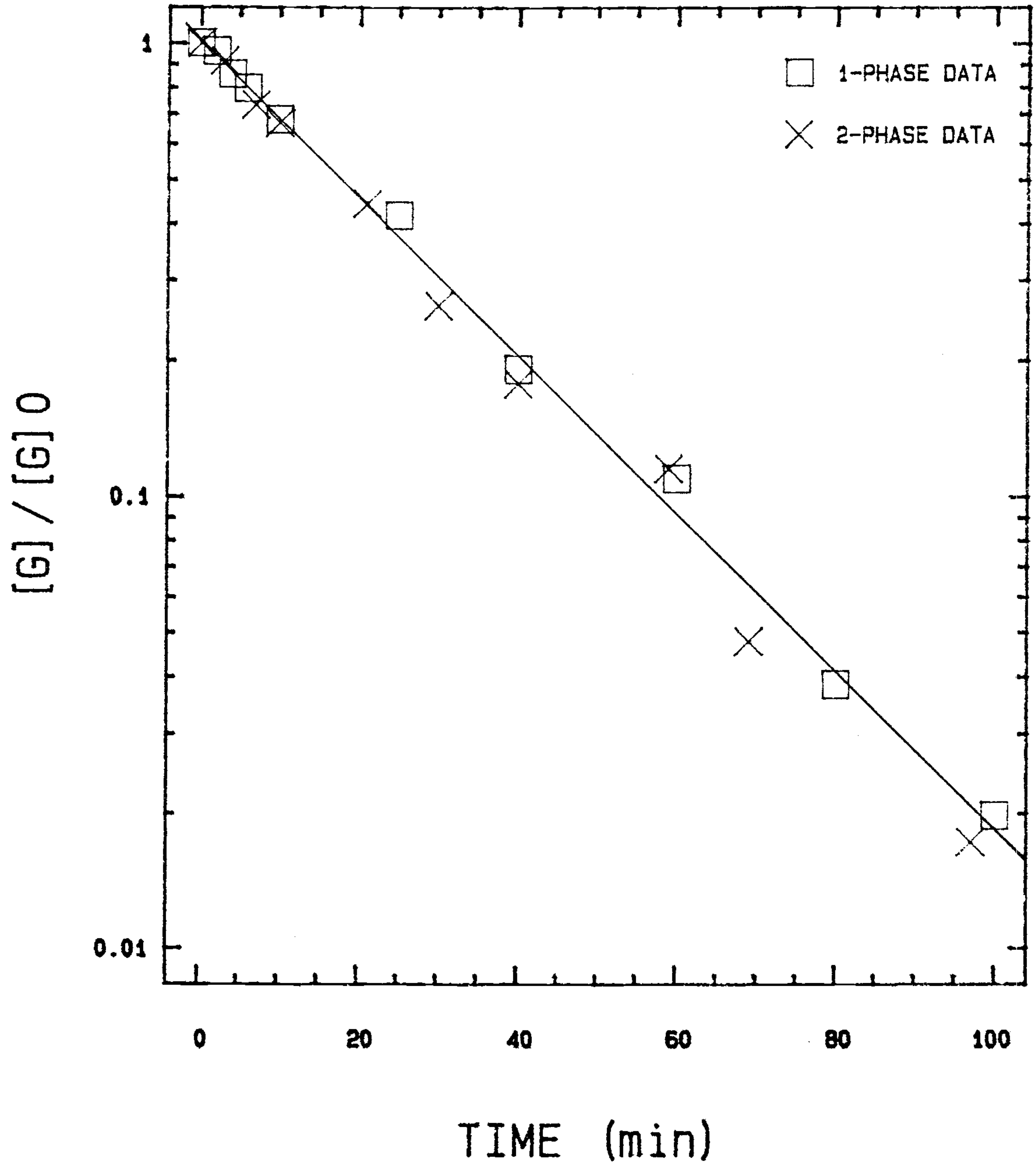


Figure 5-16

Comparison of Glucose Degradation
in One-Phase and Two-Phase Reaction Systems
T = 180°C

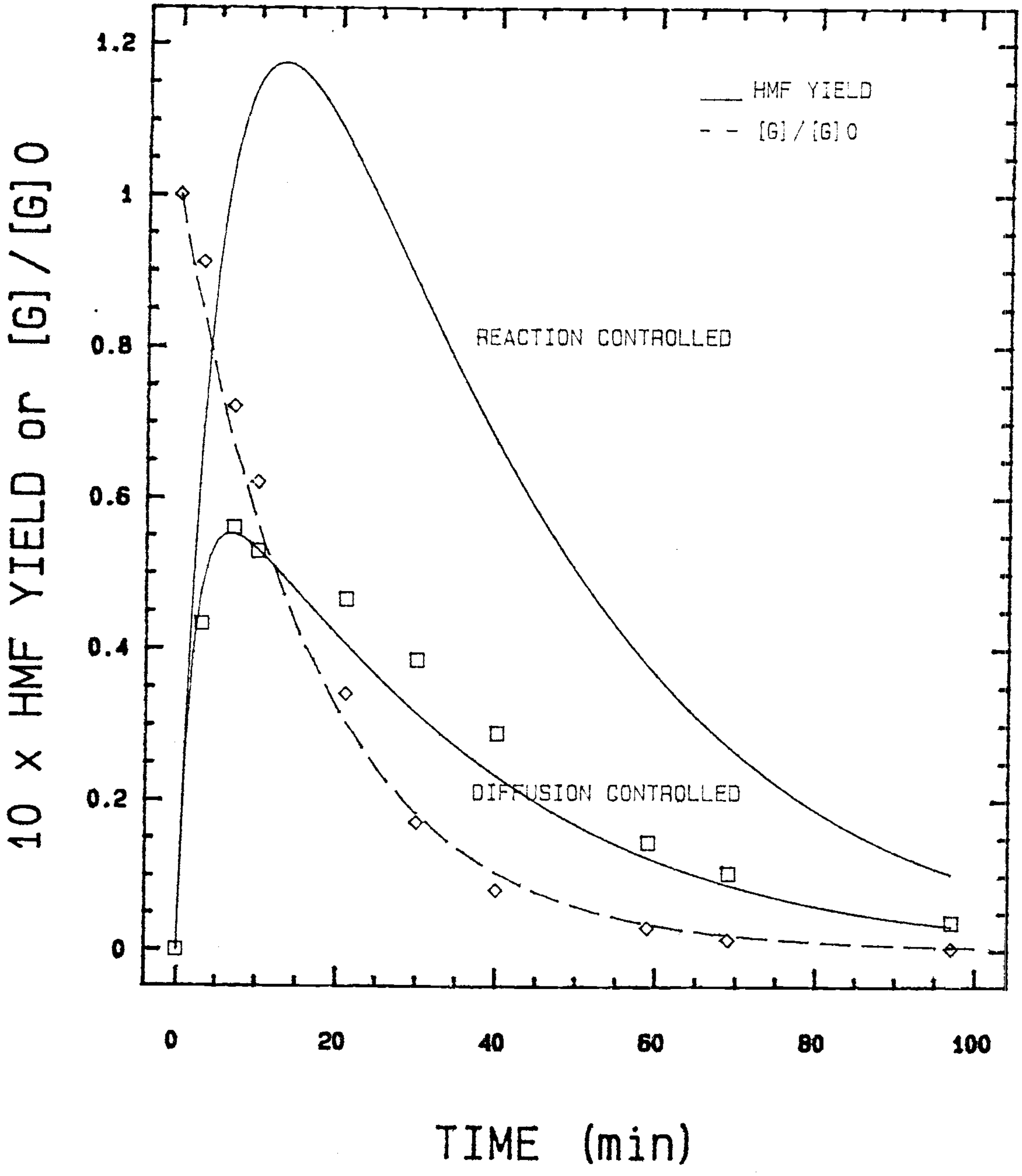


Figure 5-17

Two-Phase Concentration Profile
$[G]/[G]_0$ and $[HMF]/[G]_0$ vs Time
T = 180°C, $[H_2SO_4]$ = 0.1 M, $[G]_0$ = 0.278 M

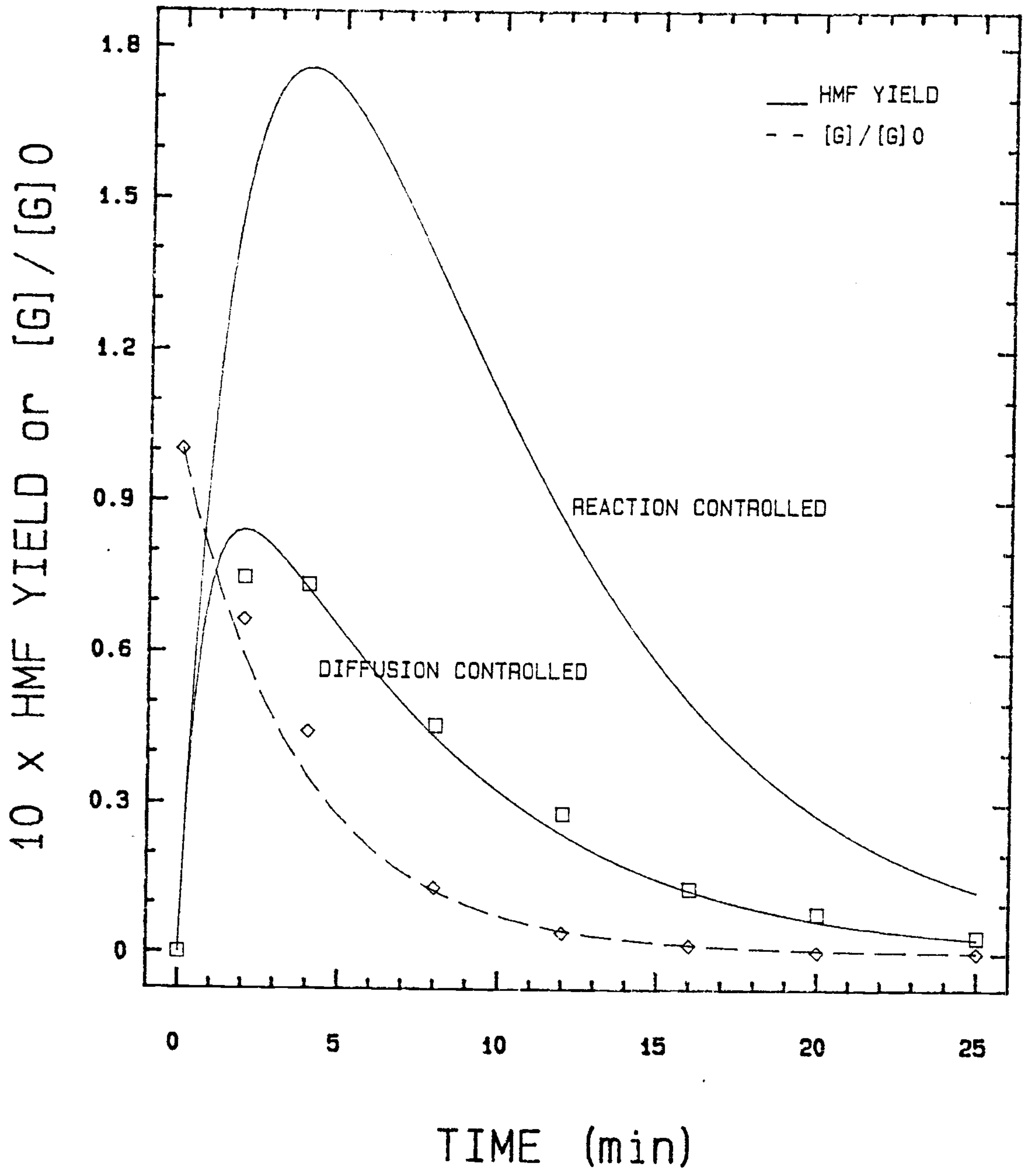


Figure 5-18

Two-Phase Concentration Profile
$[G]/[G]_0$ and $[HMF]/[G]_0$ vs Time
T = 200°C, $[H_2SO_4]$ = 0.1 M, $[G]_0$ = 0.278 M

CHAPTER 6

CONCLUSIONS

6.1 Aqueous Phase Kinetics

While the proposed three-constant model for glucose conversion to HMF:

$$\frac{d[G]}{dt} = -\,k_1[G]$$

$$\frac{d[HMF]}{dt} = k_1[G] - k_2[HMF] - k_3[G][HMF]$$

$$\frac{d[D]}{dt} = k_2[HMF]$$

is an oversimplification of the true reaction path, it adequately explains the observed phenomena. The model accurately predicts the glucose and HMF concentration profiles for sulfuric acid concentrations between 0.025 and

0.4 M and for a reaction temperature range of 160 to 220°C. The model can also be used to predict the organic acids concentration profile, as was verified for a sulfuric acid concentration of 0.1 M and for a reaction temperature range of 160 to 200°C.

The three rate constants in the above model can be fitted to a modified Arrhenius expression which accounts for the acid catalyst concentration:

$$k_i = k_{i0}[H_2SO_4]^{ai} \exp(-E_i/RT) \qquad (6\text{-}1)$$

where

$$k_1 = 1.3\text{x}10^{15}\ [H_2SO_4]^{0.86} \exp(-32500/RT)$$
$$k_2 = 4.7\text{x}10^{11}\ [H_2SO_4]^{1.06} \exp(-23100/RT)$$
$$k_1 = 2.4\text{x}10^{10}\ [H_2SO_4]^{0.71} \exp(-20300/RT)$$

Note that the activation energy for HMF production (E_1) is larger than the activation energies for HMF degradation (E_2, E_3), which means that HMF yield increases as temperature is increased.

6.2 Hydroxymethylfurfural Distribution in Aqueous and o-Nitrotoluene Phases

The HMF distribution coefficient for o-nitrotoluene, m, can be modeled by the integrated Van't Hoff equation.

$$m = 9.93 \exp(-2240/RT) \qquad (6\text{-}2)$$

The enthalpy change for the transfer of HMF from the aqueous phase to the solvent phase is positive, thus m increases with temperature. Therefore, to enhance the recovery of, HMF extraction of HMF should be performed at higher temperatures.

The values of m are small over the studied temperature range indicating that o-nitrotoluene is not a good solvent for extracting HMF from an aqueous phase.

6.3 Two Phase Kinetics

The presence of o-nitrotoluene phase does not affect the degradation of glucose. The aqueous phase kinetic model could be used in conjunction with the HMF distribution coefficient to give estimated HMF yield in the two-phase reaction system. Predicted HMF yield for diffusion-controlled condition match the experimental determined HMF yield data very well. Without agitating the two phase and with the small interfacial area of the reaction bombs, the process is diffusion-controlled.

The yield of HMF can be increased by the use of an immiscible solvent under fast mass transfer conditions, ie, when the two-phase mixture is agitated. In the limiting case, when the mass transfer is instantaneous, the HMF yield will nearly double.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE WORK

(1) To maximize HMF yield while minimizing the amount of solvent used, a solvent with a large HMF distribution coefficient is required. Studies should be conducted to measure the HMF distribution coefficients of various solvents.

(2) To increase the HMF yield, an agitated two-phase reaction system should be utilized.

(3) Different types of GC columns should be tested to separate HMF from various solvents. The behavior of HMF in the o-nitrotoluene phase is still unknown.

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APPENDICES

APPENDIX A: COMPUTER PROGRAM FOR ESTIMATING THE K_3 PARAMETERS FOR THE PROPOSED THREE-CONSTANT MODEL

```
C     --------------------------------------------------------------
C        THIS PROGRAM ESTIMATES THE K3 PARAMETERS IN THE
C     PROPOSED THREE-CONSTANT AQUEOUS PHASE KINETIC MODEL.
C     --------------------------------------------------------------


      PROGRAM K3


      DIMENSION TTIME(200),HHMF(200)
      DIMENSION EHMF(20,4)
      REAL K1,K2,K3
      COMMON K1,K2,K3,G0
      EXTERNAL DHMFDT

      OPEN ( 2, FILE = 'EHMF.DAT' )
      OPEN ( 3, FILE = 'HHMFTT.DAT' )
      OPEN ( 4, FILE = 'HHMFT.DAT' )
      OPEN ( 5, FILE = 'K3SSR.DAT' )

      READ(2,20) ( ( EHMF(I,J), J = 1,4 ), I = 1,20 )
      CLOSE (2)

5     WRITE(*,*) 'ENTER TEMPERATURE (C)'
      READ (*,*) TEMPC
      WRITE(*,*)

      IF ( TEMPC.EQ.180 ) GO TO 6
      IF ( TEMPC.EQ.190 ) GO TO 6
      IF ( TEMPC.EQ.200 ) GO TO 6
      IF ( TEMPC.EQ.220 ) GO TO 6

     WRITE(*,*) 'NO EXPERIMENT DATA FOR THIS TEMPERATURE'
     WRITE(*,*) 'TRY 180, 190, 200, OR 220 PLEASSE'
     WRITE(*,*)
     WRITE(*,*)
     GO TO 5


6     WRITE(*,*) 'ENTER [ACID] (N)'
      READ(*,*) ACIDN
      WRITE(*,*)
```

```
 IF ( ACIDN.EQ.0.05 ) THEN
        CG = 1.28
        CH = 0.81
   ELSE IF ( ACIDN.EQ.0.1 ) THEN
        CG = 1.06
        CH = 0.79
   ELSE IF ( ACIDN.EQ.0.2 ) THEN
        CG = 0.98
        CH = 0.84
   ELSE IF ( ACIDN.EQ.0.4 ) THEN
        CG = 0.99
        CH = 0.90
   ELSE IF ( ACIDN.EQ.0.8 ) THEN
        CG = 1.00
        CH = 0.97
   ELSE

WRITE(*,*) 'NO EXPERIMENT DATA FOR THIS TEMPERATURE'
WRITE(*,*) 'TRY 0.05, 0.1, 0.2, 0.4, OR 0.8 PLEASSE'
     WRITE(*,*)
     WRITE(*,*)
        GO TO 6
    ENDIF

 ACIDW = 4.9*ACIDN

 WRITE(*,*) 'ENTER GLUCOSE INITIAL CONCENTRATION'
 READ(*,*) GO
 WRITE(*,*)

 WRITE(*,*) 'ENTER MINIMUN & MAXIMUN GUESSING
&             K3*1000 VALUES'
 READ(*,*) K3MINI,K3MAXI
 WRITE(*,*)

 WRITE(*,*) 'ENTER K3 SEARCHING STEP'
 READ(*,*) K3STEP
 WRITE(*,*)

 WRITE(*,*) 'ENTER 1 FOR PRINTING [HMF]-TIME DATA'
 READ(*,*) IPHT
 WRITE(*,*)

 WRITE(*,*) 'ENTER 1 FOR SENDING HHMFT-TIME DATA'
 READ(*,*) IHTT
 WRITE(*,*)

 WRITE(*,*) 'ENTER 1 FOR SENDING HHMF-TIME DATA'
 READ(*,*) IHT
 WRITE(*,*)
```

```
      WRITE(*,*) 'ENTER 1 FOR SENDING K3-SSR DATA'
      READ(*,*) IKSSR
      WRITE(*,*)

      RT = (TEMPC + 273.16)*1.987
      K1 = 1.83E14*ACIDW**0.8634*EXP(-32506/RT)
      K2 = 2.2E11*CH*ACIDN*EXP(-23110/RT)
      HMF0 = 0.0

      TIMEMAXI = 2.0/K1

      TIMESTEP = TIMEMAXI/200

      WRITE(*,21) TEMPC
      WRITE(*,22) ACIDN, ACIDW
      WRITE(*,23) TIMEMAXI
      WRITE(*,24) TIMESTEP
      WRITE(*,25) K1
      WRITE(*,26) K2

      IF(IPHT.NE.1) WRITE(*,*) '     K3                    SSE'
      WRITE(*,*)


      DO 100 IK3 = K3MINI,K3MAXI,K3STEP

         SSE = 0.0
              K3 = IK3
         K3 = K3/1000
            TIMESTEP = TIMEMAXI/200
         HMF = 0.0
         TIME = 0.0


C     ------------------------------------------
C     OPTIMIZATION SECTION OF THE PROGRAM WHICH
C     MINIMIZES THE SUM OF THE SQUARE OF ERRORS
C     OF THE OBSERVED AND THEORETICAL HMF CONC.
C     ------------------------------------------


       CALL RUNGE( TIME, HMF, TIMESTEP, TIMEMAXI, DHMFDT,
     &             TTIME, HHMF )

         IF (IPHT.EQ.1) THEN
         WRITE(*,*) 'TIME MIN     [HMF].E.(M)    [HMF].T.(M)'
         WRITE(*,*)
         ENDIF
```

```
        IF (IHTT.EQ.1) THEN
            DO 10 I=1,200
               WRITE(3,27) TTIME(I), HHMF(I)
 10         CONTINUE
        ENDIF



        DO 15 I = 1,20
           IF (TEMPC.EQ.180) J = 1
           IF (TEMPC.EQ.190) J = 2
           IF (TEMPC.EQ.200) J = 3
           IF (TEMPC.EQ.220) J = 4

           SSE = SSE + ( 0.556*EHMF(I,J) - HHMF(10*I) )**2

           IF(IPHT.EQ.1)
             WRITE(*,28) TTIME(10*I), EHMF(I,J),
     &                   HHMF(10*I)/0.556
           ENDIF

           IF(IHT.EQ.1)
             WRITE(4,28) TTIME(10*I), EHMF(I,J),
     &                   HHMF(10*I)/0.556
           ENDIF

 15     CONTINUE



C    ------------------------------------------
C    PRINT THE SUM OF THE SQUARE OF ERRORS FOR
C    EACH VALUE OF K3 GUESSED.
C    ------------------------------------------



        IF (IKSSE.EQ.1) WRITE(5,29) K3,SSE

        IF (IPHT.EQ.1) THEN
            WRITE(*,30) K3,SSE
          ELSE
            WRITE(*,29) K3,SSE
        ENDIF

 100  CONTINUE
```

```
      WRITE(*,*)
      WRITE(*,*)
      WRITE(*,*) 'ENTER 1 FOR TRYING MORE TEMPERATURE DATA
     &            SET'
      READ(*,*) MORE
      WRITE(*,*)
      WRITE(*,*)
      IF ( MORE.EQ.1 ) GO TO 5



20    FORMAT ( 4(F5.3, 4X) )
21    FORMAT ( ////1X, 'TEMP(C) = ', F6.2 )
22    FORMAT (1X, 'H2SO4 CONC. = ', F6.3, '(N)', /13X, '= ',
     &        F6.3,'(WT%)')
23    FORMAT ( 1X, 'INTEGRATION LIMIT = ', F7.3 )
24    FORMAT ( 1X, 'STEP SIZE = ', F7.3 )
25    FORMAT ( //1X, 'K1 = ', F9.5 )
26    FORMAT ( 1X, 'K2 = ', F9.5//// )
27    FORMAT ( 1X, F6.2, 5X, F6.4 )
28    FORMAT ( 1X, F6.2, 11X, 2(F6.4, 10X) )
29    FORMAT ( 1X, F9.5, 10X, F12.9 )
30    FORMAT ( /1X, 'K3 = ', F9.5, 10X, 'SSE = ', F12.9/// )

      CLOSE (3, STATUS = 'KEEP')
      CLOSE (4, STATUS = 'KEEP')
      CLOSE (5, STATUS = 'KEEP')

      STOP
      END
```

```
C    ____________________________________________________________
C
C    THIS FOURTH ORDER RUNGE-KUTTA SUBROUTINE INTEGRATES
C    N SIMULTANEOUS  FIRST ORDER  DIFFERENTIAL EQUATIONS
C    ____________________________________________________________


     SUBROUTINE RUNGE (TIME, HMF, TIMESTEP, TIMEMAXI,
    &                  DHMFDT, TTIME, HHMF)


     DIMENSION TTIME(200),HHMF(200)
     COMMON K1,K2,K3,G0
     REAL L1,L2,L3,L4,K1,K2,K3

     M = 0

1    M = M + 1
     TIME TIME + TIMESTEP

        L1 = TIMESTEP*DHMFDT(TIME,HMF)
        L2 = TIMESTEP*DHMFDT(TIME+TIMESTEP/2.0,HMF+L1/2.0)
        L3 = TIMESTEP*DHMFDT(TIME+TIMESTEP/2.0,HMF+L2/2.0)
        L4 = TIMESTEP*DHMFDT(TIME+TIMESTEP,HMF+L3)

        HMF = HMF + (L1 + 2.0*(L2 + L3) + L4)/6.0

        TTIME(M) = TIME
        HHMF(M) = HMF

        IF(TIME.LT.TIMEMAXI) GO TO 1

     RETURN
     END


C    __________________________________________________
C
C    THIS SUBROUTINE SUPPLIES THE DIFFERENTIAL
C    EQUATIONS   TO BE INTEGRATED  BY  "RUNGE"
C    __________________________________________________


     FUNCTION DHMFDT(TIME,HMF)
     REAL K1,K2,K3
     COMMON K1,K2,K3,G0
     G = G0*EXP(-K1*TIME)
     DHMFDT = K1*G-K2*HMF-K3*G*HMF
     RETURN
     END
```

APPENDIX B: COMPUTER PROGRAM FOR MODELING HYDROXYMETHYLFURFURAL AND TOTAL ORGANIC ACIDS FORMATION

```
C     ----------------------------------------------------------------

C     THIS PROGRAM CALCULATES THE DEGRADATION OF GLUCOSE, THE
C     FORMATION AND DEGRADATION OF HYDROXYMETHYLFURFURAL, AND
C     THE FORMATION OF TOTAL ORGANIC ACIDS AS FUNCTIONS OF
C     REACTION TIME USING THE PROPOSED THREE-CONSTANT MODEL.
C     ----------------------------------------------------------------


      PROGRAM GHLFTIME


      DIMENSION T(200), TK1T(200), TK2T(200)
      DIMENSION G(200), HMF(200), FL(200)
      DIMENSION C(3),DCDT(3)
      REAL K(3)
      COMMON K, CCM
      EXTERNAL DGHFL

      OPEN ( 3, FILE = 'HHH.DAT' )
      OPEN ( 4, FILE = 'LLFF.DAT' )
      OPEN ( 5, FILE = 'GHLF.DAT' )

5     WRITE(*,*)'ENTER TEMPERATURE (C) AND ACID CONCENTRATION
     &            (M)'
      READ(*,*) TEMPC, ACIDM
      WRITE(*,*)
      WRITE(*,*) 'ENTER G0 VALUE'
      READ(*,*) G0
      WRITE(*,*)
      WRITE(*,*) 'ENTER TIME OF REACTION IN MINUTES'
      READ(*,*) TIMEMAXI
      WRITE(*,*)
      WRITE(*,*) 'ENTER 1 FOR SENDING HHMFT-TIME DATA'
      READ(*,*) IHTT
      WRITE(*,*)
      WRITE(*,*) 'ENTER 1 FOR SENDING LLFFT-TIME DATA'
      READ(*,*) ILFTT
      WRITE(*,*)
      WRITE(*,*) 'ENTER 1 FOR SENDING GHLFT-TIME DATA'
      READ(*,*) IGHLFTT
      WRITE(*,*)
```

```
       WRITE(*,*) 'ENTER 1 FOR CALCULATING THE DIFFUSION-
      &            CONTROLLED CASE AND 2 FOR THE REACTION-
      &            CONTROLLED CASE'
       READ(*,*) ICM
       WRITE(*,*)

       RT = (TEMPC + 273.16)*1.987
       K(1) = 1.3E15*ACIDM**0.86*EXP(-32500/RT)
       K(2) = 4.7E11*ACIDM**1.06*EXP(-23110/RT)
       K(3) = 2.4E10*ACIDM**0.71*EXP(-20300/RT)
       CCM = 9.93*EXP(-2240/RT)
       TIMESTEP = TIMEMAXI/200.

       WRITE(*,23) TIMEMAXI
       WRITE(*,24) TIMESTEP
       WRITE(*,25) K(1)
       WRITE(*,26) K(2)
       WRITE(*,27) K(3)
       WRITE(*,28) G0

          TIME = 0.0
          C(1) = G0
          C(2) = 0.0
          C(3) = 0.0

       IF (ICM.EQ.2) GO TO 6

          CALL RUNGE ( DGHFL, 3, TIME, C, DCDT, TIMESTEP,
      &                TIMEMAXI, T, G, HMF, FL, 1 )
          GO TO 7

 6        CALL RUNGE ( DGHFL, 3, TIME, C, DCDT, TIMESTEP,
      &                TIMEMAXI, T, G, HMF, FL, 2 )
 7        CONTINUE

          IF (IHTT.EQ.1) THEN
              DO 10 I = 1,20
                 WRITE(*,29) T(10*I), 10*HMF(10*I)/G0
                 WRITE(3,29) T(10*I), 10*HMF(10*I)/G0
 10           CONTINUE
          ENDIF


          IF (ILFTT.EQ.1) THEN
              DO 11 I = 1,20
              WRITE(*,29) T(10*I), FL(10*I)
                 WRITE(4,29) T(10*I), FL(10*I)
 11           CONTINUE
          ENDIF
```

```
      WRITE(*,*)
      WRITE(*,*) 'ENTER 1 FOR TRYING MORE DATA SET'
      READ(*,*) MORE
      WRITE(*,*)
      WRITE(*,*)
      IF ( MORE.EQ.1 ) GO TO 5


23    FORMAT (//// 1X, 'INTEGRATION LIMIT = ', F6.2 )
24    FORMAT ( 1X, 'STEP SIZE = ', F7.3 )
25    FORMAT ( 1X, 'K1 = ', F9.5 )
26    FORMAT ( 1X, 'K2 = ', F9.5 )
27    FORMAT ( 1X, 'K3 = ', F9.5 )
28    FORMAT ( 1X, 'G0 = ', F9.5//////)
29    FORMAT ( 1X, F6.2, 5X, F6.4 )

      CLOSE (3, STATUS = 'KEEP')
      CLOSE (4, STATUS = 'KEEP')
      CLOSE (5, STATUS = 'KEEP')

      STOP
      END


C     ____________________________________________________
C
C     THIS FOURTH ORDER RUNGE-KUTTA SUBROUTINE INTEGRATES
C     N SIMULTANEOUS  FIRST ORDER  DIFFERENTIAL EQUATIONS
C     ____________________________________________________


      SUBROUTINE RUNGE ( DGHFL, N, TIME, C, DCDT, TIMESTEP,
     &                   TIMEMAXI, T, G, HMF, FL, MC )


      EXTERNAL DGHFL
      DIMENSION C(N), DCDT(N), CC(10), DCL(4,10), ZL(4)
      DIMENSION T(200), G(200), HMF(200), FL(200)
      DATA ZL/0.0,0.5,0.5,1.0/

      M = 0

1     M = M + 1
      TIME = TIME + TIMESTEP

      CALL DGHFL ( TIME, C, DCDT, N, MC )
```

```
      DO 100 I = 1, N
           DCL(1,I) = TIMESTEP*DCDT(I)
100   CONTINUE

      DO 200 J = 2, 4

           TTIME = TIME + ZL(J)*TIMESTEP

           DO 150 I = 1, N
                CC(I) = C(I) + ZL(J)*DCL(J-1, I)
150        CONTINUE

           CALL DGHFL ( TTIME, CC, DCDT, N, MC )

           DO 180 I = 1, N
                DCL(J,I) = TIMESTEP*DCDT(I)
                DCL(1,I) = DCL(1,I) + DCL(J,I)/ZL(J)
180        CONTINUE

200   CONTINUE

      DO 300 I = 1, N
           C(I) = C(I) + DCL(1,I)/6
300   CONTINUE

      T(M) = TIME
      G(M) = C(1)
      HMF(M) = C(2)
      FL(M) = C(3)

      IF(TIME.LT.TIMEMAXI) GO TO 1

      RETURN
      END




C
C     ________________________________________
C
C     THIS SUBROUTINE SUPPLIES THE DIFFERENTIAL
C     EQUATIONS   TO BE INTEGRATED  BY  "RUNGE"
C     ________________________________________


      SUBROUTINE DGHFL ( TIME, C, DCDT, N, MC )
      DIMENSION DCDT(3), C(3)
      REAL K(3)
      COMMON K, CCM
```

```
IF ( MC.EQ.1 ) CM = 1.
IF ( MC.EQ.2 ) CM = 1/( 1 + 2*CCM)
DCDT(1) = - K(1)*C(1)
DCDT(2) = CM*(K(1)*C(1)-K(2)*C(2)-K(3)*C(1)*C(2))
DCDT(3) = K(2)*C(2)
RETURN
END
```