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REACTIONS OF CHLOROCARBON SPECIES WITH HYDROGEN OVER PALLADIUM ON ALUMINA CATALYST AND ZEOLITE CATALYST-DEVELOPMENT OF DEACTIVATION MODELS

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REACTIONS OF CHLOROCARBON SPECIES WITH HYDROGEN OVER PALLADIUM ON ALUMINA CATALYST AND ZEOLITE CATALYST- DEVELOPMENT OF DEACTIVATION MODELS

by

Yuh-Der Yang

Dissertation submitted to the Faculty of the Graduate School
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fulfillment of the requirements for the degree of
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ABSTRACT

Four catalytic dechlorination reactions were studied experimentally using a fixed-bed reactor at atmosphere pressure. Reaction mechanisms were proposed, and the kinetics modelled.

The first reaction is 1,2-dichloroethane with hydrogen over zeolite catalyst. Catalyst deactivation models were examined.

The second reaction was between 1,2-dichloroethane and hydrogen over palladium catalyst on alumina support. Formation of two intermediates on the catalyst surface is proposed, which then produced ethane, ethylene, and ethyl chloride. Higher conversion to ethane and ethylene was observed at temperatures above 218°C while conversion to chloroethane is higher at temperatures below 218°C. The activation energy was found to be 15 Kcal/gm-mole.

The third reaction was between chloroform and hydrogen over palladium on alumina. Once again, a free radical mechanism was also proposed to interpret the product formation of methylene chloride and methane. The activation energy is 19 Kcal/gm-mole, and conversions up to 12 % were observed.

The fourth reaction was between chlorobenzene and hydrogen over palladium on alumina catalyst. Benzene and biphenyl were the main products at temperatures between 35 and 70°C. An absorbed resonance mechanism is suggested for interpreting the production of benzene and biphenyl. A

simple first order reaction model for chlorobenzene was used to obtain kinetic parameters. The activation energy was found to be 13 Kcal/gm-mole.

The relatively low temperature requirements, and low activation energies, indicate that these catalyst systems could be used in an effective process for conversion of aromatic chlorinated species into hydrocarbons plus hydrogen chloride.

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CHAPTER 1 General Introduction

The objectives of this work are to investigate catalytic reactions of halocarbons, specifically those of chlorocarbons, over various materials in an effort to find catalysts which will promote hydrogenation/dehalogenation. The reactions would then produce a hydrocarbon, without any chlorine. The HCl product could be easily separated or neutralized. The understanding of this catalytic system and extensive study in conversion and products of reaction for various chlorocarbons would lead to a technique for production of useful materials from unwanted halocarbons. There is very little information reported in the literature regarding such reactions.

Four systems of different reactants and catalysts are investigated in this work. All four systems used a packed bed reactor to study the dehydrochlorination. Chapter 2 discusses the reaction of 1,2-dichloroethane with hydrogen over zeolite catalyst where the products are primarily vinyl chloride and HCl. Unfortunately, as with many catalysts, this commercial zeolite (zeolon 900 H, Norton company) suffers a loss of activity with time-on-stream and the operational lifetime is short. Thus, in this chapter, we focus our attention on the deactivation of zeolite and on developing accurate models to explain obtained data.

In Chapter 3 the experimental data and theory on the reactions- 1,2-dichloroethane with hydrogen and chloroform with hydrogen over palladium on alumina support- are presented. A significant conversion with products of chloroethane, ethylene, and ethane is observed for 1,2-dichloroethane, while methylene chloride and methane are formed from chloroform. The reaction of chlorobenzene with hydrogen over palladium supported on alumina is reported in Chapter 4. The main products are benzene and biphenyl.

The reaction kinetic parameters are calculated based on these assumptions:

(1) First order reaction for 1,2-dichloroethane

(2) Isothermal reactions

CHAPTER 2: Catalyst Deactivation Models: Application to Reaction of 1,2-Dichloroethane Over Zeolite in H_2 Atmosphere

2-1 INTRODUCTION

Zeolite catalysts can be used not only for cracking reaction but also for dehydrohalogenation of alkyl halides. Rapid loss in the initial activity over a period of time often accompanies the experiment because of poisioning, fouling, or sintering. The suggested method to cure the deactivation problem caused by fouling is to increase H_2 partial pressure (Carberry, 1976). Therefore, from this point of view, if the pore -mouth of catalyst is not yet blocked by carbonaceous deposit before it approachs an equilibrium amount, the catalyst activity should not go to zero. Based on this assumption, we derive two models which are obtained by modifying Levenspiel's independent deactivation model. Reaction of 1,2-dichloroethane with hydrogen over zeolite catalyst produced a large amount of carbonaceous deposit which rapidly covered the active sites on the catalyst surface and lessened the catalyst activity.

2-2 LITERATURE SURVEY

Venuto et al. (1966) have reported the reaction of dehydrohalogenation catalyzed by crystalline aluminosilicates at one atmospheric pressure and temperature in the range 65 to 370°C for 1,2-dichloroethane over REX catalyst. The main product was vinyl chloride. Kladnig et al. (1973) used a flow reactor to study the reactions of 1-

chlorobutane and 2-chlorobutane over X and A zeolites containing different cations. Their products include all 4 butene isomers for X zeolites and a carbonium ion mechanism was suggested. Feurier et al. (1979) studied the catalytic decomposition of several halomethanes over Platinum-on-alumina and also on zeolite catalysts at temperatures below 300°C, where the primary products observed were the hydrogen halides, halogens, carbon monoxide and other halocarbon species. Some of the reactions showed considerable deactivation of the catalyst.

Hatano et. al. (1981) have studied high pressure hydrodechlorination of polychlorinated biphenyl's using Raney Nickel catalysts in a batch reactor at relatively low temperatures. They observed production of biphenyl but with relatively long reaction times and low percentage yields. A few other authors have studied the catalytic hydrodehalogenation over supported metal catalysts. The work of Weiss et. al. (1966) for reactions of cis- and trans-dichloroethylene with H_2 over platinum-on-alumina catalysts, gave an activation energy of 27.5 Kcal/mole and a reaction shift from zero order to first order. The work of Lapierre et al. (1978) for the reaction of 1,1-bis(p-chlorophenyl)-2,2-dichloroethylene(p,p'-DDE) over Pd-on-alumina catalysts at 170-230°C and 40-670 Torr of hydrogen explained the relative reactiveness of aromatics and olefinic chlorides by an absorbed stabilized resonance structure. The study of Dodson et al. (1978) for the reaction of chloroform over palladium-on-charcoal catalysts, platinum-alumina, and Pt-Re/Al_2O_3 indicated that Pt/Al_2O_3 catalyst is a very good candidate for a hydrodechlorination process because of a reasonable reaction rate at atmospheric pressure and easy regeneration of fouled catalysts.

The work of Noelke et al. (1979) for the reaction of chloroform over Platnium-on-alumina catalysts claimed that the catalyst activity can be improved by means of a continuous water addition during reaction. The work of Kraus et al. (1973) for the reaction of chlorobenzene over palladium-on-charcoal catalysts suggested a mechanism for the dechlorination on palladium that chlorobenzene was attacked by a absorbed H- species.

Our study focuses on a system of 1,2-dichloroethane with hydrogen over a zeolite catalyst where the products will be shown to be primarily vinyl chloride and HCl. The results are quite encouraging in that initial conversion of the reagent being quite high (66%). However, it is accompanied by a rapid loss of catalyst activity via carbon formation.

The activity of a catalyst often decreases rapidly in reactions of organic species. Typically, deactivation of catalysts is found in the cracking of hydrocarbons over a zeolite catalyst (Yuichi,1968) as is frequently done in the petroleum industry. One common reason that deactivation of catalyst occurs is due to accumulation of carbonaceous deposits on the material surfaces. Many empirical equations have been published which try to explain (or characterize) mathematically the experimentally observed characteristics of this deactivation. Voorhies (1943), for example, has presented a frequently used relationship between carbon and reaction time.

$$C = A * t^n \qquad (1)$$

where C is the amount of carbon, A is an activity parameter t is the process time, and n is constant. Voorhies's results indicated that the coking rate was not a function of space velocity and also that it had a very small dependence on temperatures for fixed bed reactor (Hughes,1984). The independence of coking rate space on space velocity was also found by Blue and Engle (1951). But dependence on space velocity was found by Shiring et al. (Shiring et al., 1983) in the study of interparticulate coke formation during hydrocarbon cracking on zeolite catalysts. Ozawa et al. (1968) used a thermogravimentric system to continuously measure the weight of this coke production in a catalytic cracking system. Their method of measuring the coke content might have a few drawbacks, however, because the measurements also included some product and reactant species as equilibrium was approached. They found that the deposits have no significant effects on the surface area of the catalyst or on the efficient diffusion through the catalyst pore when the amount of deposits is less than 1 weight %.

Wojciechowski (1968) presented a relationship between activity and process time. The fundamental postulate of his Time-On-Stream theory is that the activity of the catalyst in a given reaction is a function of time only, and a second basic assumption of his theory is that all sites on a specific catalyst are identical. Therefore, under the condition of uniform catalytic surface, activity and concentration can be considered as separate terms. Several mechanisms for the decay of catalyst are reported by Wojciechowski (1974). He defined θ as the fraction of sites available at any time t. The general form of the function is

$$-d\theta/dt = k_d*\theta^m \qquad (2)$$

Where $m \neq 1$ and K_d is deactivation constant. After integrating this equation, one obtains the following:

$$\theta = (1/(1+(m-1)*k_d*t))^{1/(m-1)} \qquad (3)$$

When $m = 0$,

$$\theta = 1 - k_d*t \qquad (4)$$

which is the case of zero-order decay. This linear decay equation has been used by a number of authors including Crowe (1971), and Maxted (1951). The problem with this equation is that when time is very large, activity becomes negative. If the decay is not a function of reagent concentration (An example is the case where catalyst suffers sintering), this straightforward linear decay equation is expected to apply. For $m = 1$, we derive the final form

$$-d\theta/dt = k_d * \theta \qquad (5)$$

then

$$\theta = \exp(-k_d*t) \qquad (6)$$

Equation (6) is same as that used in Levenspiel's independent deactivation model (Levenspiel, 1972).

Wheeler (1955) has illustrated the case of deactivation for both pore-mouth and uniform poisoning. In uniform catalyst poisoning, he assumed that the poisoning precursor species has full access to the catalyst interior before deactivation begins, i.e. that there is no diffusional resistance to these poisoning species. This will likely occur when the catalyst particle is small, the intrinsic deactivation rate is low, or when the pores of catalysts are large. His results were

$$\text{Rate} = k*(1-\alpha) * C_o \qquad (7)$$

for slow reaction and

$$\text{Rate} = k *\sqrt{(1-\alpha)} * C_o \qquad (8)$$

for rapid reaction, where α is the fraction of the catalyst sites which are poisoned and C_o is the reactant concentration at the outer catalyst surface. The effective surface-rate constant is then

$$k_{eff} = k * (1-\alpha) \qquad (9)$$

for slow reaction and

$$k_{eff} = k *\sqrt{(1-\alpha)} \qquad (10)$$

for fast reaction.

In the pore-mouth poisoning case, he assumed that the total poisoning is at the mouth of the pore, and the rate is

$$\text{Rate} = \frac{(\pi *r*\sqrt{2*r*k*D} * \tanh(h_o*(1-\alpha))) * C_o}{1 + \alpha* h_o} \qquad (11)$$

and if $h_o*(1-\alpha) > 2$, $\tanh(h_o(1-\alpha)) \approx 1$ and the reaction rate will be

$$\text{Rate} = \frac{\pi * r * \sqrt{2 * r * k * D} * C_o}{1 + \alpha * h_o} \qquad (11')$$

where

$h_o = L * \sqrt{2 * k/r/D}$

r=pore radius

D=diffusion coefficient in the pore

L=pore length

This equation predicts that the activity will drop significantly when the catalyst suffers even very small amounts of poisoning.

Masamune-Smith (1961) solved a governing differential equation for parallel, and consecutive catalyst deactivation reactions. In this equation they assumed the reaction is irreversible, first order and isothermal. For a mechanism with coking parallel to reaction, they found the coke is deposited according to a descending profile in the catalysts' pore. For the consecutive coking mechanism, the coke profile is reverse, i.e. ascending and a maximum in the center of the catalysts. They also indicated how these results can be used with the various reactor design equations to numerically predict an overall conversion. Pachovsky et al. (1973) presented a table which lists most of the published decay functions, most of them similar to those in Levenspiel (1972). Butt et al. (1978) have indicated that the kinetic models of Szepe and Levenspiel (1970) can only be used for catalysts which have uniform surface (i.e. surface is homogeneous). In many industrial processes , however, where chemical poisoning of the catalyst occurs, the activity factor can not be separated from concentration, because the surface of catalyst is not ideal.

Internal and external diffusion may play a very important role in the catalytic reaction if the value of Thiele modulus is large. Kam et al. (1975) used an orthogonal collocation method to study isothermal fouling of catalyst pellets for the dehydration of alcohols. They indicated that at small values of the Thiele modulus, diffusion in the catalyst can be neglected regardless of time, and that the deposits are uniform through out the catalyst for parallel fouling. At high Thiele modulus, the reaction of reactant A occurs over a small region near the surface of the pellet. For series fouling, there is very little difference in the change in effectiveness factor between deactivated and fresh catalyst with increasing value of Thiele modulus.

A concentration-independent loss of activity for a first order reaction in a spherical particle which undergoes a first order deactivation was studied by Krishnaswamy et al. (1981, A; B). They concluded that the apparent deactivation rate constant can decrease below the one-half value limit for internal diffusion alone under the condition of severe internal diffusional limitation.

2-3 THEORY

Two modifications of the Levenspiel model are used in this work to fit our experimental data on reactions of 1,2-dichloroethane with hydrogen over zeolite catalysts, under the assumptions:

(1) The surface of catalyst is uniform

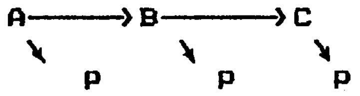
(2) Isothermal reactor

(3) Power-law kinetics

The rate equation is

$$-dC/dt = k*C*a$$

where a is activity, which is decoupled from the concentration. The reaction considered is:



where P stands for carbonaceous (deposits). Levenspiel's model predicts that activity for this independent deactivation decreases with time according to:

$$-da/dt = k_d*a$$

and

$$a = 1 \quad \text{at time} = 0$$

which upon integration gives

$$a = \exp(-k_d*t)$$

where k_d is the deactivation rate constant. This equation implies that as t ———> infinity, a ———> 0 and hence conversion will approach zero with increasing reaction time.

In this dissertation, however, hydrogen was used as a carrier gas sweeping 1,2-dichloroethane into the reactor, as well as the reagent. The conversion of reactant in this case did not approach zero as time increased, because hydrogen was capable of reducing some of the carbonaceous material on the catalyst and essentially continuously regenerating some of the catalyst activity during the reaction. Two models are developed for description of the catalyst deactivation in this reaction system.

2-3-1 Development of deactivation models

Model 1:

We define a deactivation factor η_d

$$\frac{\text{Rate of deactivation with regeneration}}{\text{Rate of deactivation without regeneration}} = \eta_d \qquad (12)$$

The rate of change in this deactivation factor with time is defined by:

$$-d\,\eta_d/dt = k_{d1} * \eta_d \qquad (12')$$

with initial condition of $\eta_d = 1$ when $t = 0$

The deactivation rate will be:

$$-da/dt = k_d * a \qquad (13)$$

where we assume $k_d = k_{do} * \eta_d$ (13')

In Levenspiel's model k_d is assumed to be a constant (deactivation), but k_d is a function of time here because of the time functionality in the deactivation factor. Solving this equation, we obtain:

$$\ln(a) = B*\exp(-k_{d1}*t)-B \tag{14}$$

where $B=k_{do}/k_{d1}$

When time ———› infinity, activity will go to the equilibrium value $a = \exp(-k_{do}/k_{d1})$.

Model 2:

If both deactivation and regeneration occur simultaniously and the deactivation order m is different from the regeneration order n, we may write the following equation:

$$-da/dt = k_d*a^m - k_r*(a^{n1}-a^{n2}) \tag{15}$$

The activity for m = 0.5 , n1 = 0.5 , and n2 = 1 is given by

$$a = ((1-b)*\exp(-k_r*t/2)+b)**2 \tag{16}$$

where $b = 1-k_d/k_r$ and $k_r = k_r'*[H_2]$, as $[H_2]$ is a constant. when t ———› infinity $a = b^2$. If there is no hydrogen present the activity is simple written as :

$$-da/dt = k_d*a \tag{17}$$

Equation 15 can not be written as

$$-da/dt = k_d* a^m-k_r*a^n.$$

Because when time is zero, the regeneration term should be zero. Here it also needs to be mentioned that, in equation 15, n_1 must be smaller than n_2 because the value of this activation term must increase to an equilibrium value.

We can derive an equation which is similar to equation 15. The loss of site concentrations with respect to time is described by the following equation:

$$-ds/dt = k'_d*S^n-k'_r*(S_o-S)^m \qquad (18)$$

where S is defined as the site concentrations available at time t, S_o is the initial value of site concentration, S_o-S is the covered site concentration, K'_d is deactivation constant, and k'_r is regeneration constant. Normalization yields

$$-d(S/S_o)/dt = (k'_d/S_o)*S^n-(k'_r/S_o)*(S_o-S)^m \qquad (19)$$

Rearrangement yields:

$$-da/dt = k_d *a^n-k_r*(1-a)^m \qquad (20)$$

where a is defined as S/S_o, k_d is $k'_d*(S_o)^{n-1}$, and k_r is $k'_r*(S_o)^{m-1}$.

2-3-2 EXTERNAL DIFFUSION AND DEACTIVATION

For a steady-state system, we can write

$$k_w*C_s*a = k_m*A_s*(C-C_s) \qquad (21)$$

where C_s is the concentration at the surface of the catalyst particles , k_m is the mass transfer coefficient (cm/s), and A_s is defined as the external specific surface of particles (cm^2/g of catalyst), C is the concentration in bulk flow, and k_w is the rate constant (cm^3/g of catalyst /time).

Let

$$k_w/k_m/A_s = D_a$$

Solving equation (21), we obtain

$$C_s = C/(1+D_a*a)$$

The reaction rate becomes

$$\text{Rate} = k_w*C*a/(1+D_a*a)=k_w*C_s*a \qquad (22)$$

The external effectiveness factor will therefore be equal to

$$\eta = k_w*C_s*a/k_w*C$$

$$\eta = a/(1+D_a*a) \qquad (23)$$

From this equation, if D_a is very small

$$\eta \approx a$$

and the reaction will be surface controlled. This situation holds for our study, since the catalyst particles are very small and we find that D_a is also very small (In this work D_a is about $3x10^{-3}$ for temperature 450°C). Combining external diffusion with the two decay models, we express the effectiveness coefficient as

$$\eta = \frac{\exp(B*(\exp(-B1)-1))}{1+D_a*\exp(B*(\exp(-B1)-1))} \qquad (24)$$

where $B = k_{do}/k_{d1}$, and $B1 = k_{d1}*t$

For our second model, the effective coefficient is

$$\eta = \frac{((1-b)*\exp(-b1)+b)**2}{1+D_a*((1-b)*\exp(-b1)+b)**2} \qquad (25)$$

where b1 = Kd *t/2. From equation 21 and 22, we find that external diffusion with deactivation will result in a lower reaction rate than in the case of only deactivation.

2-3-3 INTERNAL DIFFUSION AND DEACTIVATION

The mass conservation equation for a spherical catalyst particle which suffers deactivation and where reaction is a first order is (Bird, 1960; Krishnaswamy, 1981; Petersen, 1982):

$$D_{eff}*[d(r^2*dC/dr)/dr] = k*C*a*r^2 \qquad (26)$$

where r is the radius of particle, D_{eff} is the effective diffusion coefficient, a is the activity, and k is the rate constant (1/time). The boundary conditions are

$$(1) \qquad r = 0 \qquad dC/dr = 0 \qquad (27)$$

$$(2) \qquad r = R \qquad C = C_{As} \qquad (28)$$

To solve this equation , we let $C/C_{As} = f(r)/r$ (Bird,1960) and the solution will be

$$C = \frac{C_{As}*(R*\sinh(\sqrt{k*a/D_{eff}}\ *r))}{r*\sinh(\sqrt{k*a/D_{eff}}\ *R))} \qquad (29)$$

The molar flow at the surface is

$$W_s = -4*\pi*R^2*D_{eff}*(dC/dr)_{r=R} \qquad (30)$$

$$= 4*\pi*R*D_{eff}*C_{As}*(1-\sqrt{k*a/D_{eff}}\ *R*\coth(\sqrt{k*a/D_{eff}}\ *R)$$

The surface reaction rate is

$$r_A = -k*C_{As}$$

under condition of no deactivation or diffusion.

$$\eta = \frac{4*\pi*R*D_{eff}*C_{As}*(1-\sqrt{k*a/D_{eff}}*R*\coth(\sqrt{K*a/D_{eff}}*R)}{-\ \ 4/3*\pi*R^3*k*C_{As}} \qquad (31)$$

and after rearranging

$$\eta = \frac{\sqrt{a}\ *(\coth(\sqrt{k*a/D_{eff}}*R)-1/(\sqrt{k*a/D_{eff}}*R)}{R/3*\ (\sqrt{k/D_{eff}})} \qquad (32)$$

The total reaction rate for the fixed bed reactor is

$$-r_A = k_w*C*\ \eta \qquad (33)$$

Where k_w is in units of cm^3/g-time. For very small value of ($\sqrt{k/D_{eff}*R}$), η becomes the activity which is the case of our research. For an isothermal tubular reactor, the governing equation can be obtained from the mass balance (Smith, 1981); under assumptions of:

(1) No dispersion in radical direction

(2) Pseudo steady state

(3) Velocity is not a function of r and z

$$D_z d^2C/dz^2 - UdC/dz - k_w * C * \rho_b * \eta = 0 \qquad (34)$$

and the boundary conditions are

$$(1) z = 0 \qquad D_z dC/dz = U*(C_o - C) \qquad (35)$$

$$(2) z = L \qquad dC/dz = 0 \qquad (36)$$

where D_z is dispersion coefficient in z direction.

In terms of dimensionless parameters and conversion, equation 34 becomes

$$1/N_{pe} * d^2x/dZ^2 - dx/dZ + L * \rho_b * \eta * k_w * (1-x)/U = 0 \qquad (37)$$

the two boundary conditions are

$$(1) \; 1/N_{pe} * dx/dZ = x \quad \text{at } Z = 0 \qquad (38)$$

$$(2) \; dx/dZ = 0 \quad \text{at } Z = 1 \qquad (39)$$

where x is conversion, $Z = z/L$, and $N_{pe} = U*L/D_z$. The solution for equation (37) is

$$1-x = \frac{4*f*\exp(N_{pe}/2)}{(1+f)**2*\exp(f*N_{pe}/2) - (1-f)**2*\exp(-f*N_{pe}/2)} \qquad (40)$$

where

$$f = (\; 1+4*L*\rho_b*k_w* \; \eta/N_{pe}/U)^{0.5} \qquad (41)$$

To obtain 3 parameters (in equation (40), we used Gauss Newton nonlinear regression method. The computer program is shown in appendix A. In our study, effectiveness factor is assumed to be equal to activity.

2-3-4 INTERNAL AND EXTERNAL DIFFUSION

For a porous, spherical particle which has a homogeneous surface, the mass balance equation is identical to equation 26. if both internal and external diffusions are important, the boundary conditions are:

(1) $r = 0$ C is finite (27')

(2) $r = R$ $D_{eff}*(dC/dr) = k_m *(C_b-C_R)$ (28')

where C_b is the bulk concentration. The solution for equation (26) with the above two boundaries (equations (27') and (28')) is:

$$C/C_b = (R/r)*(Bim/\Phi/\sqrt{a})*(1/(\coth\Phi* \sqrt{a} +Bim/\Phi/ \sqrt{a} -1/\Phi/ \sqrt{a}))*(\sinh r/R*\Phi*\sqrt{a}/\sinh \Phi*\sqrt{a}) \qquad (29')$$

where $\Phi = \sqrt{k/D_{eff}}*R$ and $Bim = k_m*R/D_{eff}$.

According to the definition of effectiveness coefficient, it is:

$$\eta = (3*a/\Phi/ \sqrt{a})*(Bim/\Phi/\sqrt{a})*[(\coth \Phi*\sqrt{a} -1/\Phi/ \sqrt{a})/ (\coth\Phi *\sqrt{a} - 1/\Phi/ \sqrt{a} +Bim/\Phi/ \sqrt{a})]$$

When Bim ———> infinity , the bracket in the denominator of equation (29)' becomes $Bim/\Phi/ \sqrt{a}$, and expression of effectiveness coefficient is same as equation (32). When Bim is very small, external diffusion is important in the effectiveness coefficient which essentially becomes Da as defined in equation (23).

2-4 EXPERIMENTAL

1,2-dichloroethane was carried by hydrogen into the reactor which is in 12.5 mm OD by 10 mm ID quartz and packed with a commercial zeolite (Shell zeolon 900 H, Mordenite-hydrogen form, Norton Catalytic Products, Akron, Ohio). The catalyst is crushed to 45/60 mesh and used in quantities of 1 gram or less in the 10 mm ID reactor. Details of the experimental apparatus are shown on Figure 2-1. A summary of the catalyst properties includes:

Mordenite (Norton zeolon-900H)
Surface Area- 450 Sq Meters/gram
Effective Pore Diameter 8-9 angstroms
Ring Size- 12 Members

Hydrogen gas was input to the reactor through two calibrated rotameter assemblies. One of the H_2 lines passed through two impingers, in series, filled with 1,2-dichloroethane where the hydrogen was saturated with 1,2-dichloroethane at 0^o C for input to the reactor. The second flow meter added pure H_2 to the constant ratio H_2/1,2-dichloroethane flow from the impingers, so as to vary only

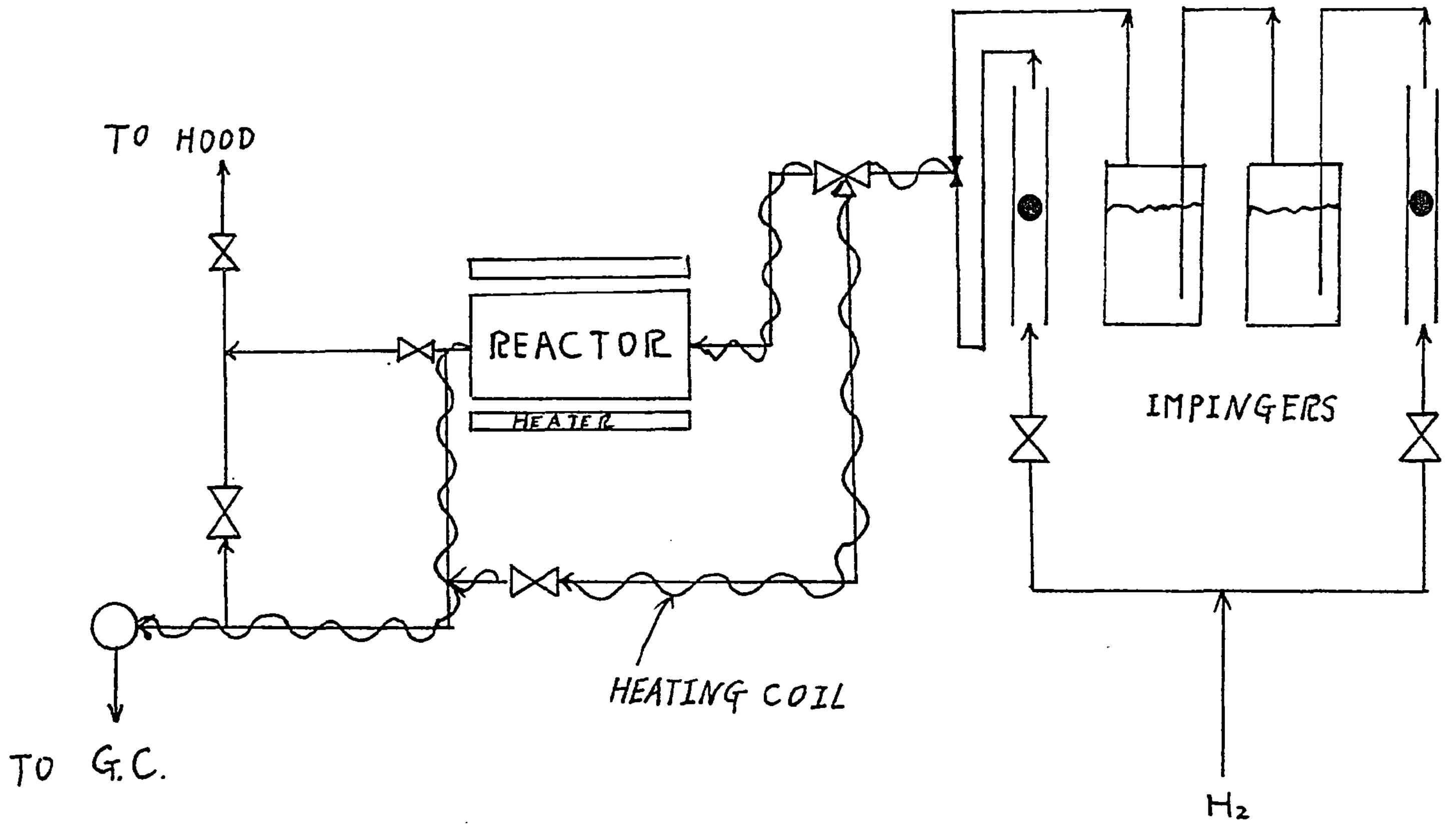


Figure 2-1 Schematic Diagram of Packed-Bed Reactor

the mole ratio of reagents. The measurement of 1,2-dichloroethane vapor pressure was calibrated in two ways. First, by measuring the total vapor flow before and after the impingers, and secondly, by monitoring the decrease of 1,2-dichloroethane liquid volume over time periods while the impingers were held at 0°C and constant hydrogen flow.

The catalyst was pretreated by passing hydrogen through the reactor for a 3 hour time period at a temperature of 450°C.

Analysis of conversion and product formation was performed using an on line gas chromatograph with a flame ionization detector and either SE 52 (5%) or SE 30 (30%) on chromosorb P, 2 meter by 1/8" stainless steel OD columns. Additional analysis was done on a separate GC using flame ionization detector and a Carbosphere micropacked column, 0.5 meter in length, with a syringe injected vapor sample for determination of methane, acetylene, ethylene and ethane products as these were not separated with the on-line GC column.

2-5 RESULTS AND DISCUSSION

Conversion, plotted as a function of time for reaction of 1,2-dichloroethane over zeolite catalyst, with excess hydrogen present, is illustrated in Figure 2-2. The results clearly show that a deactivation is occurring, and that it comes to its equilibrium value after approximatley 2 hours of reaction. Levenspiel and Bischoff (1963) have developed a equation for equal conversions in plug flow-axially dispersed reactor

$$W_{(dispersion)}/W_{(plug\ flow)} = 1+L*\rho_b*k_w/U/N_{pe} \qquad (42)$$

where L is bed length, U is velocity, N_{pe} is peclet number with a definition of $U*L/D_z$. If one requires that the increased catalyst loading, due to axial dispersion, not exceed 5 %, we obtain Mears's criterion (Mears, 1971)

$$L*\rho_b*k_w/U/N_{pe} < 0.05 \qquad (43)$$

According to Mears's criterion, we can not neglect axial dispersion, since for temperature 350 °C, the criterion is about 0.1417, which is larger than 0.05. Therefore, for short reactors, and very fast reaction, the effects of axial dispersion in the isothermal packed bed reactor can not be neglected. The calculated results of N_{pe} are listed in Table 2-1.

The experimental data as shown in Figure 2-2 have complicated the kinetic analysis due to the large deactivation that is occuring. The reaction products observed are primarily vinyl chloride and hydrogen chloride gas with smaller amounts of acetylene, ethane, and ethylene.

The following discussion is an attempt to characterize this observed deactivation which is shown in Figure 2-2. The hydrogen concentration was always held in excess (greater than a factor of 10) and considered constant over the reaction time. The expansion factor was always less

Table 2-1

Calculated Peclet number

T(^{o}C)	R_e	S_{cf}	$R_e * S_{cf}$	N_{pe}
350	0.0755	1.2295	0.0928	2.45
400	0.0714	1.2388	0.08845	2.34
450	0.0678	1.241	0.0841	2.22

$R_e = d_p * G/\mu$

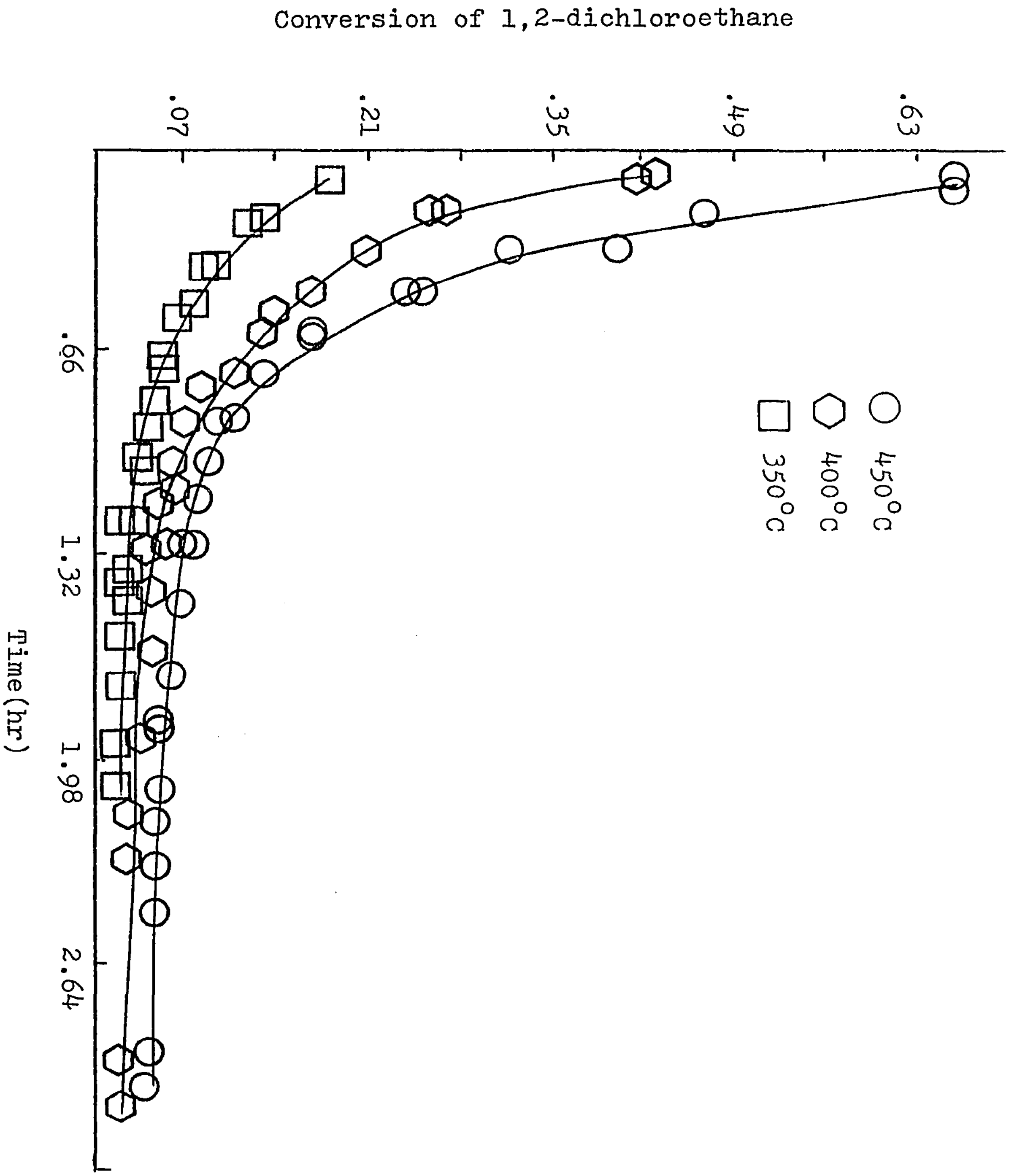
$S_{cf} = \mu/ \rho/D_{AB}$

D_{AB} = diffusion coefficient.

$N_{pe} = U*L/D_z$

* Wen, C.Y. and Fan, L.T.. " Models for Flow System and Chemical Reactor ", Marcel Dehker Inc. New York.

Figure 2-2 The Plot of Conversion with Respect to Time-on-Stream



than 0.05, because of the H_2 excess, and was not considered in the calculations, as it had a negligible effect on the data.

The first deactivation mechanism used in attempting to fit the data is the simple model of Levenspiel, where the deactivation constant, k_d, was held constant. The results of this model are shown in Tables 2-2 ,2-3, and 2-4 (temperature 350, 400, and 450°C). To show differences between X_{exp} and X_{cal}, we plot X_{exp} vs X_{cal} in Figure 2-3 , 2-4, and 2-5, using a best fit K_d, where they are compared against the experimental data. The differences between the calculated and experimental data are significant, especially, the initial points and terminal points. The average error are 13 and 26.94 % for temperature 350 and 450°C respectively. Similar poor fits of the data were obtained for 400°C. Those poor fits are expected due to faster deactivation in the present experiment which is not well modelled by the Levenspiel's theory.

The modified Levenspiel model, model 1, where k_d equals a function of time was the first deactivation mechanism that gave a reasonable fit to the experimental data with results shown as the solid lines in figure 2-6 for data at 350, 400 and 450°C. Table 2-5, 2-6, and 2-7 and Figure 2-7, 2-8, and 2-9 demonstrate that the average error between calculated and experimental data is consistently less than 10% for the 350, 400, and 450° C results.

The second model, (Model 2) where an activation term is included in the activity equation also correlated well

TABLE 2-2

Levenspiel's model-Comparison between calculated (Xcal) and experimental (Xexp) conversions for temperature 350°C

TIME (Hr.)	XEXP	XCAL	ERROR
0.0988	0.18	0.1148	0.3623
0.2292	0.13	0.0997	0.2333
0.2428	0.12	0.0982	0.1816
0.3720	0.094	0.0852	0.0933
0.3883	0.087	0.0837	0.0378
0.5147	0.075	0.0728	0.0299
0.5481	0.064	0.0701	-0.0953
0.6769	0.054	0.0607	-0.1236
0.7111	0.057	0.0584	-0.0178
0.8189	0.048	0.0517	-0.0768
0.9031	0.043	0.0470	-0.0924
1.0550	0.036	0.0418	-0.1618
1.0478	0.039	0.0398	-0.0212
1.2008	0.033	0.0334	-0.0127
1.2114	0.024	0.0330	-0.3756
1.3536	0.028	0.0280	-0.0009
1.4097	0.024	0.0263	-0.0944
1.4660	0.026	0.0246	0.0534
1.5744	0.022	0.0217	-0.0134
1.7347	0.021	0.0180	0.1420
1.9258	0.019	0.0144	0.2410
2.0664	0.0201	0.0122	0.3881

TABLE 2-3

Levenspiel's Model- Comparison between Xcal and Xexp for temperature 400°C.

TIME(Hr.)	XEXP	XCAL	ERROR
0.0908	0.43	0.1783	0.5853
0.0947	0.42	0.1777	0.5768
0.2044	0.27	0.1619	0.4002
0.2067	0.26	0.1616	0.3784
0.3400	0.21	0.1441	0.3139
0.3797	0.17	0.1392	0.1813
0.4703	0.16	0.1286	0.2438
0.5394	0.14	0.1209	0.1362
0.6117	0.13	0.1134	0.1276
0.7450	0.11	0.1006	0.0852
0.7825	0.085	0.0973	-0.1444
0.8933	0.071	0.0880	-0.2389
0.9075	0.071	0.0868	-0.2230
1.0283	0.063	0.0777	-0.2339
1.1167	0.065	0.0717	-0.1374
1.1694	0.054	0.0682	-0.2638
1.2842	0.059	0.0613	-0.1153
1.3011	0.044	0.0604	-0.3723
1.4328	0.049	0.0534	-0.1122
1.4408	0.041	0.0530	-0.2923
1.6281	0.046	0.0444	0.0331
1.9186	0.039	0.0337	0.1353
2.1560	0.033	0.0269	0.1854
2.3050	0.031	0.0233	0.2483
2.9678	0.022	0.0123	0.4412
3.0960	0.022	0.0109	0.5065

TABLE 2-4
Levenspiel's Model- Comparison between Xcal and Xexp for temperature 450^{o}C.

TIME(Hr.)	XEXP	XCAL	ERROR
0.0889	0.66	0.2272	0.6557
0.1394	0.66	0.2194	0.6676
0.2061	0.47	0.2093	0.5547
0.3278	0.40	0.1918	0.5204
0.3308	0.32	0.1914	0.4018
0.4719	0.25	0.1728	0.3089
0.4755	0.23	0.1723	0.2508
0.5997	0.17	0.1572	0.0753
0.6064	0.17	0.1564	0.0799
0.7364	0.13	0.1419	−0.0916
0.8742	0.11	0.1278	−0.1619
0.8900	0.096	0.1263	−0.3154
1.0225	0.089	0.1141	−0.2815
1.1417	0.081	0.1040	−0.2836
1.2839	0.077	0.0930	−0.2080
1.2900	0.074	0.0926	−0.2510
1.4739	0.069	0.0800	−0.1600
1.7119	0.061	0.0662	−0.0846
1.8418	0.054	0.0596	−0.1033
1.8729	0.051	0.0581	−0.1401
2.0819	0.051	0.0490	0.0388
2.1866	0.048	0.0450	0.0625
2.3242	0.047	0.0402	0.1447
2.4758	0.047	0.0355	0.2450
2.9186	0.044	0.0246	0.4412
3.0389	0.041	0.0222	0.4575

Figure 2-3 Levenspiel's model- The comparison between X_{cal} and X_{exp} at temperature 350°C

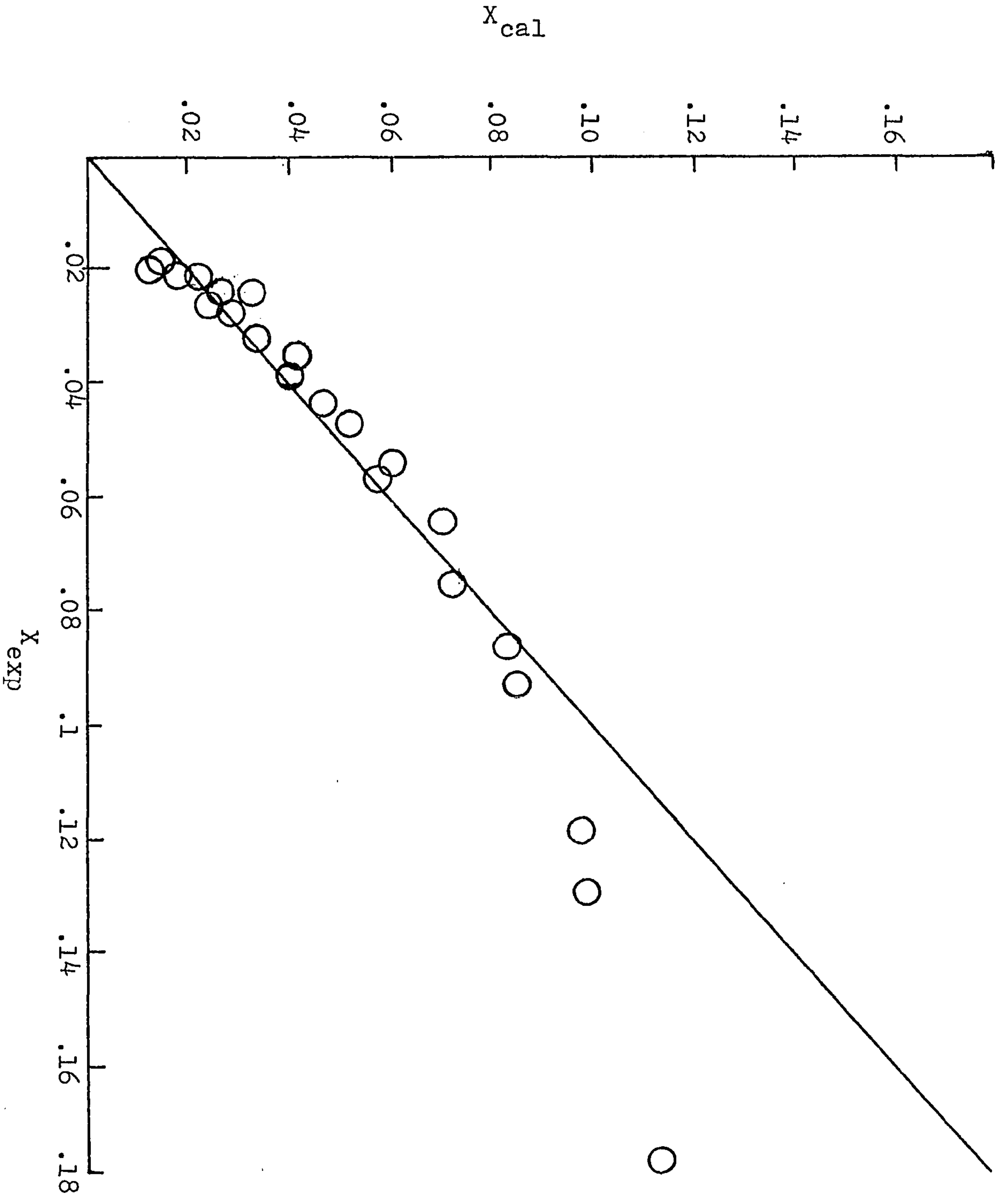


Figure 2-4 Levenspiel's Model- The Comparison Between X_{cal} and X_{exp} at Temperature 400°C

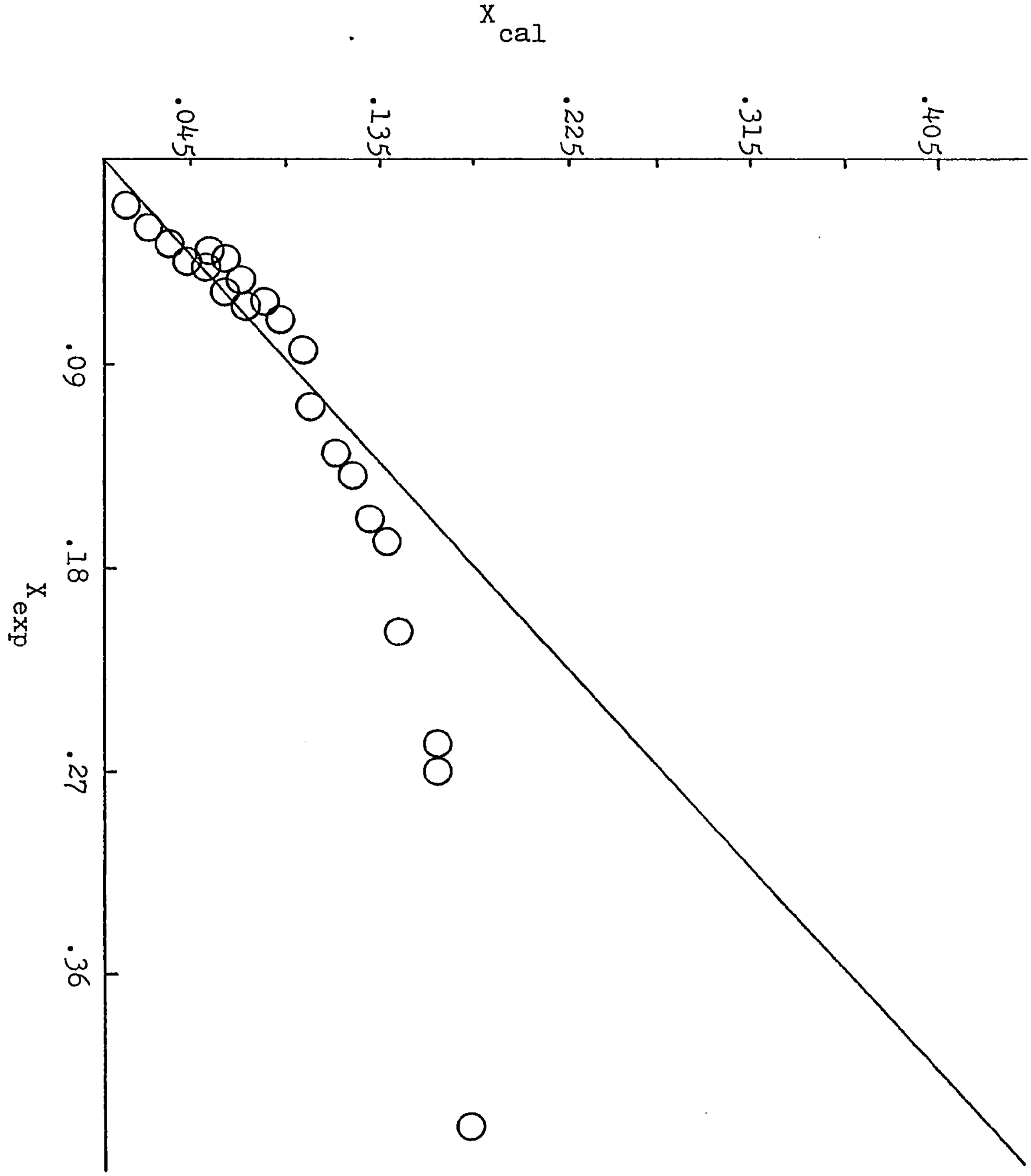


Figure 2-5 Levenspiel's Model- The Comparison Between X_{cal} and X_{exp} at Temperature 450°C

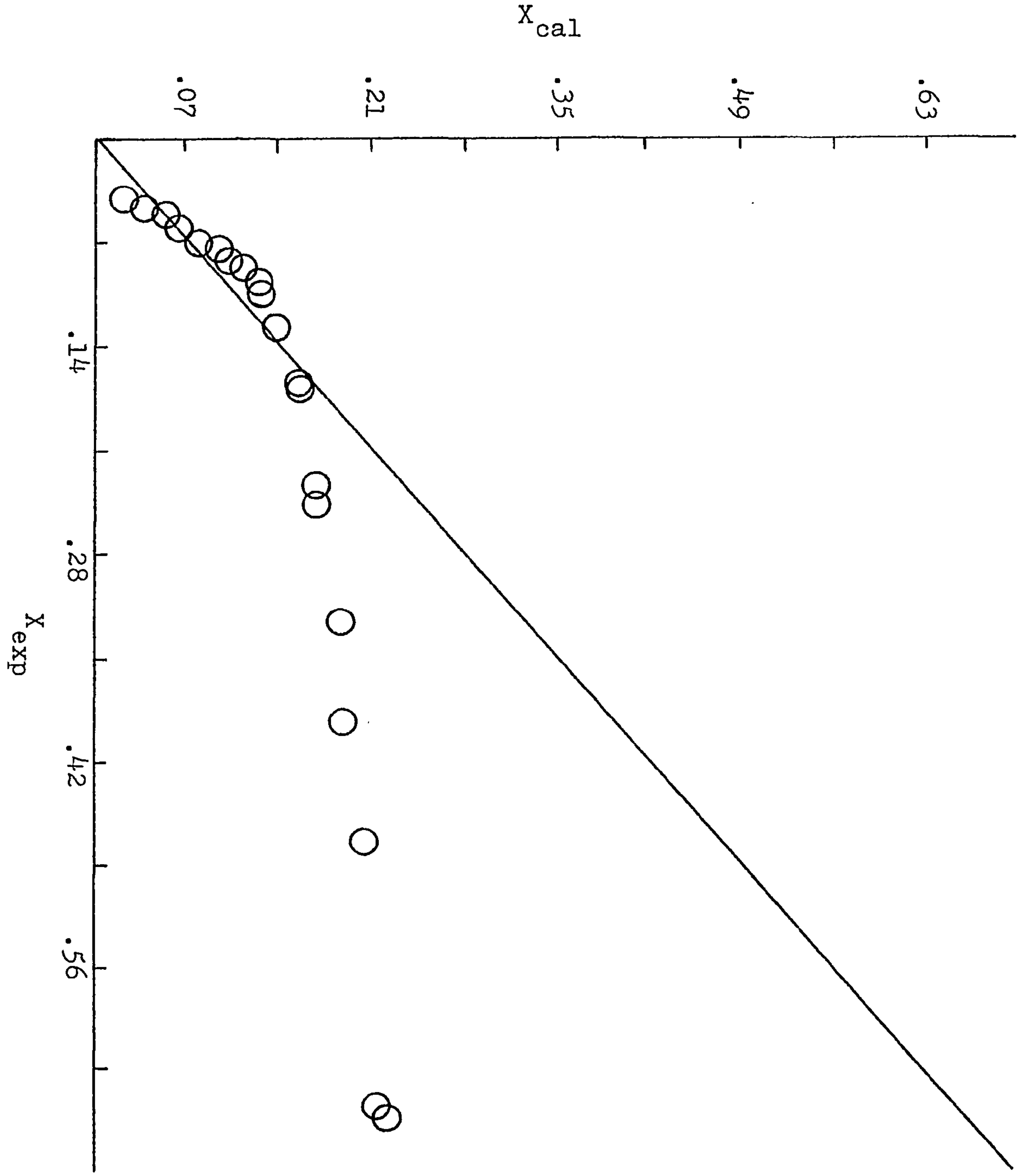


Figure 2-6 Fitting Results for Model 1

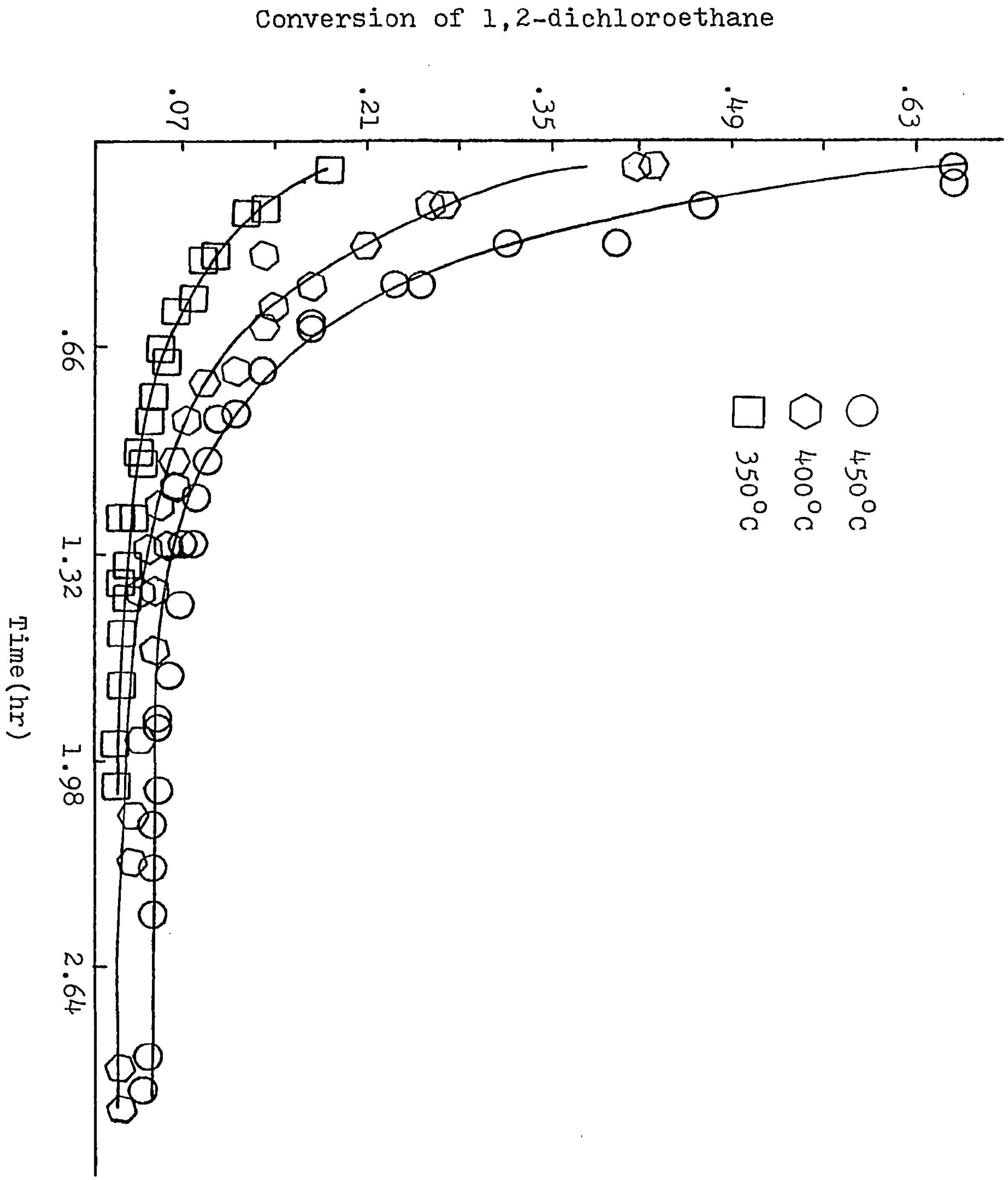


TABLE 2-5

Model 1- Comparison between Xcal and Xexp for temperature 350°C

TIME(Hr.)	XEXP	XCAL	ERROR
.0988	.18	.1759	.0225
.2292	.13	.1282	.0136
.2428	.12	.1243	-.0358
.3720	.094	.0941	-.0013
.3883	.087	.0911	-.0469
.5147	.075	.0718	.0428
.5481	.064	.0677	-.0584
.6769	.054	.0551	-.0200
.7111	.057	.0524	.0813
.8189	.048	.0452	.0592
.9031	.043	.0407	.0542
1.005	.036	.0363	-.0071
1.0478	.039	.0347	.1110
1.2008	.033	.0300	.0904
1.2114	.024	.0297	-.2393
1.3566	.028	.0266	.0513
1.4097	.024	.0255	-.0632
1.4660	.026	.0246	.055
1.5744	.022	.0230	-.0446
1.7347	.021	.0211	-.0046
1.9258	.019	.0194	-.0206
2.0664	.020	.0184	.0794

TABLE 2-6

Model 1- Comparison between Xcal and Xexp for temperature 400°C.

TIME(Hr.)	XEXP	XCAL	ERROR
.0908	.43	.3767	.1240
.0947	.42	.3731	.1116
.2044	.27	.2859	-.0589
.2067	.26	.2843	-.0936
.3400	.21	.2088	.0055
.3797	.17	.1914	-.1258
.4703	.17	.1583	.0690
.5394	.14	.1381	.0133
.6117	.13	.1208	.0706
.7450	.11	.0965	.1228
.7825	.085	.0910	-.0709
.8933	.071	.0775	-.0922
.9075	.071	.0761	-.0714
1.0283	.063	.0653	-.0358
1.1167	.063	.0590	.0634
1.1694	.054	.0558	-.0334
1.2842	.055	.0599	.0924
1.3011	.044	.0492	-.1173
1.4328	.048	.0440	.0827
1.4408	.041	.0438	-.0673
1.6281	.043	.0384	.1075
1.9186	.039	.0328	.1597
2.1560	.033	.0297	.0987
2.3050	.031	.0283	.0867
2.9678	.022	.0245	-.1144
3.0960	.022	.0241	-.0948

TABLE 2-7

Model 1- Comparison between Xcal and Xexp for temperature 450°C.

TIME(Hr.)	XEXP	XCAL	ERROR
.0889	.66	.6708	-.0164
.1394	.66	.5891	.1074
.2061	.47	.4902	-.0431
.3278	.40	.3478	.1305
.3308	.32	.3449	-.0779
.4719	.25	.2379	.0485
.4755	.23	.2358	-.0251
.5997	.17	.1773	-.0431
.6064	.17	.1748	-.0284
.7364	.13	.1360	-.0459
.8742	.11	.1090	.0087
.8900	.096	.1066	-.1105
1.0225	.089	.0900	-.0113
1.1417	.081	.0794	.0199
1.2839	.077	.0703	.0874
1.2900	.074	.0699	.0548
1.4739	.069	.0620	.1018
1.7118	.061	.0554	.0916
1.8418	.054	.0530	.0192
1.8719	.051	.0525	-.0290
2.0819	.051	.0498	.0242
2.1866	.048	.0488	-.0158
2.3242	.047	.0477	-.0148
2.4758	.047	.0468	.0046
2.9186	.044	.0452	-.0263
3.0389	.041	.0449	-.0949

Figure 2-7 Model 1- Comparison Between X_{cal} and X_{exp} at Temperature 350°C

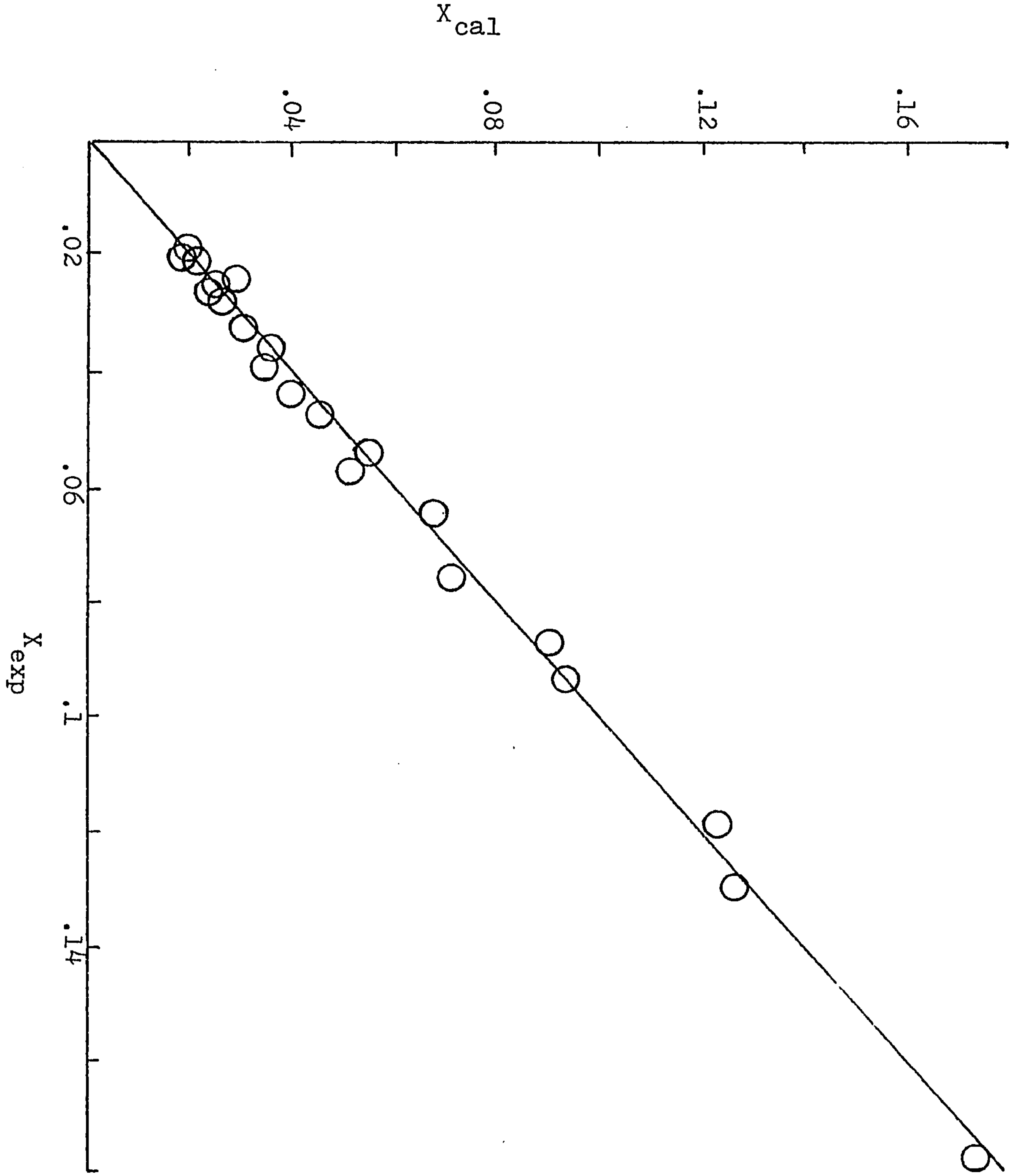


Figure 2-8 Model 1- Comparison Between X_{cal} and X_{exp} at Temperature 400°C

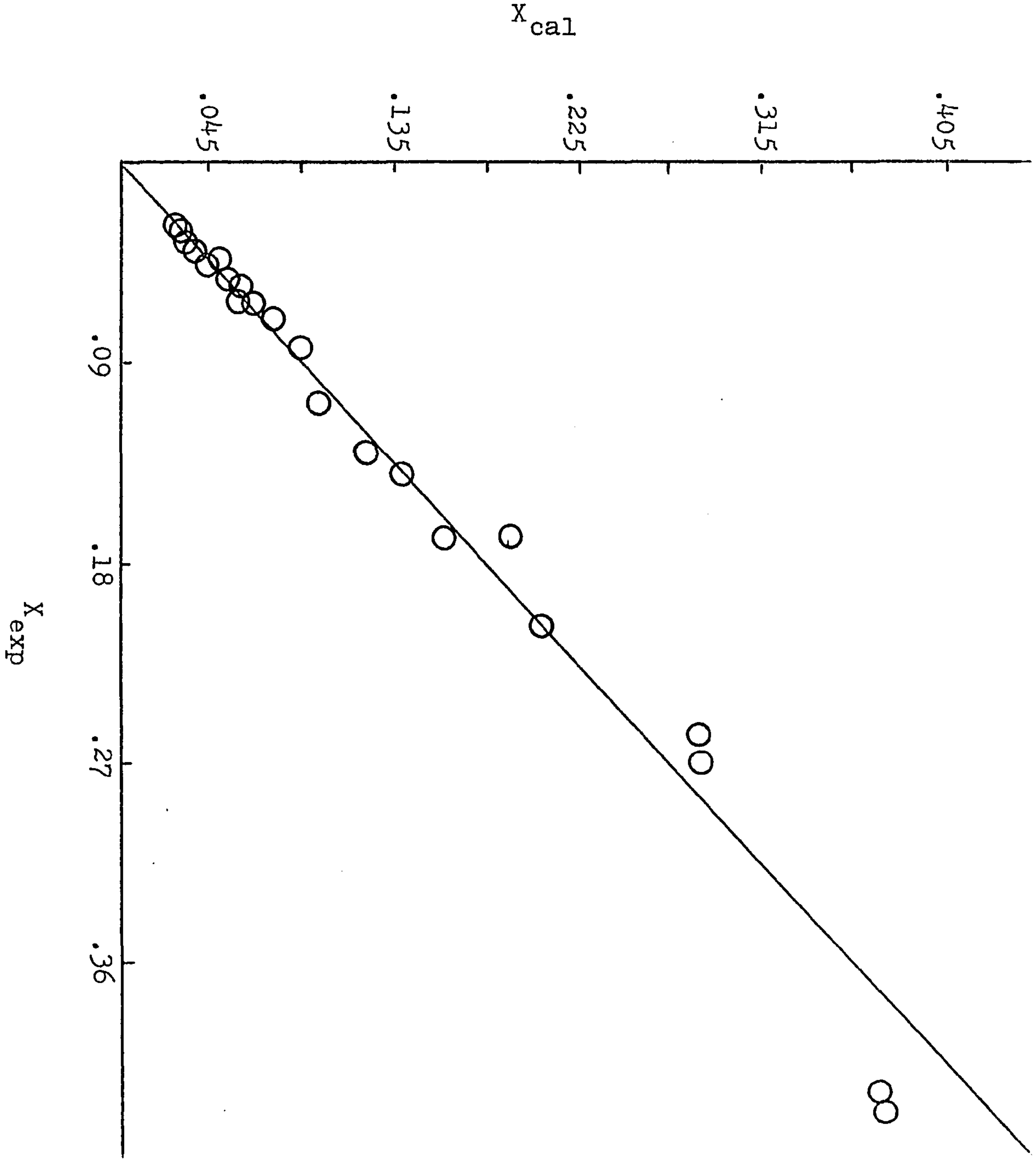
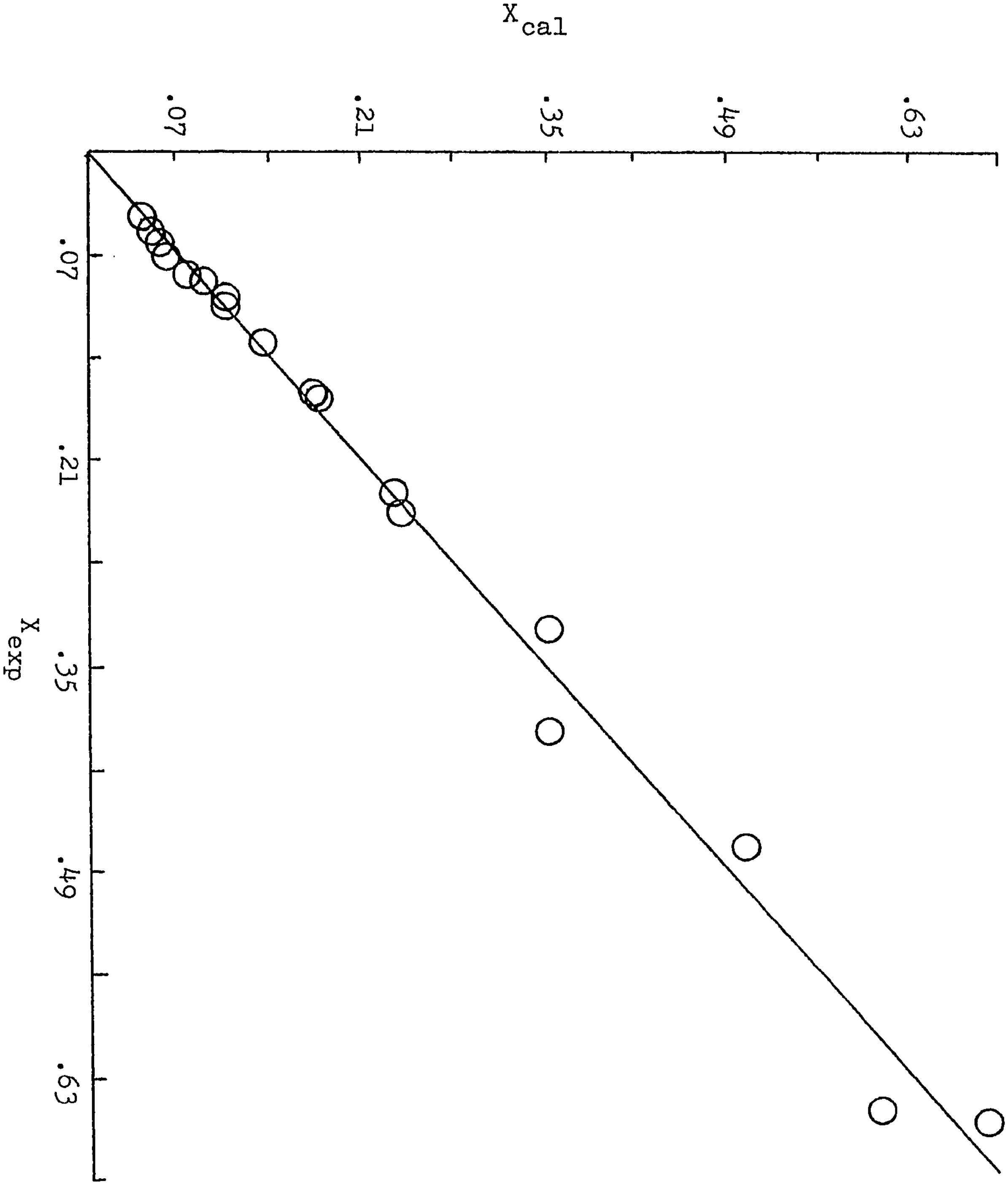


Figure 2-9 Model 1- Comparison Between X_{cal} and X_{exp} at Temperature 450°C



with the experimental data with results shown in Figure 2-10 as the solid lines represent the three previous temperatures. Tables 2-8, 2-9, and 2-10 and Figures 2-11, 2-12, and 2-13 compare the calculated data with the experimental and again demonstrate that the fit is quite good.

Rate constants and deactivation parameters are shown in Tables 2-11 and 2-12 for both Model 1 and Model 2 respectively. Graphs of ln(k) versus (1/T) for use in calculation of the activation energies for this reaction are shown in Figure 2-14 and 2-15 for Models 1 and 2 respectively.

The data to test for isothermality in the particle is presented in Table 2-13 along with heat capacity and heat of reaction. According to Anderson's criterion(1963), the observed rate will deviate from the rate under isothermal conditions by less than 5 % if

$$\frac{|\Delta H| * (-rate) * r_p^2}{\lambda * T_s} < \frac{R * T_s}{E} \qquad (44)$$

where $|\Delta H|$ is absoulte value of heat of reaction, λ is thermal conductivity of catalysts, (-rate) is reaction rate, r_p is particle radius, and T_s is temperature at particle surface. In our study, the left side of equation (44) is about .00055 and right side is 0.068 based on highest reaction rate and reaction at 450°C:

$$CH_2ClCH_2Cl \longrightarrow CH_2{=}CHCl + HCl$$

Figure 2-10 Fitting Results for Model 2

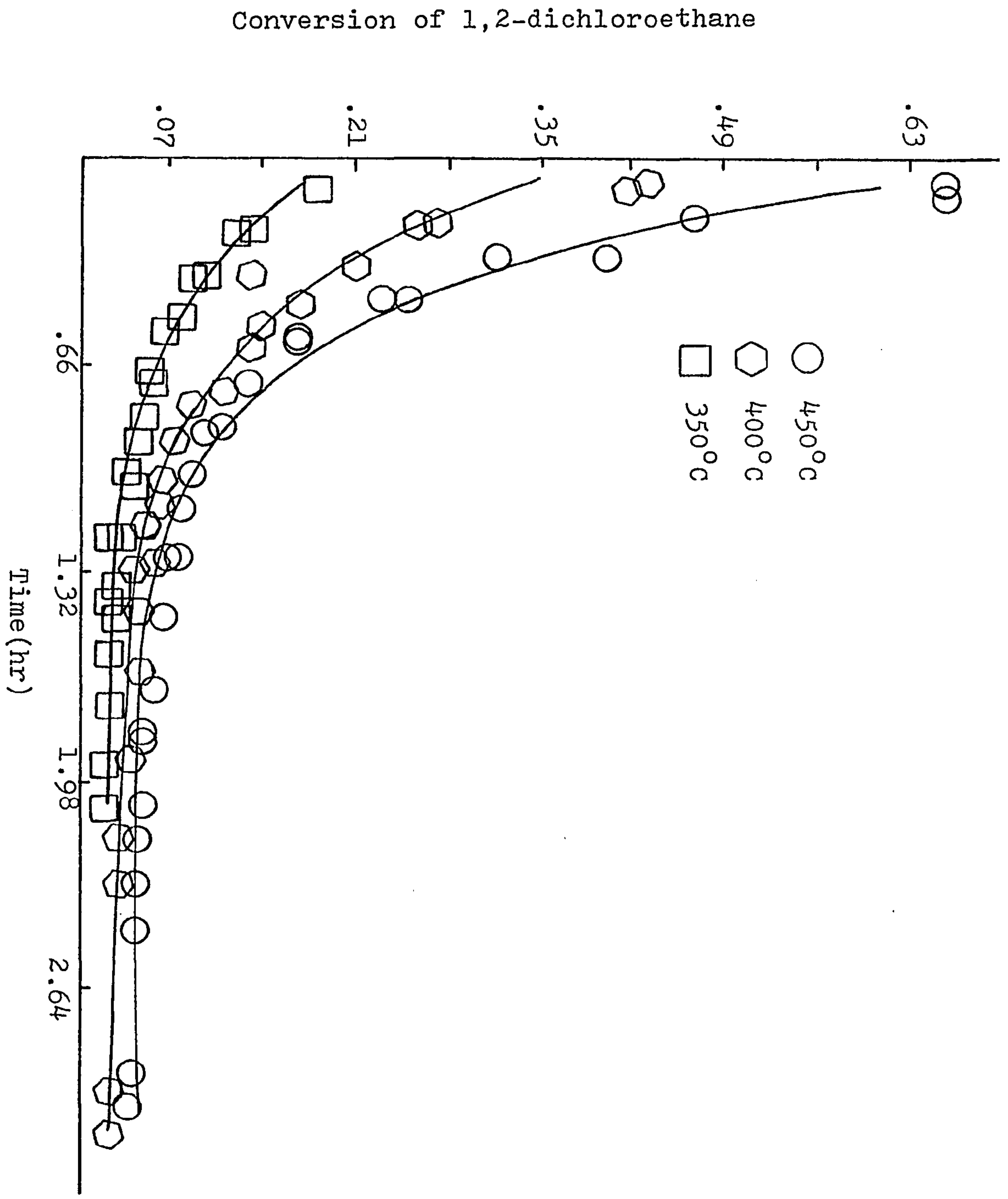


TABLE 2-8

Model 2- Comparison between Xcal and Xexp for temperature 350°C.

TIME(Hr.)	XEXP	XCAL	ERROR
.0988	.18	.1677	.0682
.2292	.13	.1272	.0213
.2428	.12	.1237	-.0309
.3720	.094	.0955	-.0264
.3883	.087	.0925	-.0632
.5147	.075	.0732	.0241
.5481	.064	.0690	-.0785
.6769	.054	.0558	-.0337
.7111	.057	.0530	.0709
.8189	.048	.0453	.0556
.9031	.043	.0406	.0561
1.0050	.036	.0360	.0011
1.0478	.039	.0343	.1201
1.2008	.033	.0296	.1042
1.2114	.024	.0293	-.2203
1.3536	.028	.0262	.0659
1.4097	.024	.0252	-.0480
1.4660	.026	.0243	.0670
1.5744	.022	.0228	-.0364
1.7347	.021	.0211	-.0071
1.9258	.019	.0197	-.0393
2.0664	.020	.0190	.0501

TABLE 2-9

Model 2- Comparison between Xcal and Xexp for temperature 400°C.

TIME(Hr.)	XEXP	XCAL	ERROR
.0908	.43	.3474	.1920
.0947	.42	.3448	.1790
.2044	.27	.2776	-.0283
.2067	.26	.2764	-.0629
.3400	.21	.2117	-.0080
.3797	.13	.1956	-.1509
.4703	.17	.1639	.0360
.5394	.14	.1437	-.0263
.6117	.13	.1257	.0327
.7450	.11	.0997	.0937
.7825	.085	.0937	-.1027
.8933	.071	.0789	-.1109
.9075	.071	.0772	-.0879
1.0283	.063	.0653	-.0362
1.1167	.065	.0584	.0730
1.1694	.054	.0549	-.0169
1.2842	.059	.0486	.1167
1.3011	.044	.0478	-.0859
1.4328	.048	.0424	.1162
1.4408	.041	.0421	-.0279
1.6281	.046	.0368	.1450
1.9186	.039	.0316	.1903
2.1560	.033	.0291	.1197
2.3050	.031	.0280	.0983
2.9678	.022	.0255	-.1584
3.0960	.022	.0243	-.1483

TABLE 2-10

Model2- Comparison between Xcal and Xexp for temperature 450°C.

TIME(Hr.)	XEXP	XCAL	ERROR
.0889	.66	.6076	.0794
.1394	.66	.5478	.1700
.2061	.47	.4725	-.0052
.3278	.40	.3532	.1170
.3308	.32	.3506	-.0956
.4719	.25	.2480	-.0079
.4755	.23	.2459	-.0690
.5997	.17	.1840	-.0824
.6064	.17	.1813	-.0663
.7364	.13	.1381	-.0624
.8742	.11	.1079	-.0190
.8900	.096	.1052	-.0959
1.0225	.089	.0870	.0226
1.1417	.081	.0758	.0644
1.2839	.077	.0666	.1347
1.2900	.074	.0663	.1039
1.4739	.069	.0589	.1458
1.7119	.061	.0535	.1225
1.8418	.054	.0517	.0420
1.8719	.051	.0514	-.0078
2.0819	.051	.0497	.0263
2.1866	.048	.0491	-.0226
2.3242	.047	.0485	-.0325
2.4758	.047	.0481	-.0235
2.9186	.044	.0475	-.0792
3.0386	.041	.0474	-.1563

Figure 2-11 Model 2- Comparison Between X_{cal} and X_{exp} at Temperature 350°C

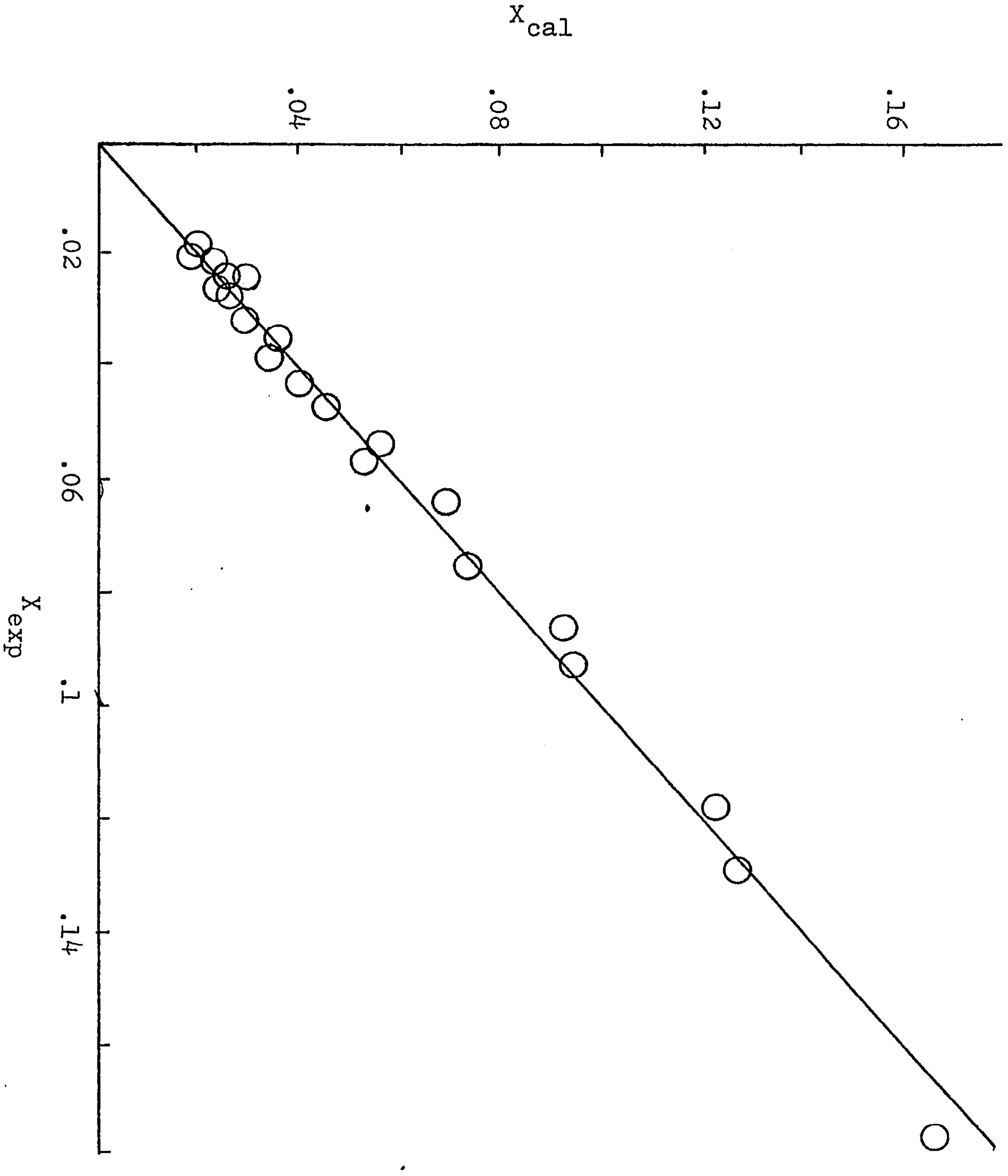


Figure 2-12 Model 2- Comparison Between X_{cal} and X_{exp} at Temperature 400°C

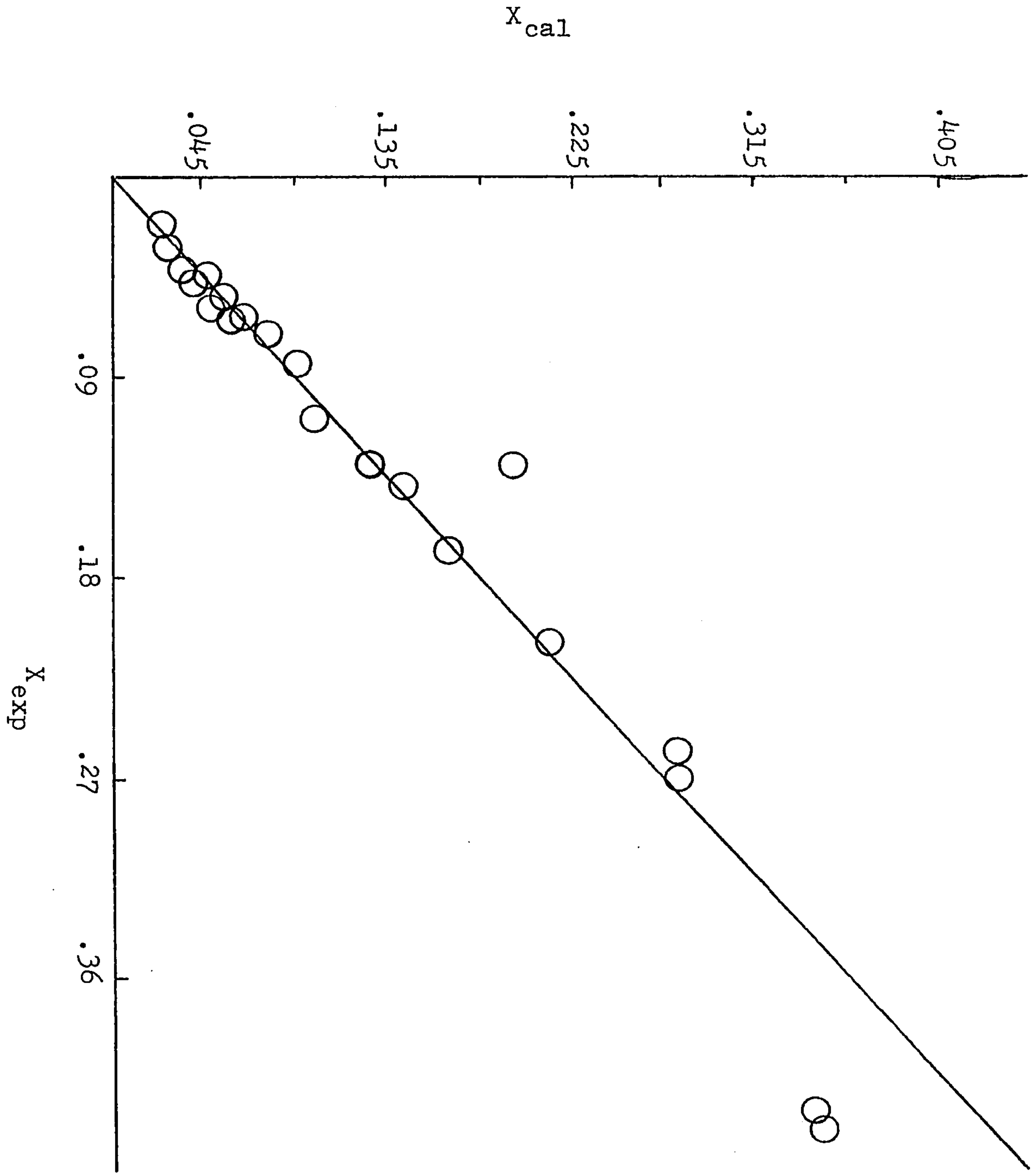


Figure 2-13 Model 2- Comparison Between X_{cal} and X_{exp} at Temperature 450°C

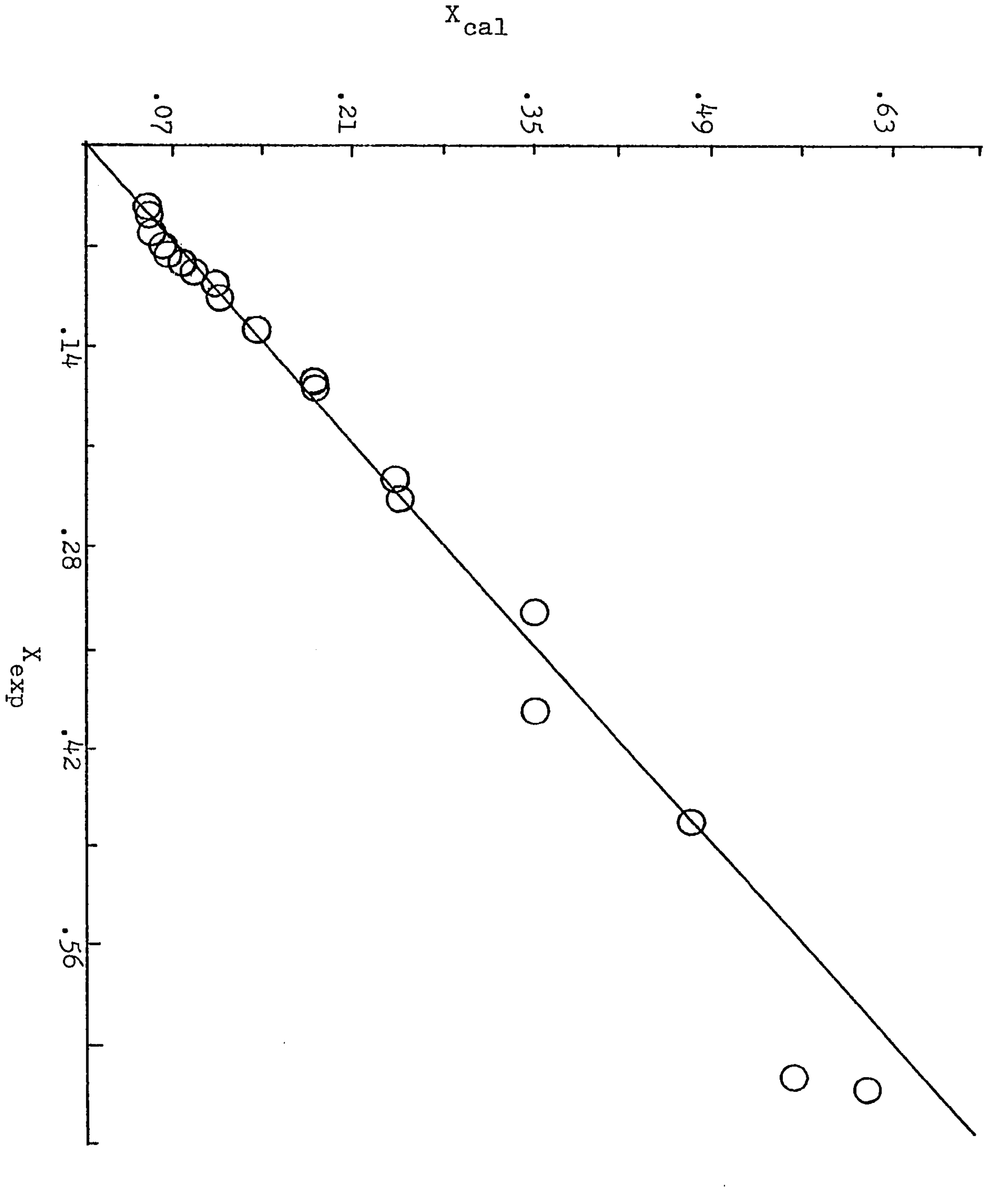


TABLE 2-11 Rate constants and deactivation parameters for model 1

TEMP (^{o}C)	K_{v} (1/sec)	K_{do} (1/hr)	K_{d1} (1/hr)
350	8.26	3.28	1.087
400	24.04	3.86	1.092
450	87.67	6.55	1.629

E=21 K_{cal}/MOLE

A_{o}=1.9E 8 /sec

E_{d}=6.1 Kcal/Mole

A_{od}=425 /Hr

TABLE 2-12

Rate constants and deactivation parameters for model 2

TEMP(^{o}C)	K_v(1/sec)	K_d(1/Hr)	K_r(cm^3/hr-mole)
350	7.39	2.59	1.84E5
400	19.68	2.77	1.99E5
450	59.13	4.15	3.05E5

E=19 K_{cal}/mole

A_o=2.29E7 (1/sec)

Figure 2-14 Arrhenius' Plot for Model 1

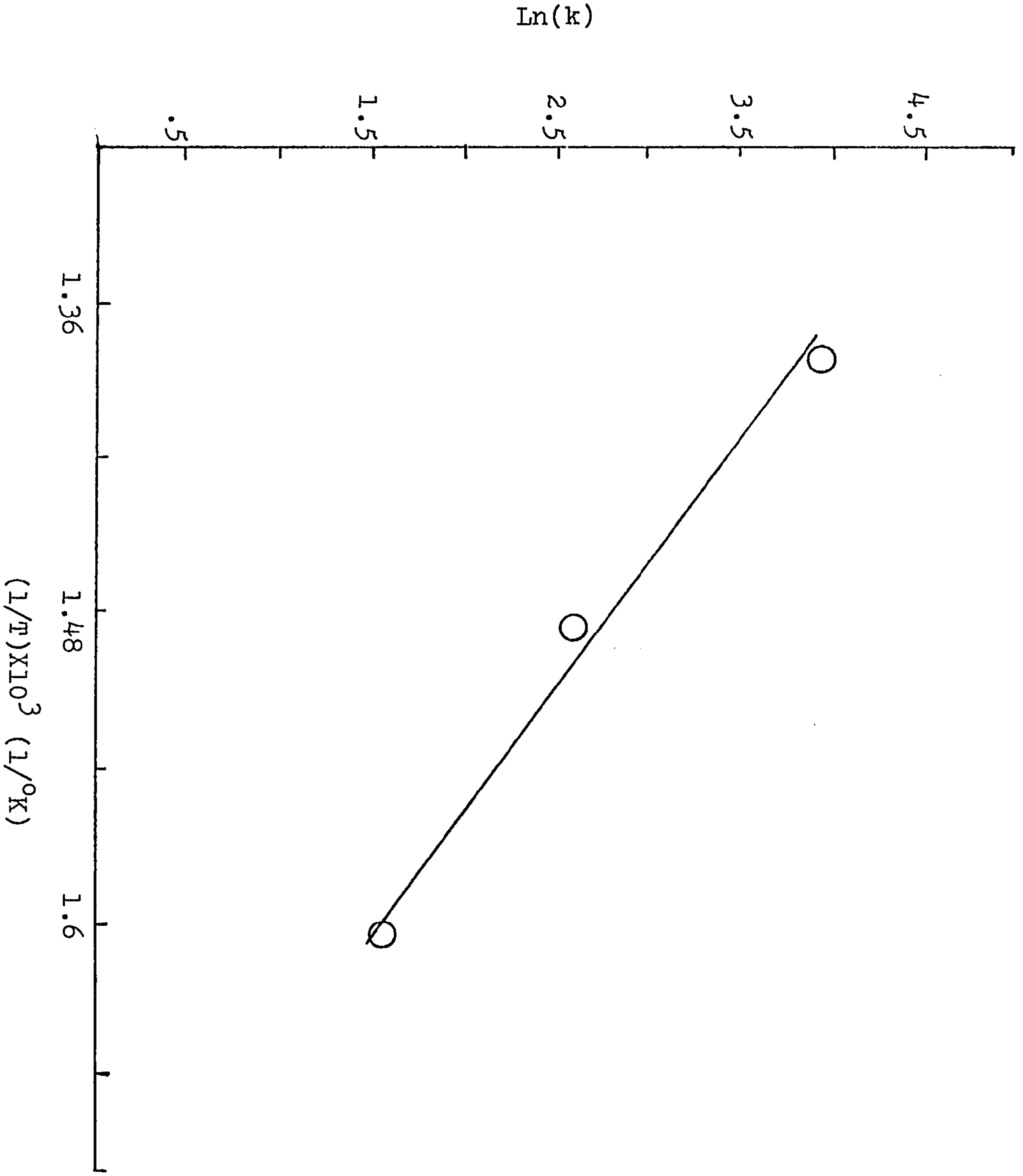


Figure 2-15 Arrhenius' Plot for Model 2

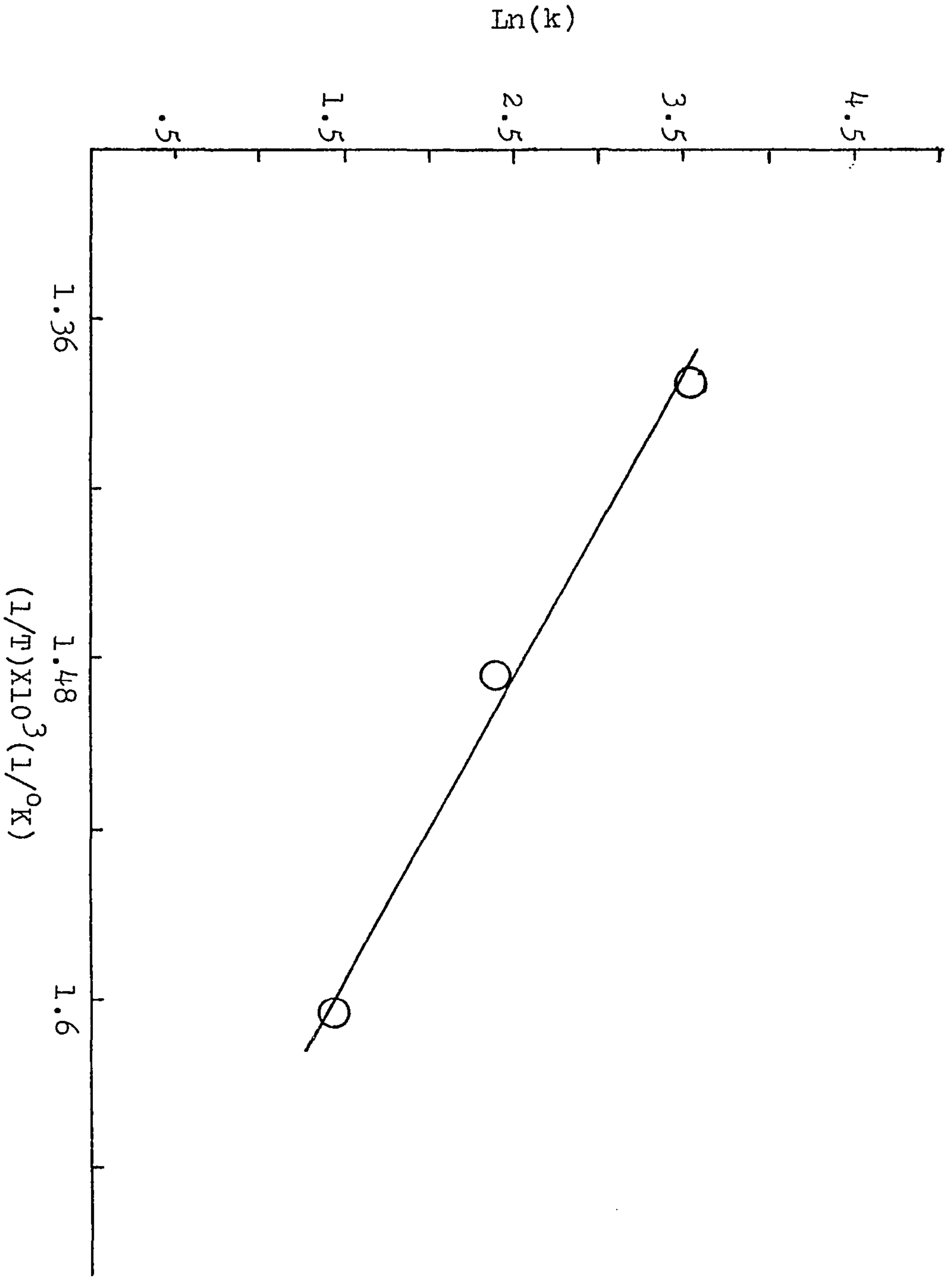


TABLE 2-13 HEAT CAPACITY AND HEAT OF REACTION

$$C_p = A + B * T + C * T^2 + D * T^3 \text{ (Cal/g mole-}^\circ\text{K)}$$

COMPOUND	A	B*10E2	C*10E5	D*10E9
1,2-DCE	4.893	5.518	-3.435	8.094
VINYL CHLORIDE	1.421	4.823	-3.669	11.4
HCl	7.235	-0.172	0.2976	-.931

Where 1,2-DCE = 1,2-Dichloroethane

REACTION: 1,2-DCE --------> Vinyl chloride + HCl

TEMPERATURE	H
350°C	17.5 (Kcal/mole)
400°C	17.4 (Kcal/mole)
450°C	17.35 (Kcal/mole)

These results indicate that isothermal conditions in the catalyst is maintained.

A pore diffusion test is also examined. When Φ_s is less than 1

$$\Phi_s = (R/3)**2*k/D_{eff} < 1 \qquad (45)$$

pore diffusion can be neglected (Levenspiel, 1972). Table 2-14 summarizes kinetic parameters with the diffusion calculation results for Model 1 and Table 2-15 for Model 2. Φ_s are all smaller than 1 in both models, indicating that pore diffusion can be omitted. Equation (45) only need be condsidered for the initial condition at which activity is 1. However, when activity is smaller, equation (32) and Figure 2-16, indicate that pore diffusion can still be neglected, because the effectiveness factor approaches the activity value over a larger range of $R*\sqrt{K/D_{eff}}$ than that at activity 1. This is illustrated further by using two examples: when activity is 1 and $R*\sqrt{k/D_{eff}}$ is 0.9, effectiveness factor is 0.95 which allows one to neglect pore diffusion. When activity is 0.8 and $R*\sqrt{k/D_{eff}}$ is 0.9, effectiveness factor is 0.77 which is still larger than 0.8*0.95 = 0.76.

TABLE 2-14

EFFECTIVENESS FACTOR FOR MODEL 1

TEMP(^{o}C)	K_v(1/sec)	D_{eff}(cm^2/sec)	$(K_v/D_{eff})^{0.5}*R$	η
350	8.26	4.2E-3	.6596	.9721
400	24.04	4.375E-3	1.0999	.92764
450	87.67	4.535E-3	2.1128	.7900

Levenspiel's Criterion

$L.C.=k_v*(R/3)^2/D_{eff} < 1$

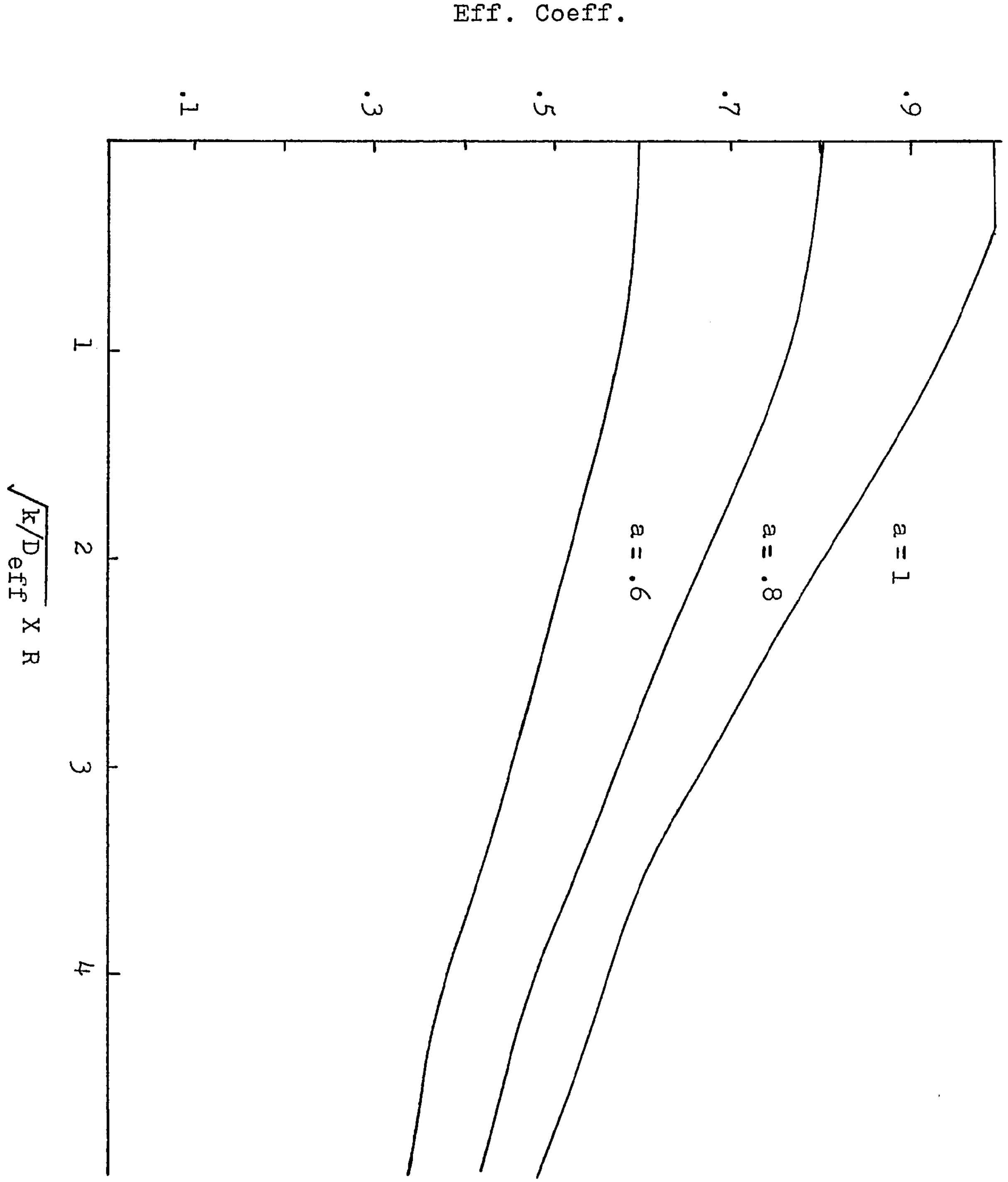
temp(^{o}C)	L.C.
350	.04834
400	.1344
450	.4960

TABLE 2-15

EFFECTIVENESS FACTOR FOR MODEL 2

TEMP(^{o}C)	k_v(1/sec)	η
350	7.39	.9748
400	19.68	.9395
450	59.13	.84413

Figure 2-16 Effectiveness Factor with Respective to $R*\sqrt{(k/D_{eff})}$

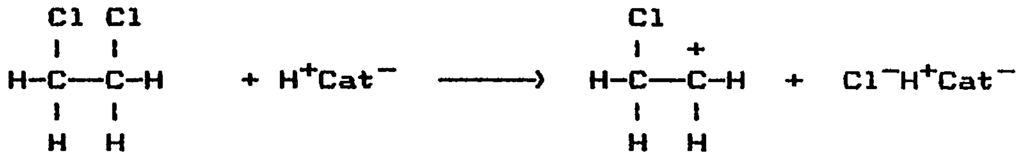


2-6 Reaction Mechanism

An ionic mechanism was proposed by Noller et. al. (1965) in their study of HCl elimination from gaseous 2,3-dichloroethane on Al_2O_3. HCl elimination from 2-chloro-2 butene which is one of the products in their experiment was also explained by a carbonium ion mechanism.

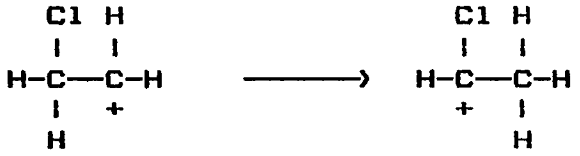
Mochida et. al. (1967) also indicated that acid catalyst behaved as the Bronsted acid and that the intermediate in the elimination reaction of HCl from chloroethanes was a carbonium ion. Vinyl chloride was produced by HCl elimination from 1,2-dichloroethane on acid catalyst in their study. The carbonium ion mechanism for paraffin hydrocarbons in the catalytic cracking reactions was postulated by a number of workers. These include: Thomas (1949) who suggested that the mechanism of cracking reactions on silica-alumina catalyst be carbonium ion after olefins are produced by thermal decomposition; Greensfelder (1949) also agreed with Thomas's carbonium ion mechanism for paraffines over acid catalysts; Emmett (1965) explained the catalytic reaction of cetane by a carbonium ion mechanism in a fixed bed reactor; Satterfield (1980) indicated that a paraffin may react as a week Lewis base which donated a hydride to a Lewis acid catalyst with a carbonium ion intermediate produced.

Considering that the strength of C-Cl bond is weaker than that of C-H bond, we propose that Cl is more easily released from a carbon than H. We further propose a carbonium ion mechanism occuring in the hydrodechlorination reaction of 1,2-dichloroethane over zeolon catalyst. First, 1,2-chloroethane behaves as a Lewis base approaching the catalyst which plays a role of Bronsted acid and then a carbonium ion intermediate is produced



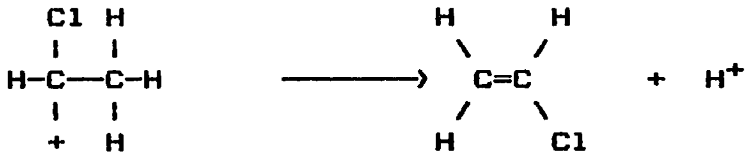
$$ClH_2C{-}CH_2Cl + H^+Cat^- \longrightarrow ClH_2C{-}C^+H_2 + Cl^-H^+Cat^-$$

Hydrogen migration to the carbon adjacent to the C-Cl bond results in a more stable intermediate because of the possible resonant forms involving conjugation of P electron of chloride with vacant carbon orbital (Noller, 1965).



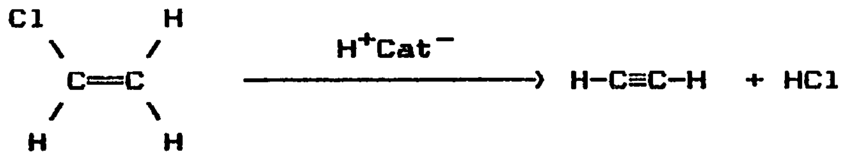
$$ClH_2C{-}C^+H_2 \longrightarrow ClHC^+{-}CH_3$$

A proton then leaves the carbonium to produce vinyl chloride



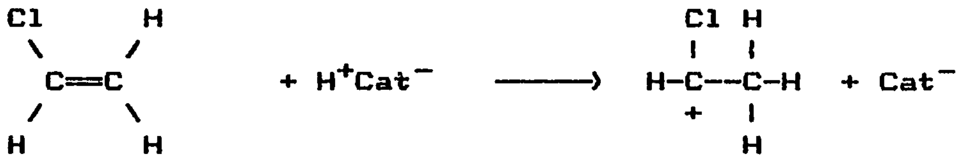
$$ClHC^+{-}CH_3 \longrightarrow H_2C{=}CHCl + H^+$$

Elimination of HCl from vinyl chloride will produce acetylene



$$ClHC{=}CH_2 \xrightarrow{H^+Cat^-} H{-}C{\equiv}C{-}H + HCl$$

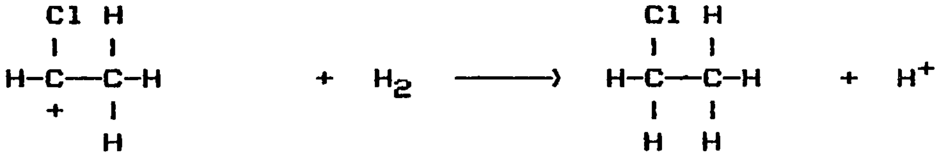
It is of interest that a carbonium ion is also formed from vinyl chloride attacked by a proton on the catalyst surface (Venuto, 1966)



$$\mathrm{CHCl{=}CH_2} + \mathrm{H^+Cat^-} \longrightarrow \mathrm{H{-}\underset{+}{\overset{Cl}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + \mathrm{Cat^-}$$

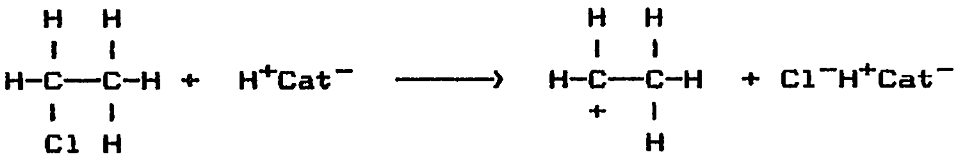
This intermediate is the same as the first step of mechamism; again, vinyl chloride is produced.

The reaction in our study occured in a hydrogen atmosphere; consequently addition of hydrogen to the carbonium ion and formation of chloroethane are possible



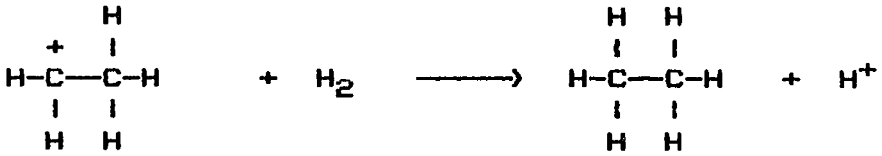
$$\mathrm{H{-}\underset{+}{\overset{Cl}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + \mathrm{H_2} \longrightarrow \mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + \mathrm{H^+}$$

Once chloroethane is produced in the system, it should follow the same mechanism as 1,2-dichloroethane. Here, a lower reaction rate can be predicted, because of the lower reactivity of chloroethane than that of 1,2-dichloroethane (Venuto, 1966).



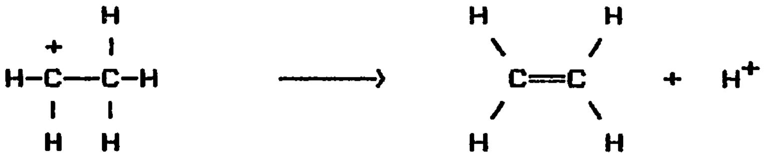
$$\mathrm{H{-}\underset{Cl}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + \mathrm{H^+Cat^-} \longrightarrow \mathrm{H{-}\underset{+}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + \mathrm{Cl^-H^+Cat^-}$$

Ethane can be obtained by hydrogenation of ethylene when hydrogen is present,



$$\mathrm{H\!-\!\overset{+}{C}H_2\!-\!CH_2\!-\!H + H_2 \longrightarrow H\!-\!CH_2\!-\!CH_2\!-\!H + H^+}$$

or a proton leaves the carbonium ion to form ethylene



From the proposed mechanism, we expect that the quantities of ethane, ethene, and acetylene produced will be small, and that higher concentration of these species will be observed at higher temperatures.

CHAPTER 3 Reactions of 1,2-Dichloroethane and Chloroform with Hydrogen Over Palladium Supported on Alumina

3-1 Introduction

The formation of hydrocarbons and hydrogen chloride from reactions of chlorocarbons and hydrogen is thermodynamically favourable. We have used the above catalyst (zeolite) to facilitate this reaction. It has been mentioned in Chapter 2 that the purpose of our study is to discover and develop means for complete and efficient destruction of toxic chlorocarbons and simultaneously to convert them into useful products. Perhaps more importantly, in addition, we wish to obtain some insights into the chemical and engineering aspect of the reactive processes and catalyst deactivation. Since zeolite suffers rapid loss of activity, one may question the value of using it as a catalyst. Therefore, for this chapter, we changed from zeolite to palladium which has been extensively used in liquid phase dehydrochlorination reaction for olefinic species (Rylander, 1967; Freifelder, 1971)

3-2 Literature Survey

Although the reaction rates of aliphatic chlorides is much lower than that of olefinic chlorides (Lapierre, et al., 1978), a number of saturated halogenated compounds have been hydrodehalogenated by various methods to produce lower Cl content compounds having the same numbers of carbon atoms; for example, vinyl chloride can be produced by passing 1,2-dichloroethane with hydrogen over H-Y mordenite zeolite(Yang and Bozzelli et al. 1984) or without catalysts (Lee and Bozzelli et. al. 1985). J.A. Ward et. al. (1975) have used alumina plus 1 to 10% La_2O_3 and, alumina plus 10% La_2O_3 plus 0.25 to 2% Pt or Pd as a catalyst to dehydrohalogenate many compounds including species with three or more carbon atoms with two or more halogen atoms, such as dichloropropenes and trichlorobutanes . The useful compounds produced includes vinyl chloride, 1,2- and 1,3-dichloropropane, and allyl chloride. Dodson et. al. (1978) discovered that methylene chloride can be produced by chloroform over palladium on charcoal, platinum on alumina and Pt-Re on alumina reforming catalyst, and that coke deposit and metal agglomeration were the causes of resulting catalyst deactivation. The coke which is a chlorinated polymeric hydrocarbon could be removed by regenerating catalyst with hydrogen at high temperatures. The reaction of chloroform with hydrogen over platinum on alumina in the temperature range 150 to 305°C has been studied by Mullin et. al. (1971). The production of methane increases at higher temperatures (208-305°C), but the conversion to methyl chloride is higher in temperature range (150 - 177°C). This type of results also appears in our study of 1,2-dichloroethane in hydrogen atmosphere over palladium (0.5%) on alumina support.

Mochida et. al. studied the elimination reaction of hydrogen chloride from chloroethanes (1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-

trichloroethane) on solid acid (silica-alumina, alumina-boria, alumina) at temperature 300°C with the pulse technique (Mochida et al., 1967. A), and from 1,1,2-trichloroethane on ion-exchange molecular sieves (H-Y, Mg-10X, 5A, 4A) at 300°C. The elimination reaction was nearly first order under experimental conditions for all chloroethanes used in their studies. The main products observed were vinyl chloride for 1,1-dichloroethane and 1,2-dichloroethane; $CCl_2=CH_2$ for 1,1,1-trichloroethane; $CCl_2=CH_2$, trans-CHCl=CHCL, and cis-CHCL=CHCL for 1,1,2-trichloroethane; and $CCL_2=CHCL$ for 1,1,2,2-tetrachloroethane. The ratio of trans-1,2-dichloroethylene to cis-1,2-dichloroethylene is higher for the elimination reaction of HCl from 1,1,2-trichloroethane on molecular sieves. Mochida et. al. (1967, B) also found that alumina had an extremely high reactivity with methylene chloride to produce methyl chloride in the temperature range 300 to 450°C.

We have studied the conversion of 1,2-dichloroethane and chloroform in hydrogen over palladium on alumina supported catalysts respectively and observed significant conversion with products of chloroethane, ethylene, and ethane for 1,2-chloroethane system and methylene chloride and methane for chloroform system .

3-3 Experimental

3-3-1 Reaction with 1,2-Dichloroethane

A 0.7-cm-ID by 35-cm-length Pyrex tube was used as reactor to study the reaction of 1,2-dichloroethane and over palladium (0.5 %) on alumina catalyst in a hydrogen atmosphere, temperature range 100 to 245°C. The catalysts in the form of extruded 1/8" by 1/8" pellets were crushed, sieved, and screened to 60/80 mesh before being used. 0.2 to 0.3 grams of 60/80 mesh catalysts with 0.2 grams 80/100 mesh glass beads were mixed uniformly and used for each experimental run. Both ends of the packed bed, length of 3 cm, were supported by glass wool plugs. A schematic diagram of the apparatus is shown in Figure 2-1. Teflon tubing before and after the reactor was heated by heating tapes and wrapped with high quality insulating material to avoid condensation or adsorption of products and reactants which may have high boiling point. Two thermocouples (chromel-alumel) were used on both sides for measuring the temperatures in the axial direction. Two series impingers were used as saturators; and kept in an ice bath. 1,2-dichloroethane from both impingers was brought into the reactor by a hydrogen flow which passed through a calibrated flow meter. The two impingers were used to assure saturation of 1,2-dichloroethane with hydrogen at the 0°C bath temperature.

The reactor effluent stream was analyzed for 1,2-dichloroethane and products using an on-line Carle Model

9500 gas chromatograph(GC) with a flame ionization detector, and 20% SP-2100 on 80/100 SUPELCOPORT, 1.6 meter by 1/8" OD stainless steel column. A Hewelett-Packard 3390 A recorder/integrator was connected to the output of GC for quantitative determination of all reactants and products. A GC/MS spectrometer was used to confirm the identification of the sample products. The equipment used was a Carlo Erba Strumentizione Fractovap 4160 series GC interfaced with Kratos MS 25 double focusing magnetic sector Mass Spectrometer.

3-3-2 Reaction with chloroform

The apparatus used was almost same as those of 1,2-dichloroethane system, except:

(1) Reactor diameter: 0.4 cm ID

(2) GC :Perkin-Elmer 900 (same as that of used in reaction 1,2-dichloroethane with hydrogen over zeolite)

0.1 grams of 45/60 mesh catalysts with 0.1 grams 80/100 mesh glass beads were mixed uniformly and used for each experimental run.

3-4 Results and Discussion

3-4-1 1,2-Dichloroethane

Conversion of 1,2-dichloroethane to ethane, ethylene and chloroethane was observed at temperatures of 100 to 245°C. Figure 3-1 shows the observed changes in total conversion of 1,2-dichloroethane with respect to time on

Figure 3-1 Total Conversion of 1,2-Dichloroethane with Respective to Time-on-Stream at Temperature 245°C

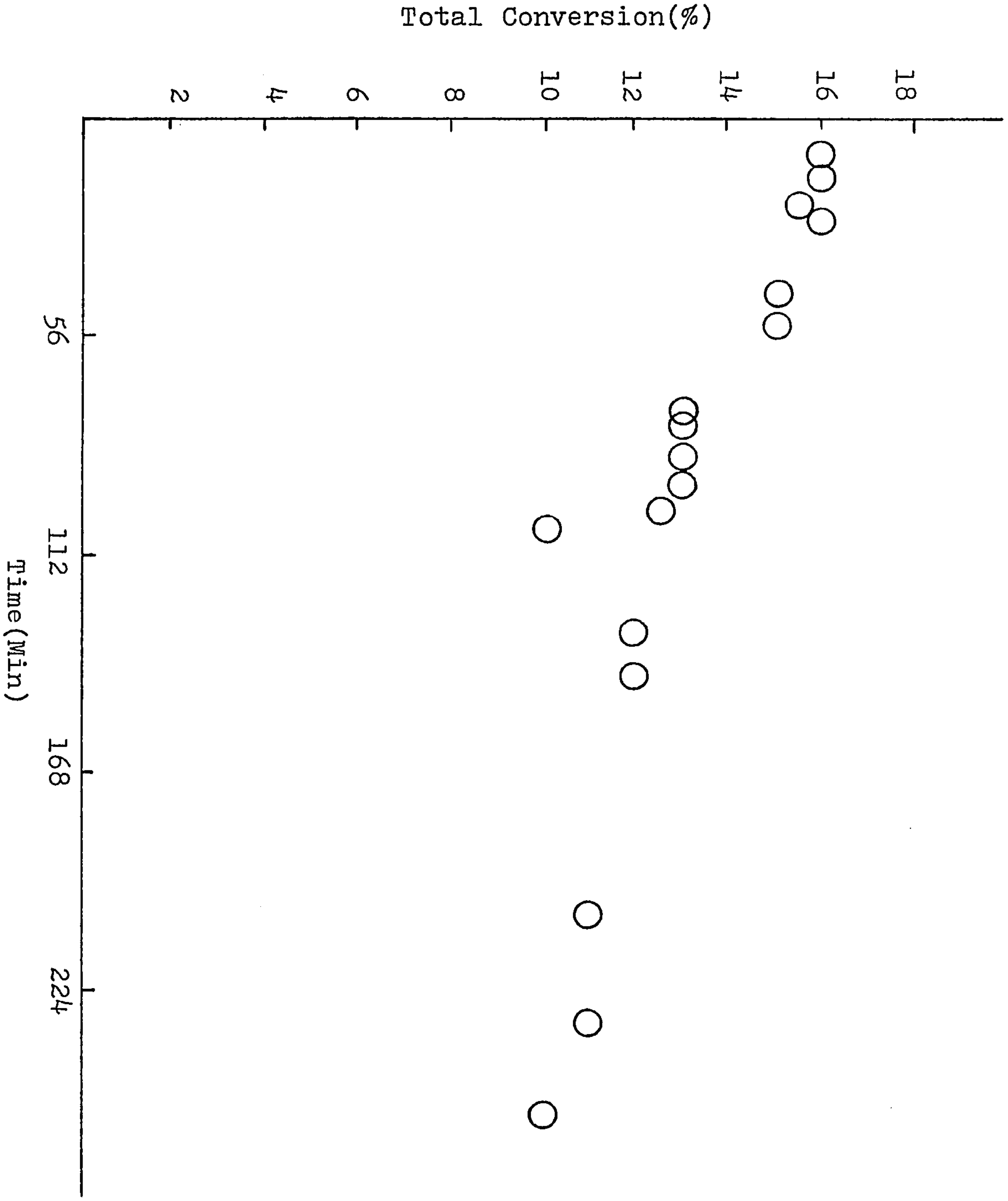


Figure 3-2 Product Distribution with Respect to Residence Time at Temperature 100°C

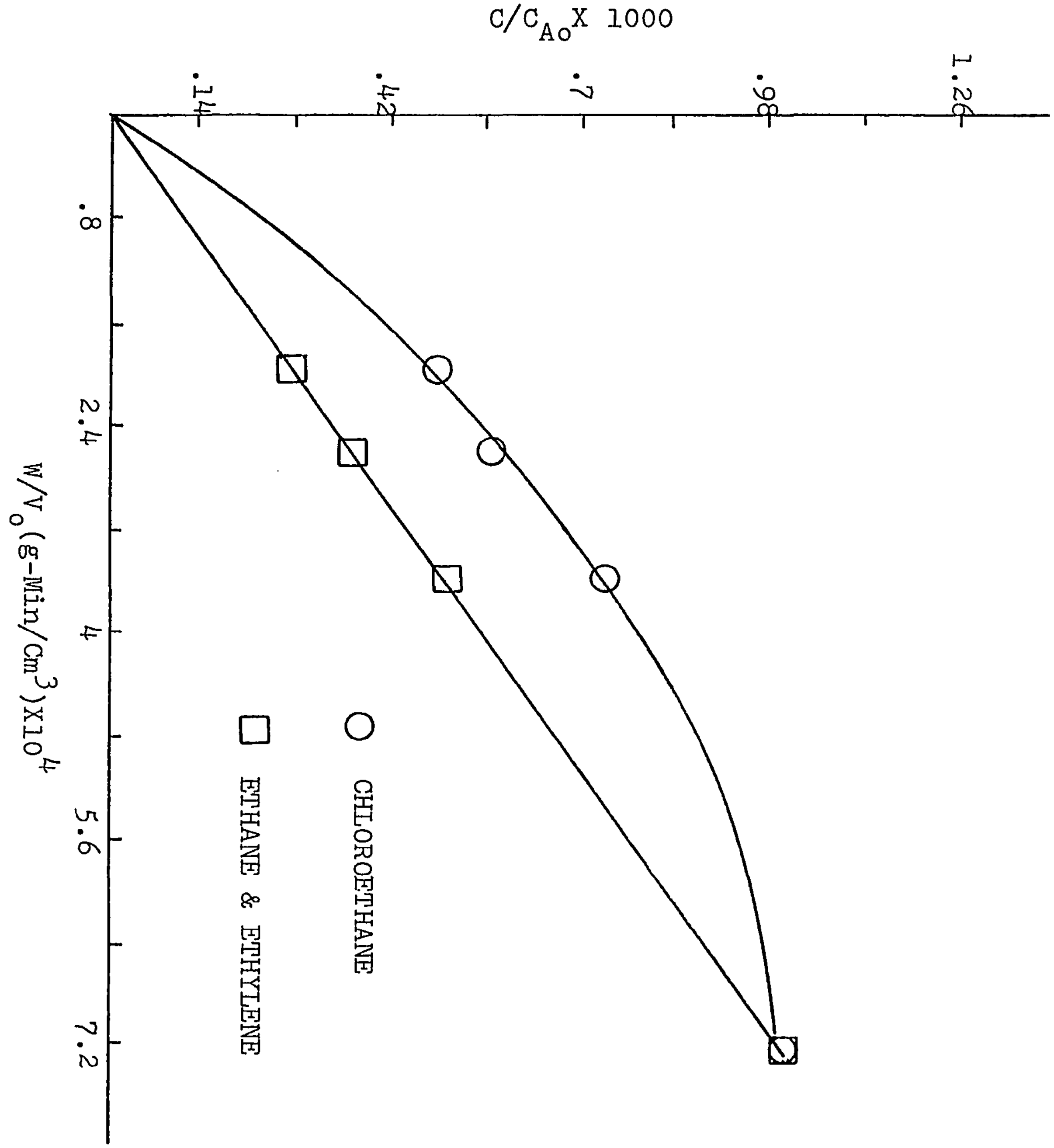


Figure 3-3 Product Distribution with Respect to Residence Time at Temperature 120°C

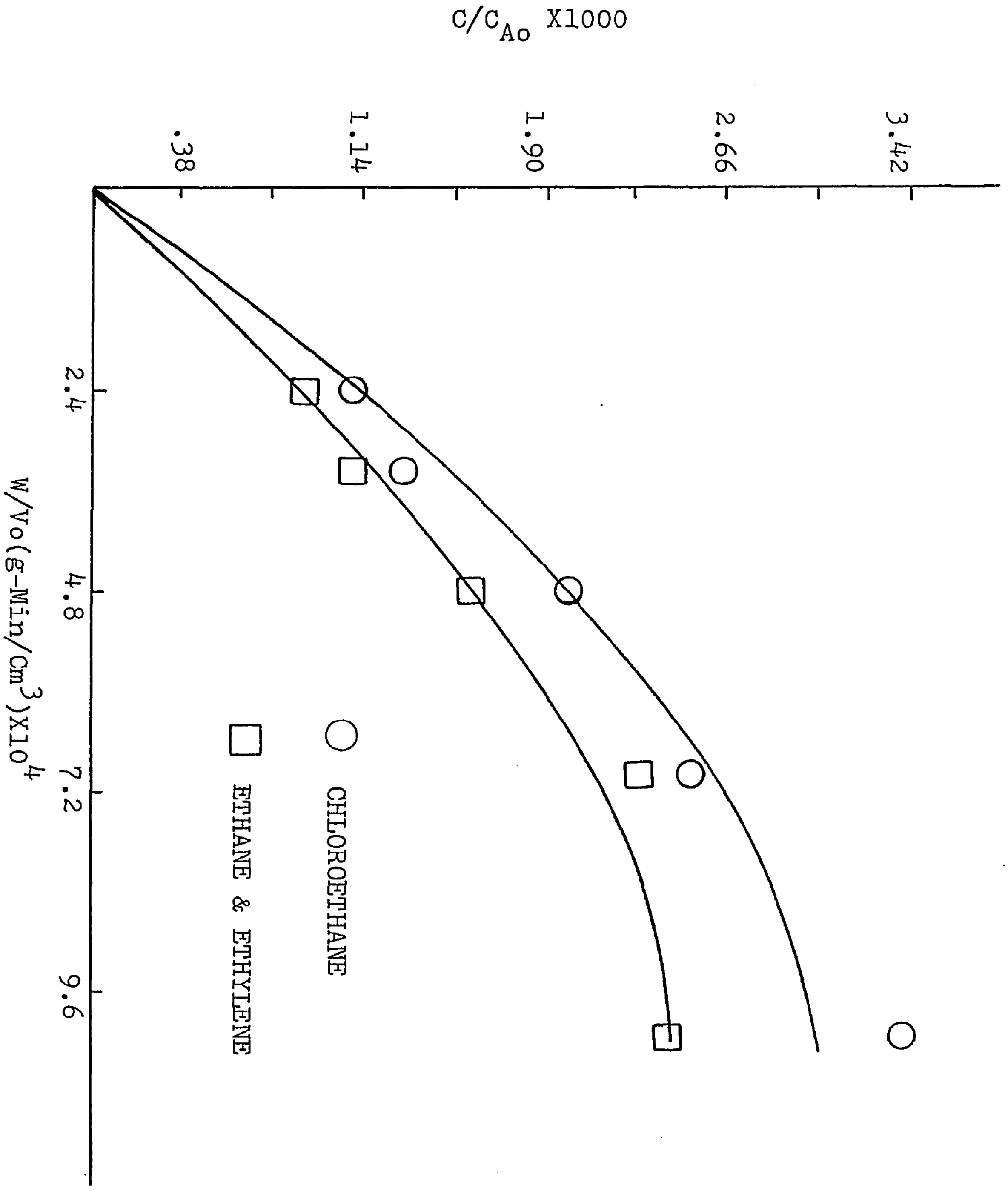


Figure 3-4 Product Distribution with Respective to Residence Time at Temperature 150°C

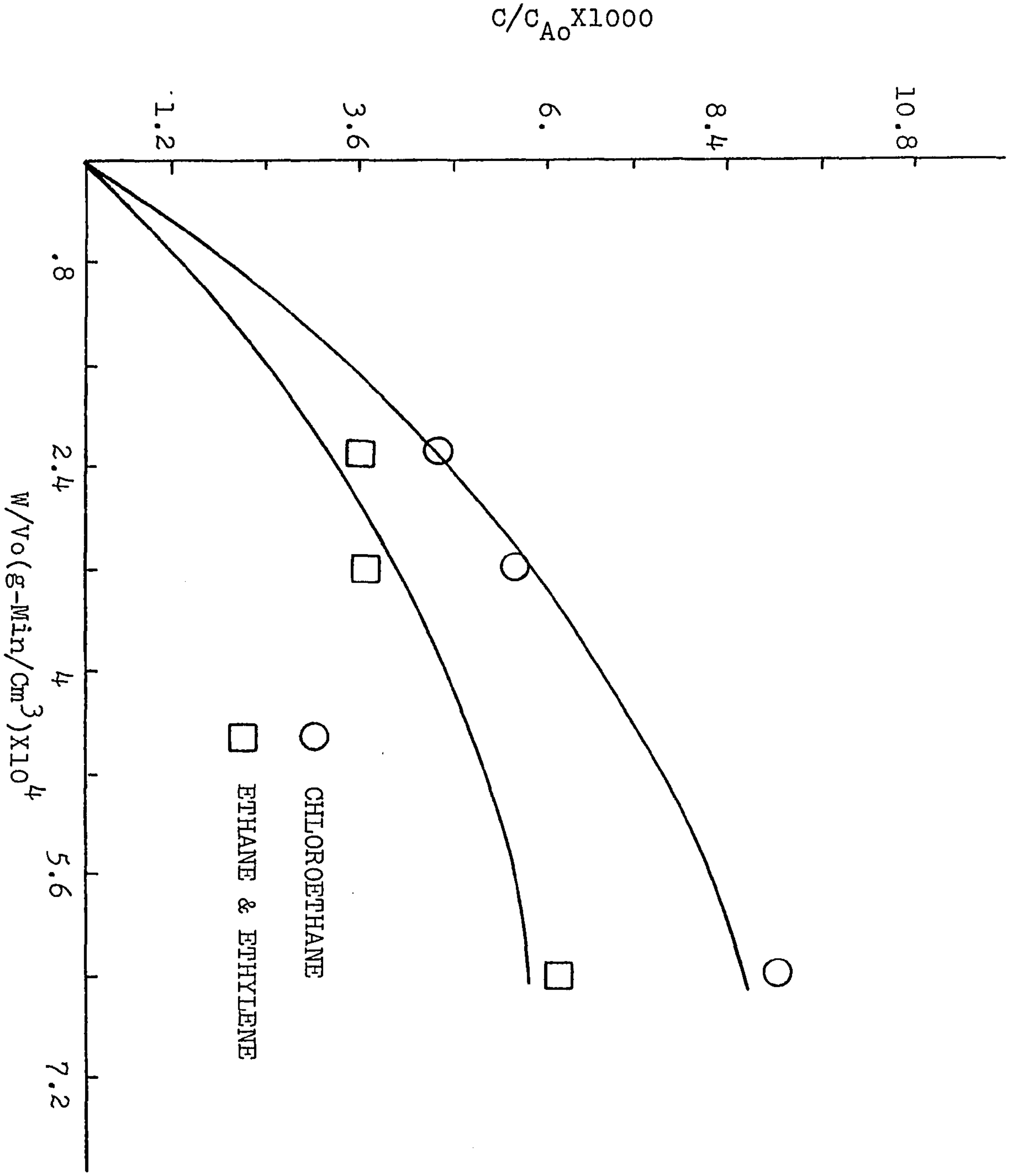


Figure 3-5 Product Distribution with Respect to Residence Time at 177°C

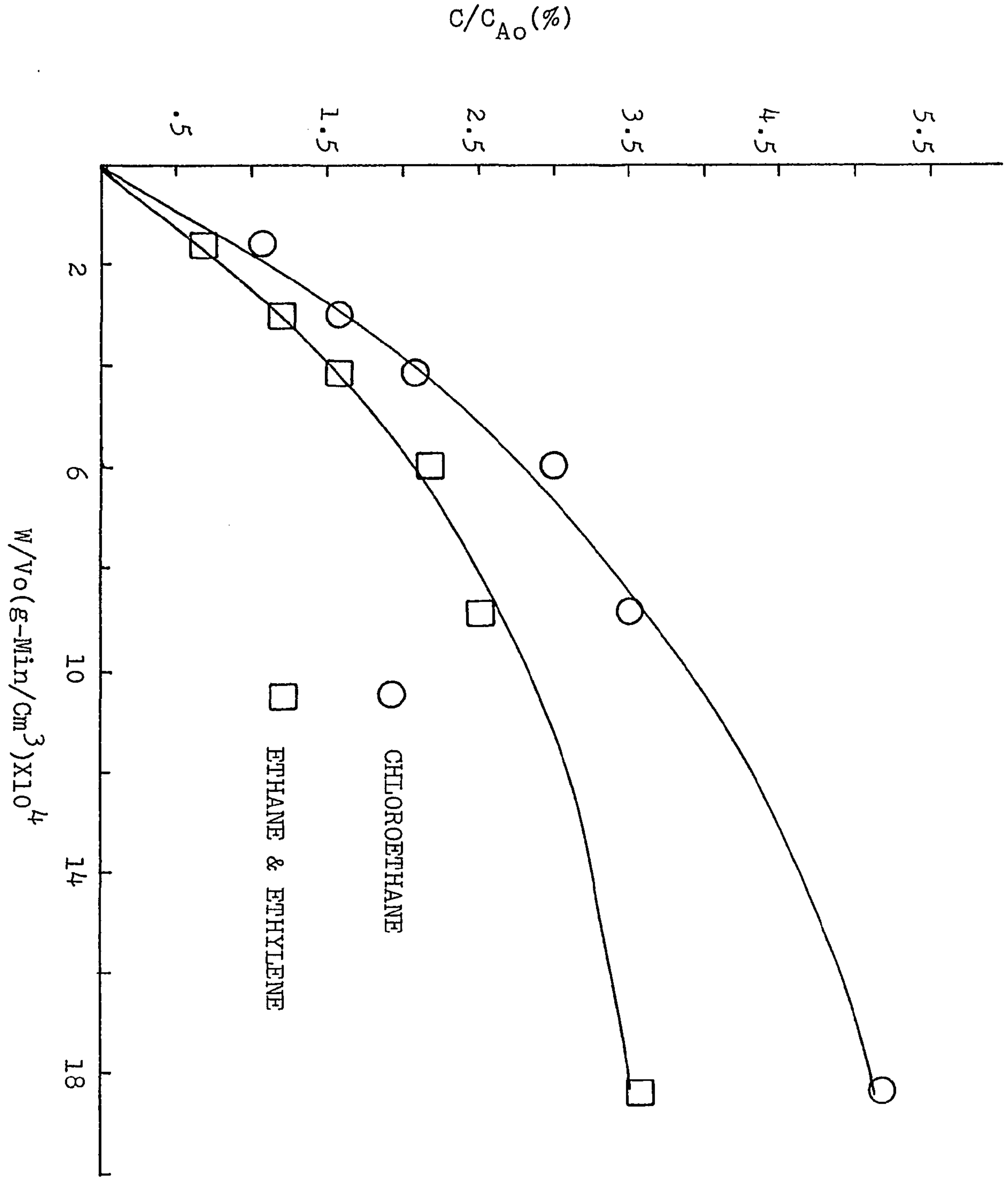


Figure 3-6 Product Distribution with Respect to Residence Time at 218°C

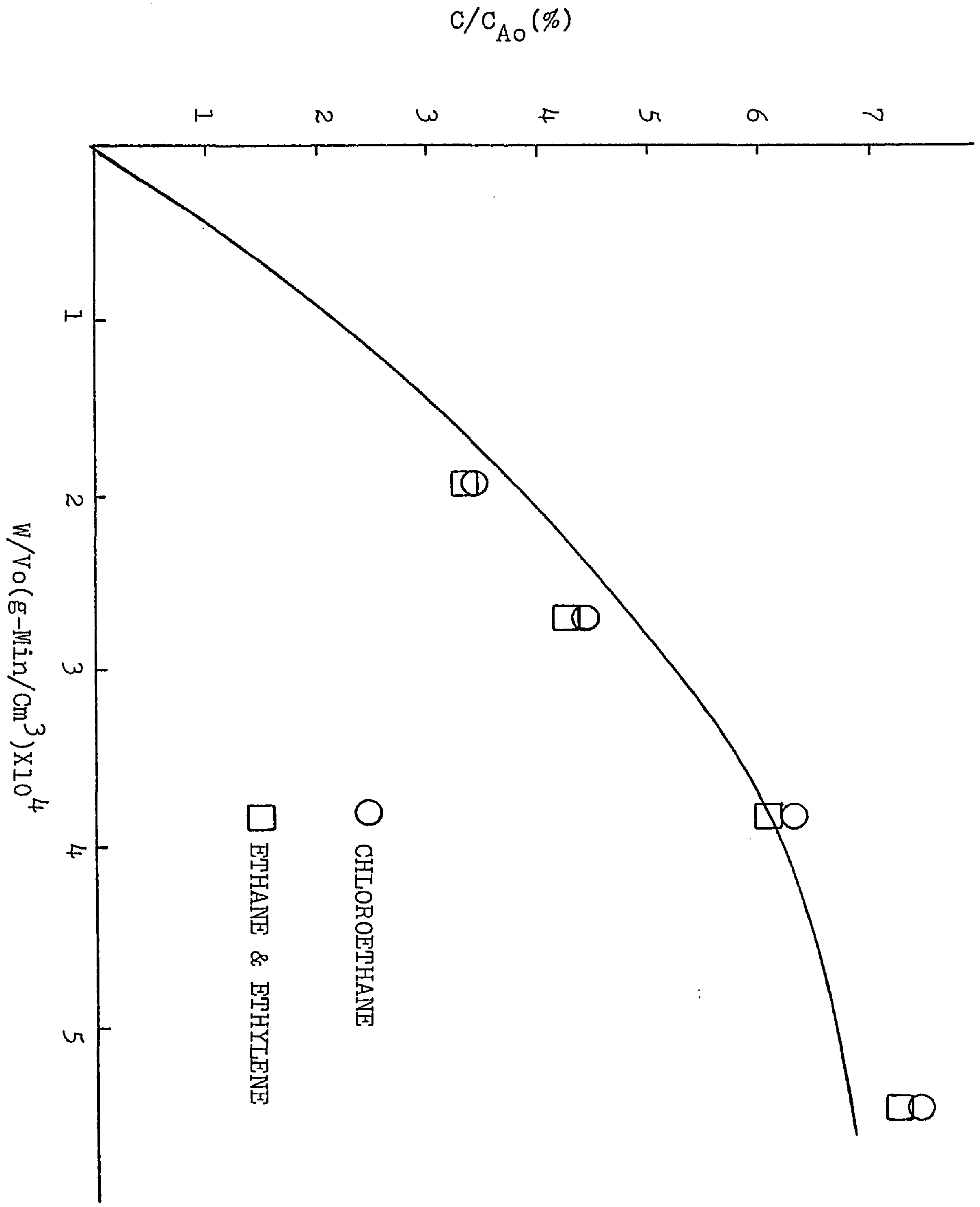
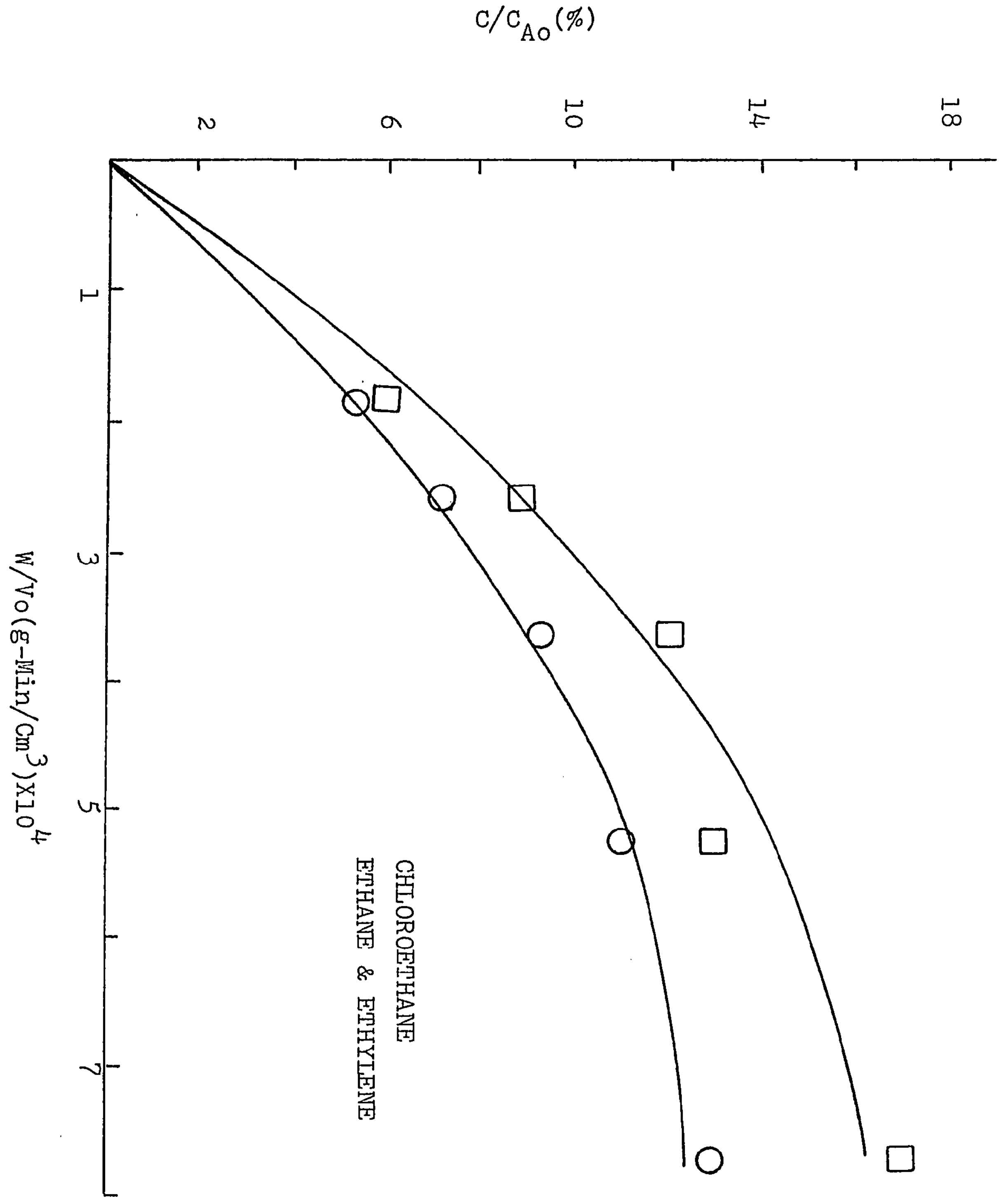


Figure 3-7 Product Distribution with Respect to Residence Time at 245°C



stream at 245°C. The conversion within one hour period remained essentially constant. The distribution of products is shown in Figure 3-2 to 3-7 for temperature 100, 120, 150, 177, 218, and 245°C respectively.

It is interesting to note that the higher conversion to ethane plus ethene is observed at higher temperature, but the conversion to chloroethane is lower at higher temperatures.

An integral method was used to fit data under assumption of first order reaction with respect to 1,2-dichloroethane. The performance equation is

$$\ln(1/(1-X)) = \tau k$$

where X is conversion of 1,2-dichloroethane, k is rate constant, τ is defined as w/v_o, w is weight of catalyst and v_o is volume flow rate. Table 3-1 shows kinetic parameters for this reaction:

TABLE 3-1

Kinetic parameters for reaction 1,2-dichloroethane with hydrogen over palladium on alumina catalyst.

T(°C)	k_w(cm^3/Min-g)
100	3.1
120	5.8
150	23.1
177	86.4
218	341.4
245	656.5

The Arrhenius' plot shown in Figure 3-8 yields an apparent activation energy of 15 Kcal/mole.

Pore diffusion may play a very important role in the catalytic reaction, and we therefore can not ignore it. If $r_p^2 * k_v / D_{eff}$ is smaller than 1, according to Mears's(1971) criterion, there will be no resistance to pore diffusion. Here r_p is particle radius, D_{eff} is effective diffusion coefficient, and k_v is rate constant, unit of sec^{-1}. In this experiment at temperature 245°C, $r_p^2 * k_v / D_{eff} = 0.44$ which is smaller than 1; therefore the pore diffusion effects may be neglected.

It is common to find that catalysts need to be regenerated after a prolonged operation. Figure 3-9 shows the effect of regeneration on the catalyst activity. After 4.3 hours the flow of reactant was stopped. The reactor was then kept at same temperature (245°C) and pure hydrogen was purged into reactor at a flow rate of 20 cm^3/sec. After 13.5 hours of regeneration, the activity recovered to about 68% of initial and further deactivation was slowed (from the slope shown on Figure 3-9). The same results were shown for each run after first regeneration step, but at time 36.8 hour, after 12 hours regeneration, the activity only recovered to 56% of initial. This indicates that the catalyst may undergo sintering and some fraction of the surface is covered by carbonaceous material (fouling). Regeneration at higher temperatures may also be more efficient.

Figure 3-8 Arrhenius' Plot for Reaction of 1,2-Dichloroethane with Hydrogen Over Palladium on Alumina Catalyst

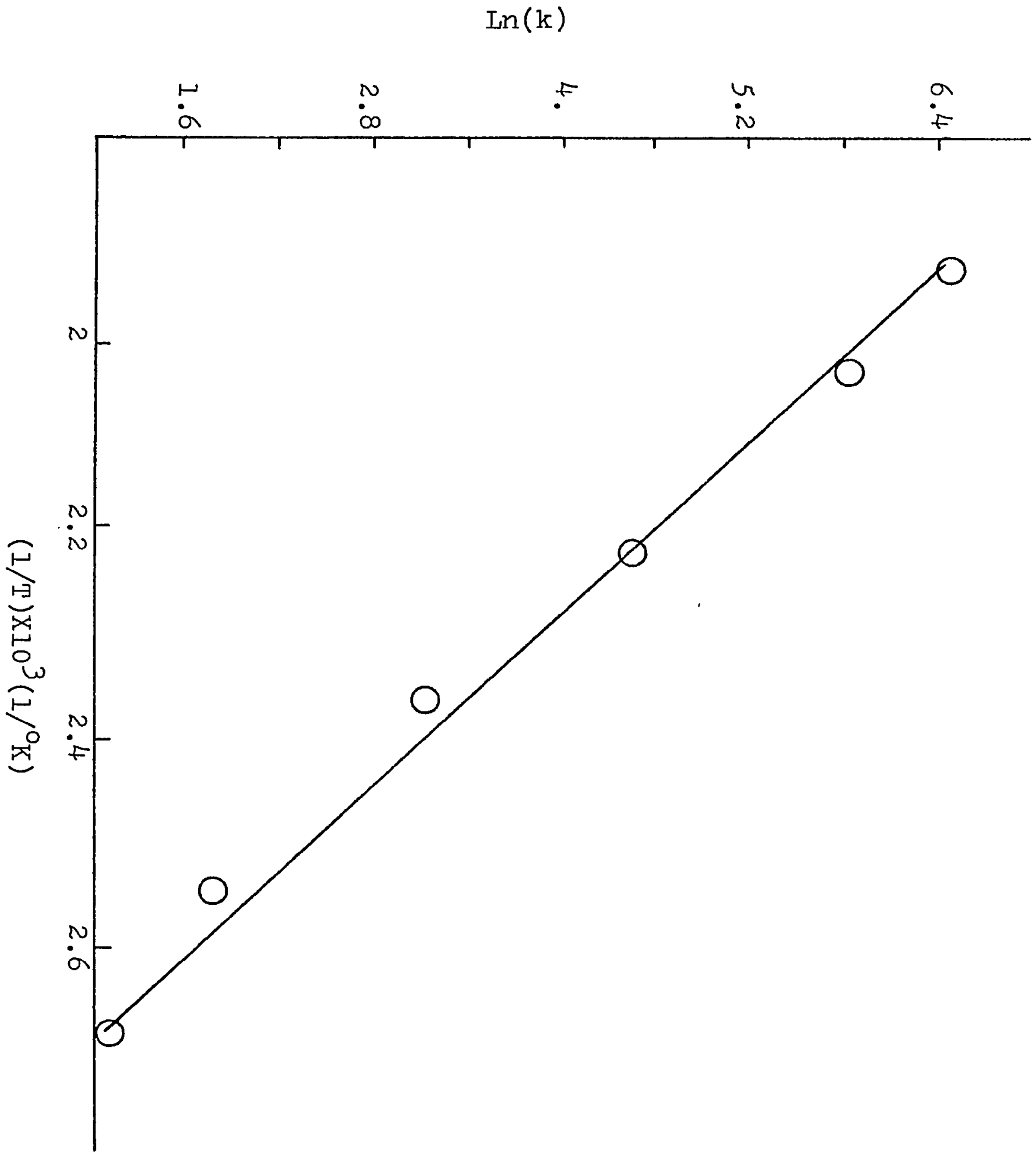
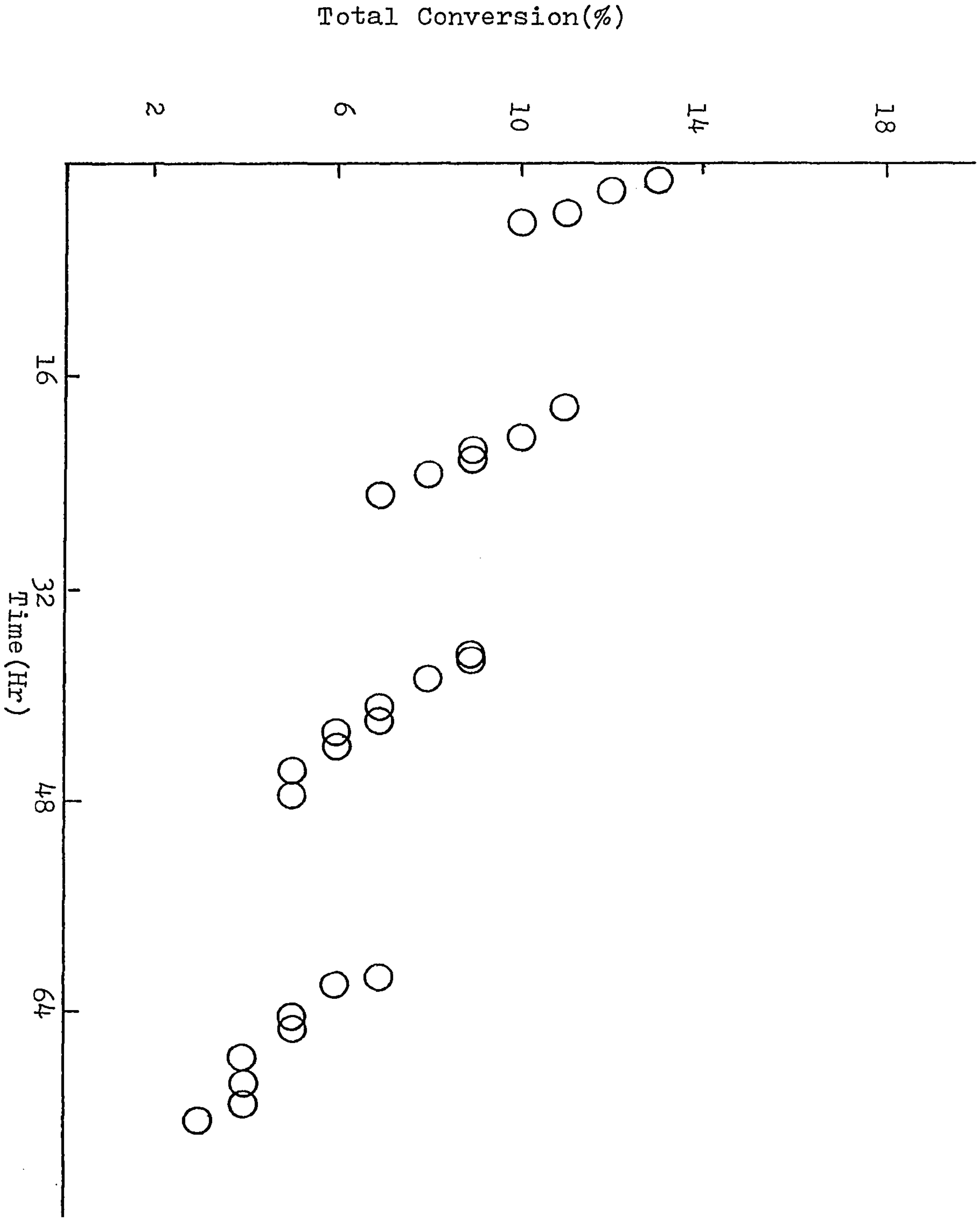


Figure 3-9 Regeneration of Catalyst with Respect to Time at 245°C



3-4-2 chloroform:

More deactivation occured in this reaction and therefore we cannot determine the conversions as we did in the reaction of 1,2-dichloroethane system. Fortunately, the deactivation is not very rapid at the begining of the reaction time as shown in Figure 3-10 at temperature 100°C; therefore we determined the conversion by extrapolating the conversion around 10 minutes to that of time zero.

A first order with respect to chloroform was used to calculate kinetic parameters. The results were given in Table 3-2:

TABLE 3-2
Kinetic Parameters for reaction chloroform with hydrogen over palladium on alumina catalyst

Temperature(°C)	k_w(cm^3/sec-g)
61	.0424
82	.149
102	.853
122	3.07
143	8.2608

The Arrhenius' plot shown in Figure 3-11 yields an apparent activation energy of 19 Kcal/mole.

3-5 Reaction Mechanisms

3-5-1 With 1,2-Dichloroethane

Lapierre et. al. (1978) suggested that aliphatic

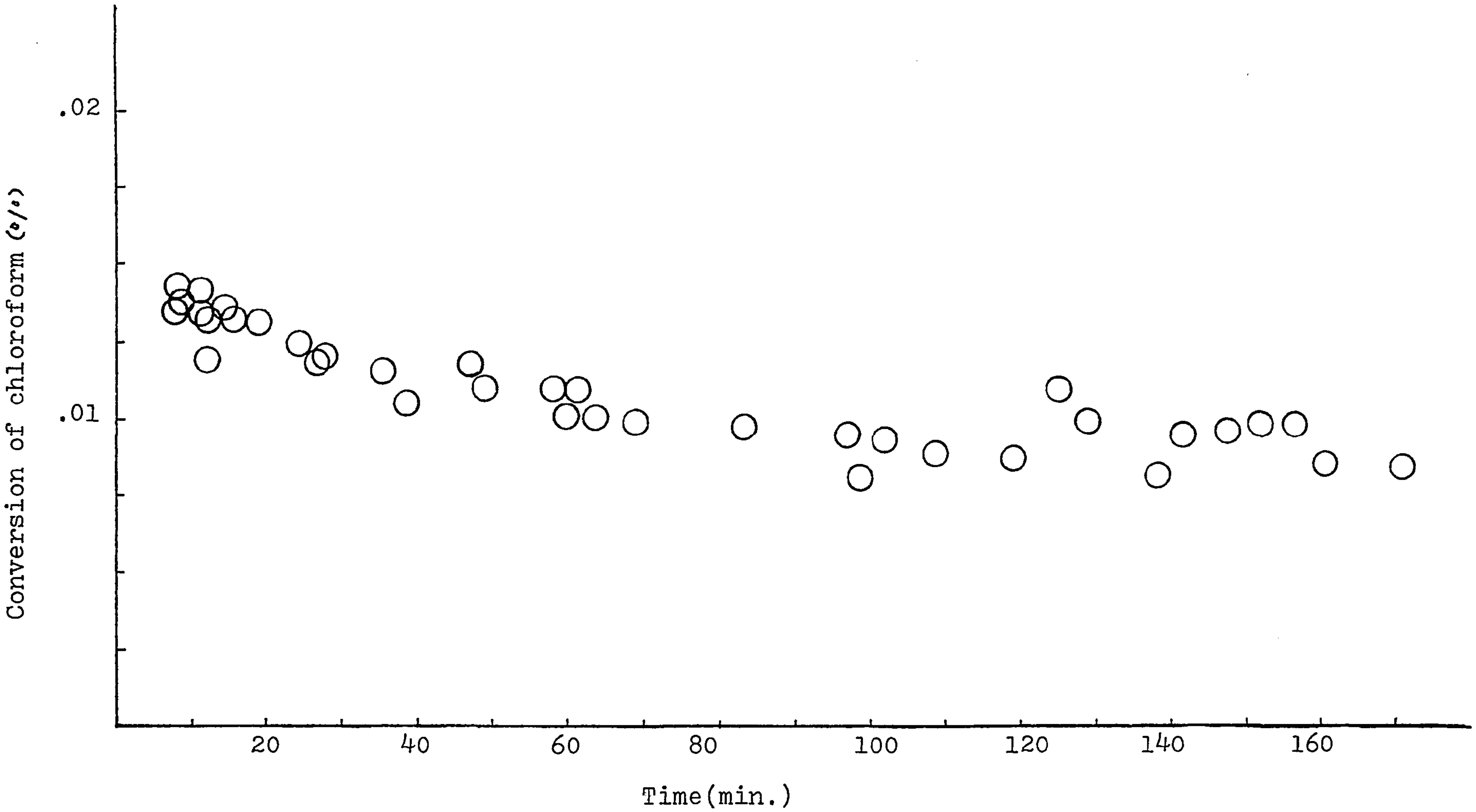
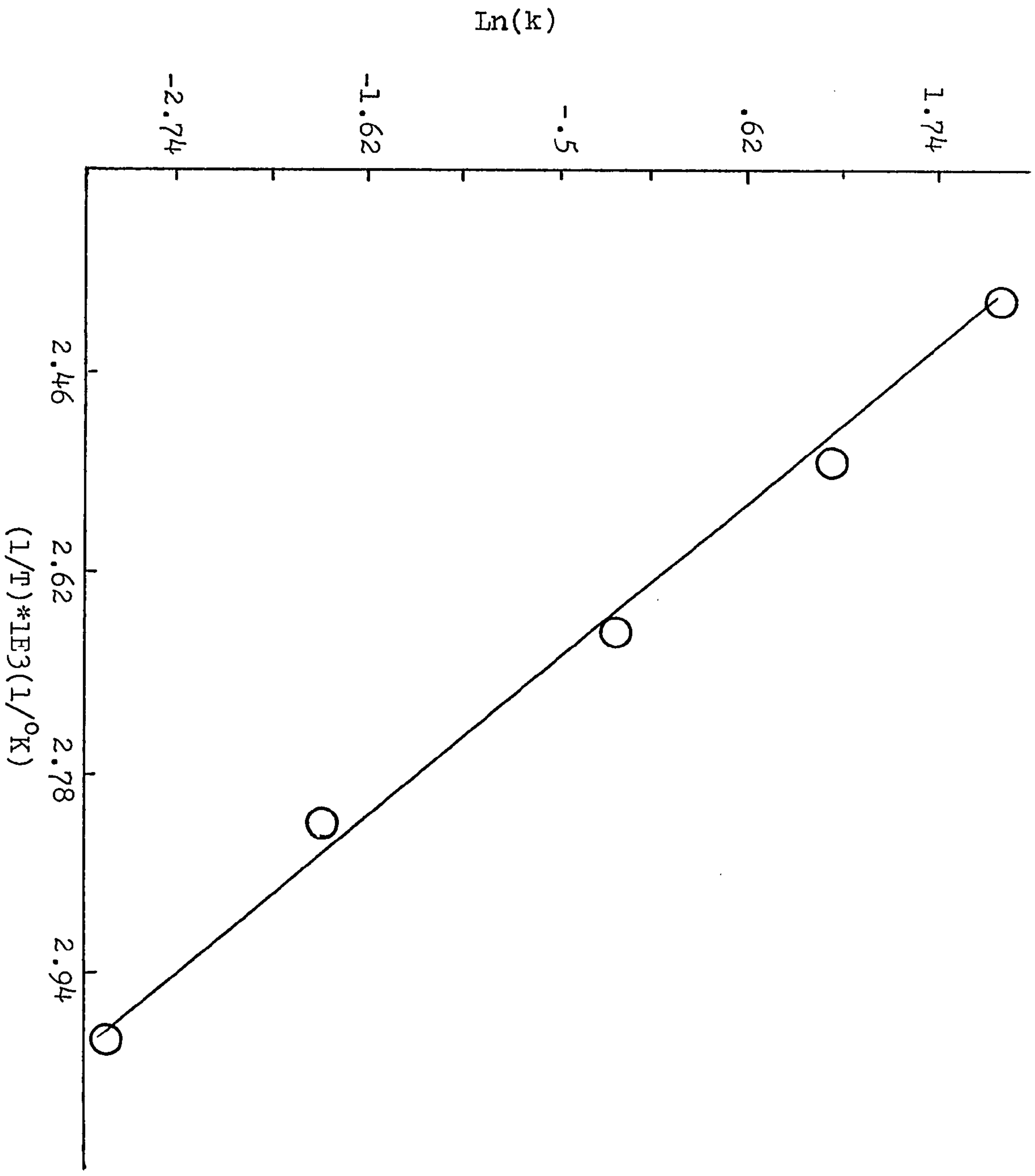
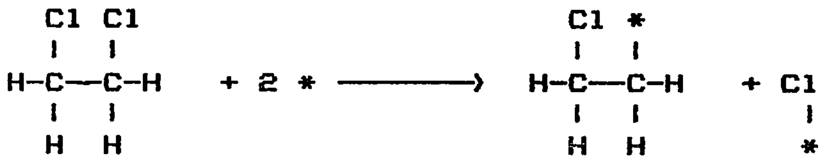


Figure 3-10 Total Conversion of Chloroform Vs. Time-on-Stream at 100°C

Figure 3-11 Arrhenius' Plot for Reaction of Chloroform with Hydrogen Over Palladium on Alumina



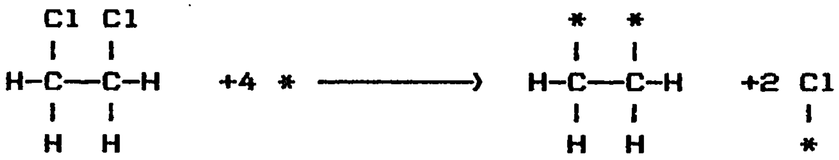
chloride occcurs by radical type mechanism over supported metal catalysts. We propose similar reaction steps in our experiment. 1,2-dichloroethane must undergo dissociative adsorption, and two possible radical intermediates are produced



$$\mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{Cl}{C}}{-}H} + 2\,* \longrightarrow \mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{*}{C}}{-}H} + \underset{*}{\mathrm{Cl}}$$

(I)

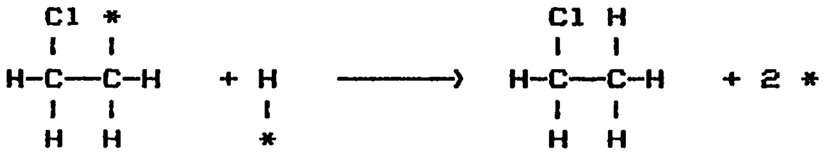
or



$$\mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{Cl}{C}}{-}H} + 4\,* \longrightarrow \mathrm{H{-}\underset{H}{\overset{*}{C}}{-}\underset{H}{\overset{*}{C}}{-}H} + 2\,\underset{*}{\mathrm{Cl}}$$

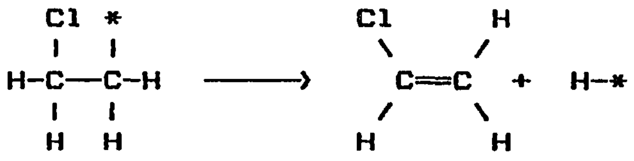
(II)

This type of intermediate (II) has been reported by Keii(1954,1955). The intermediate (I) is then attacked by a hydrogen radical on the catalyst surface to produce ethyl chloride.



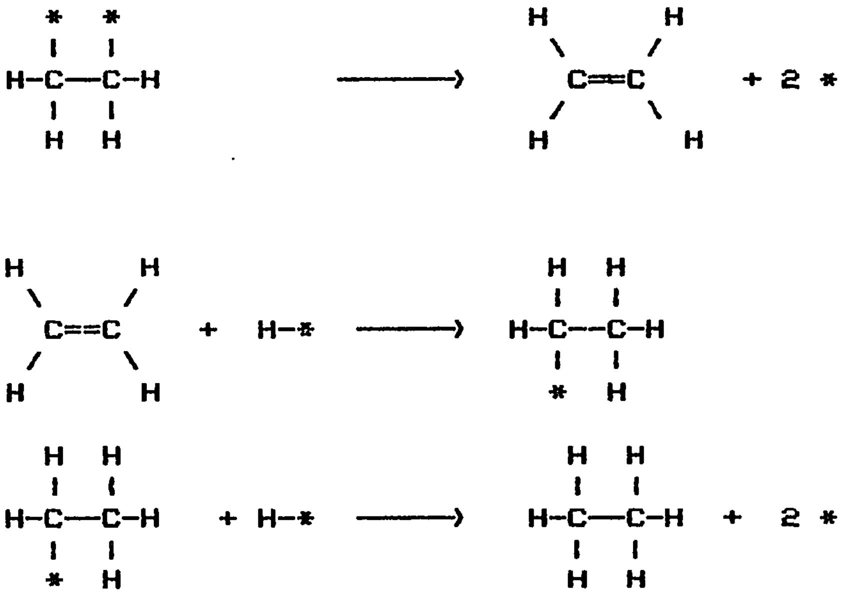
$$\mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{*}{C}}{-}H} + \underset{*}{\mathrm{H}} \longrightarrow \mathrm{H{-}\underset{H}{\overset{Cl}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + 2\,*$$

It seems likely that a H-* can leave intermediate (I), and vinyl chloride is produced; the reaction rate should be low because the reaction is under hydrogen atmosphere and the chance of intermediate (I) meeting with H-* is high.

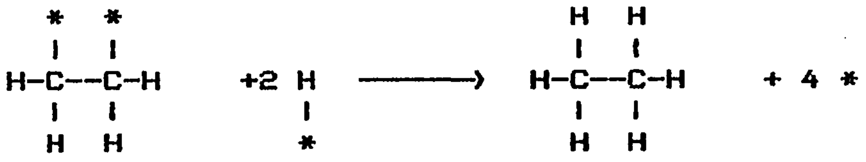


Vinyl chloride will be quickly converted to ethane because of a stable resonance intermediate being produced (Lapierre,1978).

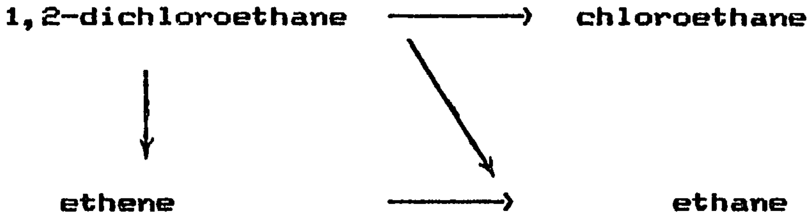
Intermediate (II) has two possible reaction paths. The first is production of ethene, and hydrogenation of ethene, then occurs:



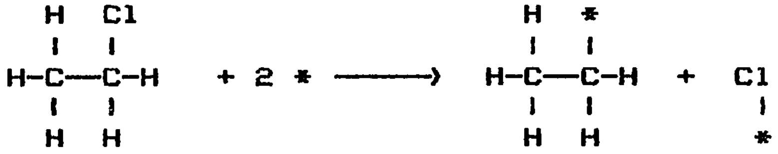
or intermediate (II) can also react with two hydrogen atoms on catalyst surface to produce ethane:



According to the mechanism we suggest, the reaction type would be :

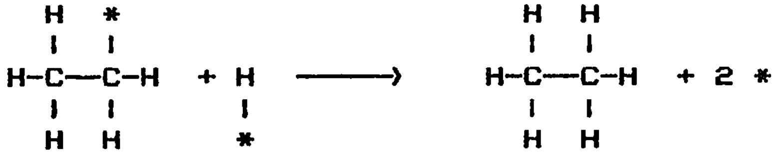


It is possible that chloroethane, one of the products, can undergo secondary reaction and becomes a radical:



$$\mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{C}}}\mathrm{{-}H} + 2\,* \longrightarrow \mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{*}{|}}{\mathrm{C}}}\mathrm{{-}H} + \underset{\underset{*}{|}}{\mathrm{Cl}}$$

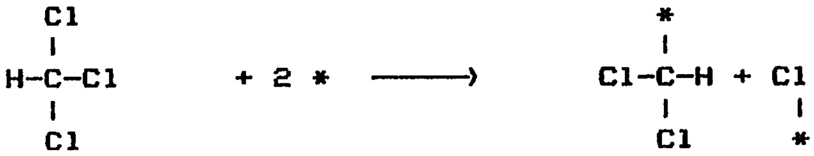
which then produces ethane by:



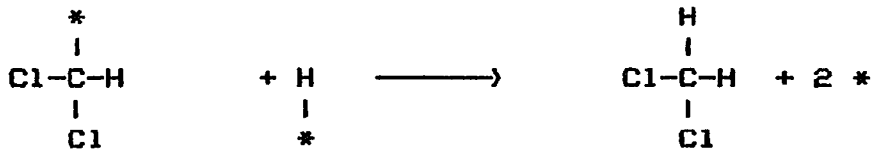
$$\mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{*}{|}}{\mathrm{C}}}\mathrm{{-}H} + \underset{\underset{*}{|}}{\mathrm{H}} \longrightarrow \mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}H} + 2\,*$$

3-5-2 With Chloroform

The products in this reaction are methylene chloride and methane. According to the formation of products, we proposed that the mechanism for this reaction is similiar to that of the reaction 1,2-dichloroethane with hydrogen over palladium on alumina:



$$\mathrm{H{-}}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{C}}}\mathrm{{-}Cl} + 2\,* \longrightarrow \mathrm{Cl{-}}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{*}{|}}{\mathrm{C}}}\mathrm{{-}H} + \underset{\underset{*}{|}}{\mathrm{Cl}}$$



$$\overset{\overset{*}{|}}{\underset{\underset{Cl}{|}}{Cl-C-H}} \quad + \underset{\underset{*}{|}}{H} \longrightarrow \overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{Cl-C-H}} + 2\,*$$

then methylene chloride is converted to methane.

3-6 Isothermal Test For Particles

To verify isothermal conditions for catalyst particles, Anderson's criterion (Anderson, 1963) was used. (see equation 44, chapter 2). The calculation results of Anderson's criterion which demonstrate isothermality of the particles are listed in table 3-3.

All of the results we have shown include the assumption, that film diffusion is insignificant. Film diffusion is not a significant factor when

$$(-Rate)*r_p/C_b/K_m < 0.15/n$$

According to Mears's criterion. Where (-Rate) is reaction rate, r_p is particle radius, C_b is the bulk concentration, K_m is mass transfer coefficient, and n is reaction order. In the experiment of 1,2-dichloroethane system $(-Rate)*r_p/C_b/K_m = 0.00115$ and 0.15/n is 0.15; therefore film diffusion is negligible here. Values of the parameters are listed in Table 3-3.

TABLE 3-3

Parameters of Mears's and Anderson's criterion (based on flow rate 327 cm^3/min. at temperature 23°C)

Parameters	100°C	120°C	150°C	171°C	218°C	245°C
Re	.481	.462	.439	.42	.396	.38
N_{pe}	77.2	74.6	70.8	68.0	64.4	62.2
k_m (cm/sec)	34.1	36.4	40.1	43.3	48.3	51.5
K_v (1/sec)	0.051	0.096	0.385	1.44	5.69	11.
D_{eff} (cm^2/sec)	2.35E-3	2.42E-3	2.51E-3	2.59E-3	2.7E-3	2.8E-3
Φ	.0024	.0045	.017	.062	.24	.44
$\frac{\lvert\Delta H\rvert*(-rate)*r_p^2}{\lambda * T_s}$	$1.5x10^{-6}$	$2.6x10^{-6}$	$9.x10^{-6}$	$3.x10^{-5}$	$9.9x10^{-5}$	$1.7x10^{-4}$
$\frac{E}{R*T_s}$	.049	.052	.056	.059	.065	.069

Where Φ represents $r_p^2*k_v/D_{eff}$, (-rate) is reaction rate, and $|\Delta H|$ is absoutle value of ΔH. Δ H was based on largest value of heat of reaction:

$$CH_2ClCH_2Cl + H_2 \longrightarrow C_2H_6 + HCl$$

Calculated values of the reaction rate are those of the fastest rate. Table 3-3 also shows that internal diffusion can be ignored because all Φ are smaller than 1, which was the upper limit for Mears's criterion.

Table 3-4

Mears's and Anderson's parameters for system of chloroform with hydrogen over palladium (based on flow rate 5.1 cm^3/sec at 61°C):

Parameters	61°C	82°C	102°C	122°C	145°C
Re	3.97	3.77	3.60	3.45	3.30
N_{pe}	1.48	1.47	1.45	1.44	1.43
K_m (cm/sec)	54.4	58.5	62.5	66.6	71.0
k_v (1/sec)	.04	.15	.85	3.1	8.3
$D_{eff} \times 10^3$ (cm^2/sec)	2.03	2.09	2.15	2.20	2.26
Φ	.0047	.016	.089	.31	.82
$\dfrac{\lvert\Delta H\rvert * (-rate) * r_p^2}{\lambda * T_s}$	5.6×10^{-6}	1.9×10^{-5}	9.4×10^{-5}	3.1×10^{-4}	7.4×10^{-4}
$\dfrac{R * T_s}{E}$	.035	.037	.039	.041	.044

The above data demonstrate internal and external diffusion can be neglected. The reaction rate shown in Table 3-4 is the largest one. ΔH was calculated at temperature 145°C for this reaction

$$CHCl_3 + H_2 \longrightarrow CH_2Cl_2 + HCl$$

CHAPTER 4 Reaction of Chlorobenzene with Hydrogen Over Palladium Catalyst Supported on Alumina

4-1 Introduction:

It is of interest that low and narrow range temperatures are needed for gas phase metal catalytic dehydrochlorination of chlorocarbon species which have a olefinic and aromatic structure (this study; Chen, 1986; Lapiere, 1978 A and B; Kraus, 1973).

For comparison with the reaction of 1,2-dichloroethane (Aliphatic structure) with hydrogen on the palladium/Al_2O_3 and to test the resonance theory suggested by several authors (Weiss, 1966; Lapiere, 1978 A and B), we chose chlorobenzene as a next reagent. Kinetic parameters were determined using the simple first order reaction. It is hoped that this data will lead to the design of an optimum system for effeciently converting toxic chlorocarbon waste into safe and useful compounds. The possibility of converting chlorocarbons, especially chloro-aromatic species, to hydrocarbons and HCl without the presence of oxygen, essentially eliminates the formation of dioxanes or furans, as well as chloro-furans and dioxans, and is an extremely appealing concept.

4-2 Literature Survey

Acid catalysts such as alumina, H-Y zeolite, and molecular sieves have been studied in the removal of chlorine from chlorohydrocarbon substances, but are not practical because the reaction is almost always accompanied by rapid catalyst deactivation. Crystalline alummosilicate has actively catalyzed the dechlorination of two-carbon chlorohydrocarbons between temperatures of 65-370 °C as studied by Venuto et al. (1966); vinyl chloride was the major product from reaction of 1,2-dichloroethane over the molecular sieve catalysts, and a carbonium ion mechanism was suggested for the dehydrochlorination reactions.

Mochida et al. (1967) studied the elimination reaction of HCl from chloroethanes on acid catalysts at 300°C with a pulse technique. The main product, vinyl chloride, showed an overall elimination reaction from 1,2-dichloroethane as a reagent. HCl elimination from gaseous 2,3-dichlorobutane on acidic Al_2O_3 in the temperature range 150 to 370°C with the pulse technique gave results indicating that the lifetime of the carbonium ion was shorter on these acid catalysts than on $CaCl_2$ and CaO catalysts. They also reported that more cis-2-chloro-2-butene was produced from the meso form of 2,3-dichlorobutane. A carbonium ion mechanism was also suggested in the HCl elimination reaction from 1-chlorobutane and 2-chlorobutane over X and A zeolites containing Ca, Mg, Co, Ni, Cu, and Zn cations with the exception of NaX, NaA, and ZnA (Kladnig ,1973).

Palladium on a support such as carbon or calcium carbonate, has been suggested as the best catalyst for dehalogenation reactions in neutral media because it is least affected by the substrate or resulting hydrogen halide

(Freifelder,1971). Rylander(1967) indicated the importance of palladium by showing that catalytic dehalogenation of benzyl chloride was extremly fast by using palladium on carbon catalyst relative to Platinum/carbon and rhodium/carbon.

4-3 Materials:

Hydrogen and Nitrogen were purchased as commercial grade from MG Industries Company(North branch, NJ).

Chlorobenzene: From Aldrich Chemical Company, Inc.

Catalyst: A commercial catalyst, from Strem Chemical Inc. (Newburyport, MA); palladium(0.5%) on alumina with a surface area of approximately 100 m^2/gram. This catalyst is in the form of extruded 1/8" x 1/8" pellets. The catalyst was crushed to 45/60 mesh before being used. A quantity of 0.2 to 0.3 grams of crushed catalyst was used in all of experiments. The catalyst bed was 1.5 cm long and was supported at both ends by glass wool. Pretreatment of catalyst using a hydrogen flow at temperature 300°C for 3 hrs was done before each experiment.

4-4 Experimental

Temperature range: 35 - 70°C

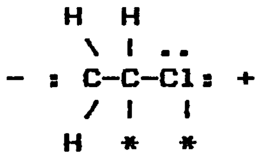
The apparatus are same as those in chapter 3 as shown in Figure 2-1.

Analysis: A Perkin-Elmer 900 Gas Chromatograph equipped with flame ionization and thermal conductivity detectors was used for all analysis. A Hewlett-Packard 3390A recording integrator was used to calculate the peak areas.

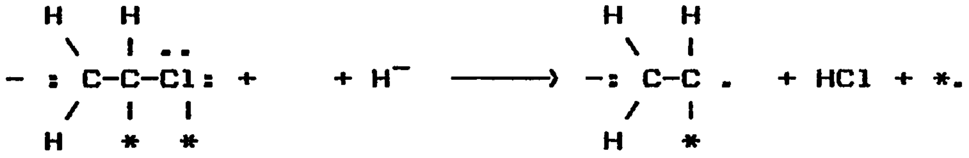
4-5 Results and Discussion:

4-5-1 Possible mechanisms

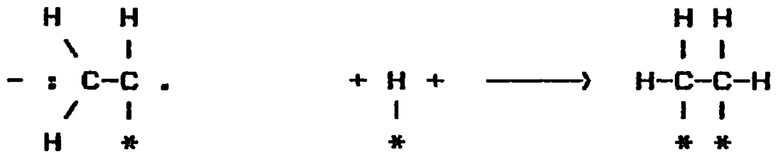
There are three possible mechanisms for explaining dehalogenation reactions occuring on palladium catalyst; the first one is ionic in nature. Weiss(1966) has pointed out that vinyl chloride and cis- and trans-dichloroethylenes react rapidly with H_2 over Pt on an Al_2O_3 reforming catalyst. He proposed that olefinic chlorides were adsorbed on the surface of catalyst in a stabilized resonance form, such as the absorbed resonance intermediate of vinyl chloride.



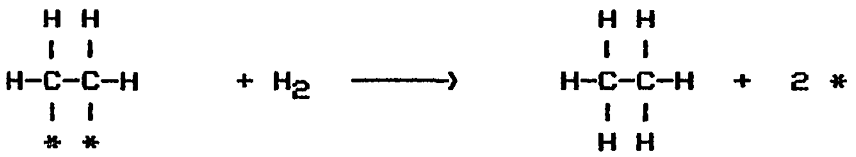
This intermediate is then attacked by a hydride ion H^- (Lapierre et al.,1978,A)



to produce HCl and a non-chlorine intermediate on the catalyst surface. This non-chlorine intermediate then reacts with a proton on the catalyst to produce an adsorbed C_2H_4



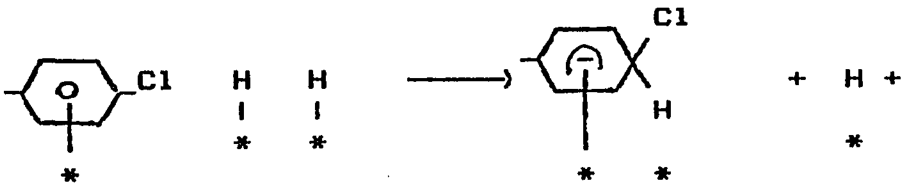
The absorbed C_2H_4 then reacts with hydrogen to produce ethane.



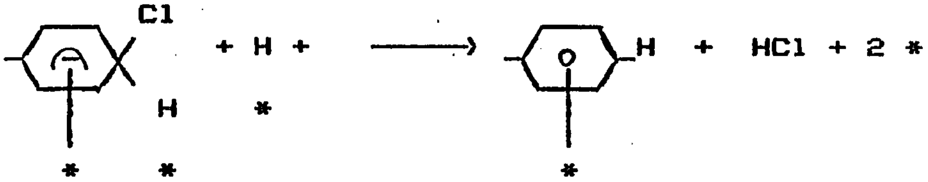
$$\mathrm{H{-}\underset{*}{\overset{H}{C}}{-}\underset{*}{\overset{H}{C}}{-}H} + \mathrm{H_2} \longrightarrow \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H} + 2\ *$$

An adsorbed resonance mechanism was also proposed in Lapierre's studies (Lapierre et al., 1978. A, B) to illustrate hydrodechlorination of 1,1-bis (p-chlorophenyl) 2,2-dichloroethylene (p,p'-DDE) and polychlorinated biphenyl.

A somewhat different second mechanism for chlorobenzene reaction with hydrogen over Pd on carbon has been proposed by M. Kraus et. al. (1973) who suggested that the mechanism requires hydridic species H^- to be present on the surface in equilibrium with H^+. The H^+ reacts with chlorine Cl- , and H^- then attacks the benzene to produce a very stable phenyl ion .

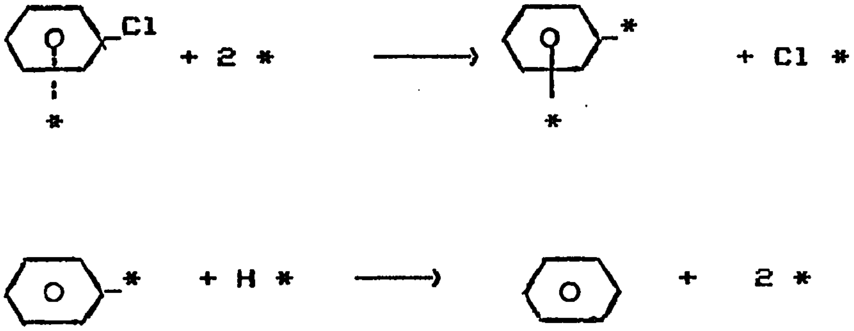


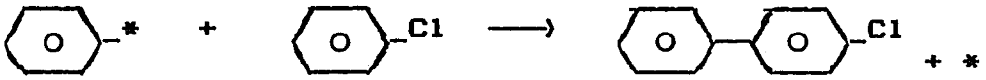
This ion then reacts with a proton to produce benzene and HCl.



A similar mechanism was also reported by Kieboom et al.(1971) who studied the substituent effect in the hydrogenolysis of benzyl alcohol derivatives over palladium.

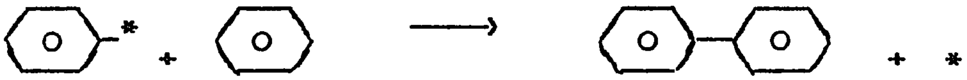
A third mechanism has been suggested by Garnett (1966) and is a free radical mechanism. The chlorine atom on chlorobenzene is attacked by a metal atom, and the intermediate is then attacked by a proton to give benzene. This intermediate can also attack a chlorobenzene to form chlorobiphenyls:





+ other isomers

The intermediate can also react with benzene to produce biphenyl:



4-5-2 Results

No deactivation was observed within one hour of reaction time as shown in Figures 4-1 and 4-2 at temperature 50° and 70°C respectively, so the observed average conversion in this time period (after 10 minutes) was used for calculation of the kinetic parameters. Figures 4-3 to 4-6 show the product distribution plots at 35, 50, 60, and 70°C. The observed products include benzene and biphenyl.

The reaction rate can be expressed by a simple model first order in chlorobenzene

$$-\text{Rate} = k * C_A$$

where the concentration of hydrogen on the surface is incorporated into k because H_2 was in excess and its concentration is constant. C_A represents concentration of chlorobenzene, and k is the rate constant. Since only one fluid phase is present, the rate can be found as with homogeneous reactions. For a steady-state plug flow system the performance equation is:

Figure 4-1 Conversion of Chlorobenzene Vs. Time-on-Stream at Temperature 50°C

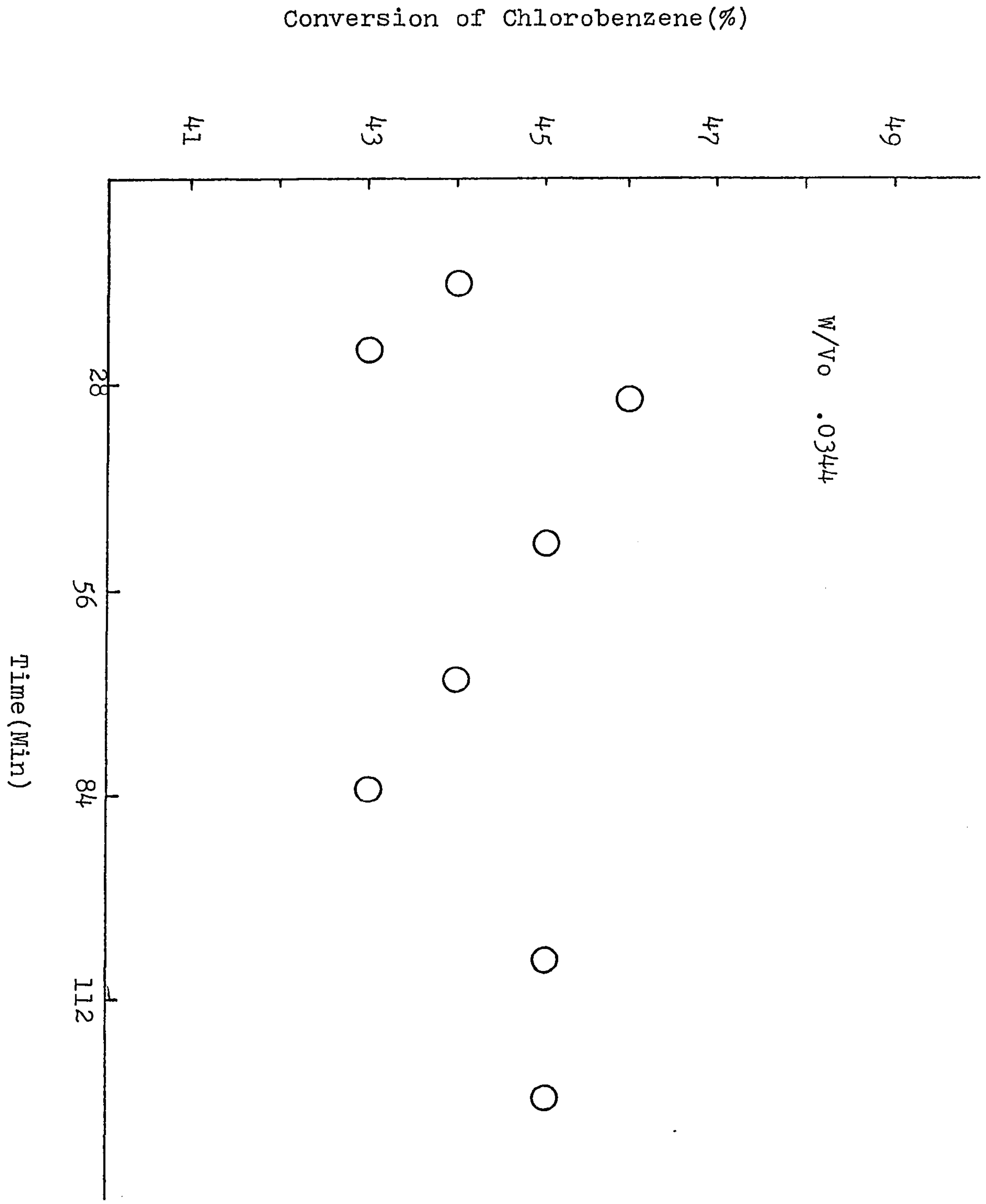


Figure 4-2 Conversion of Chlorobenzene Vs. Time-on-Stream at Temperature 70°C

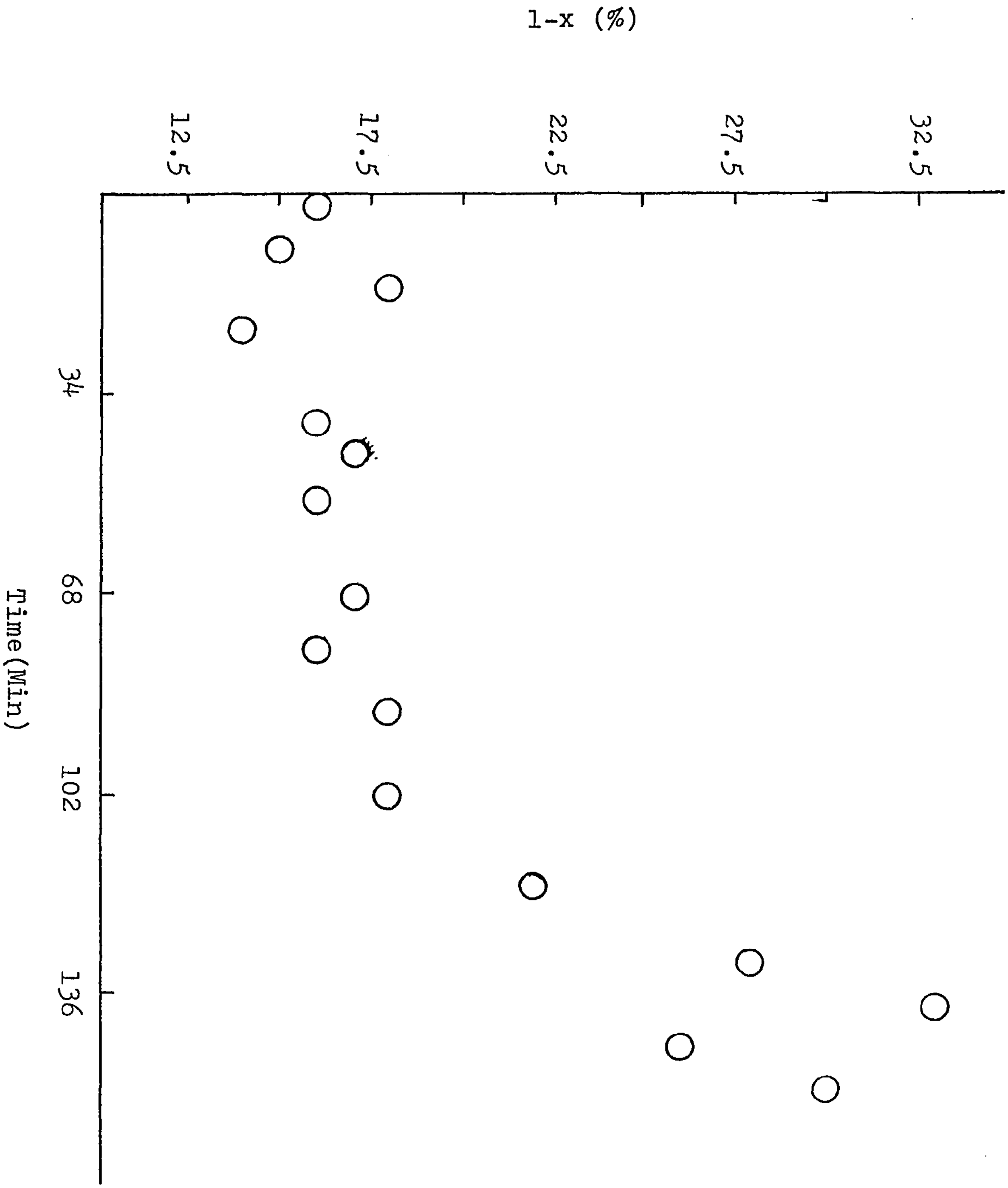


Figure 4-3 Product Distribution Plot Against Residence Time at Temperature 35°C for Reaction of Chlorobenzene with Hydrogen Over Palladium on Alumina Catalyst

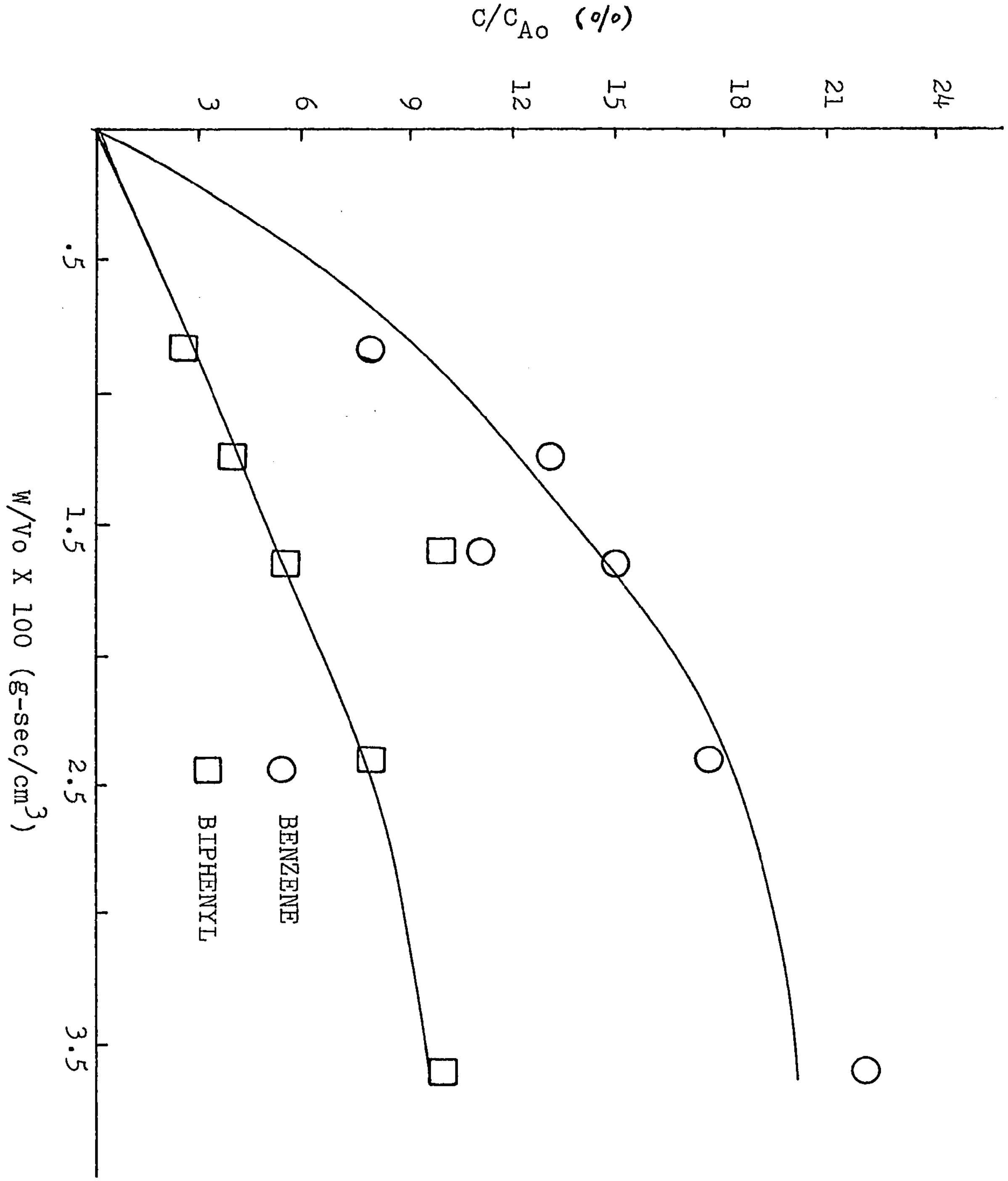


Figure 4-4 Product Distribution Plot Against Residence Time at Temperature 50°C for Reaction of Chlorobenzene with Hydrogen Over Palladium on Alumina Catalyst

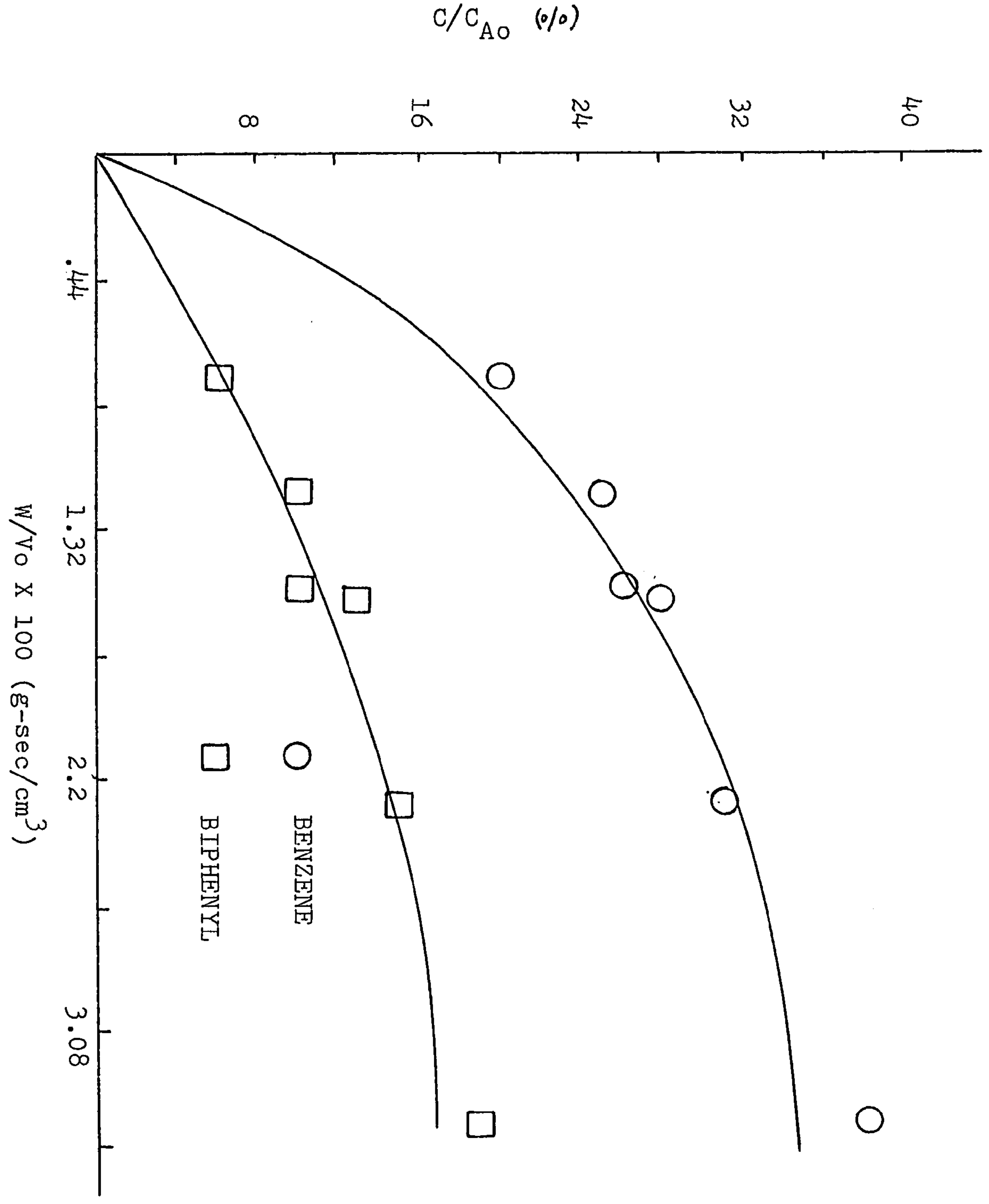


Figure 4-5 Product Distribution Plot Against Residence Time at Temperature 60°C for Reaction of Chlorobenzene with Hydrogen Over Palladium on Alumina Catalyst

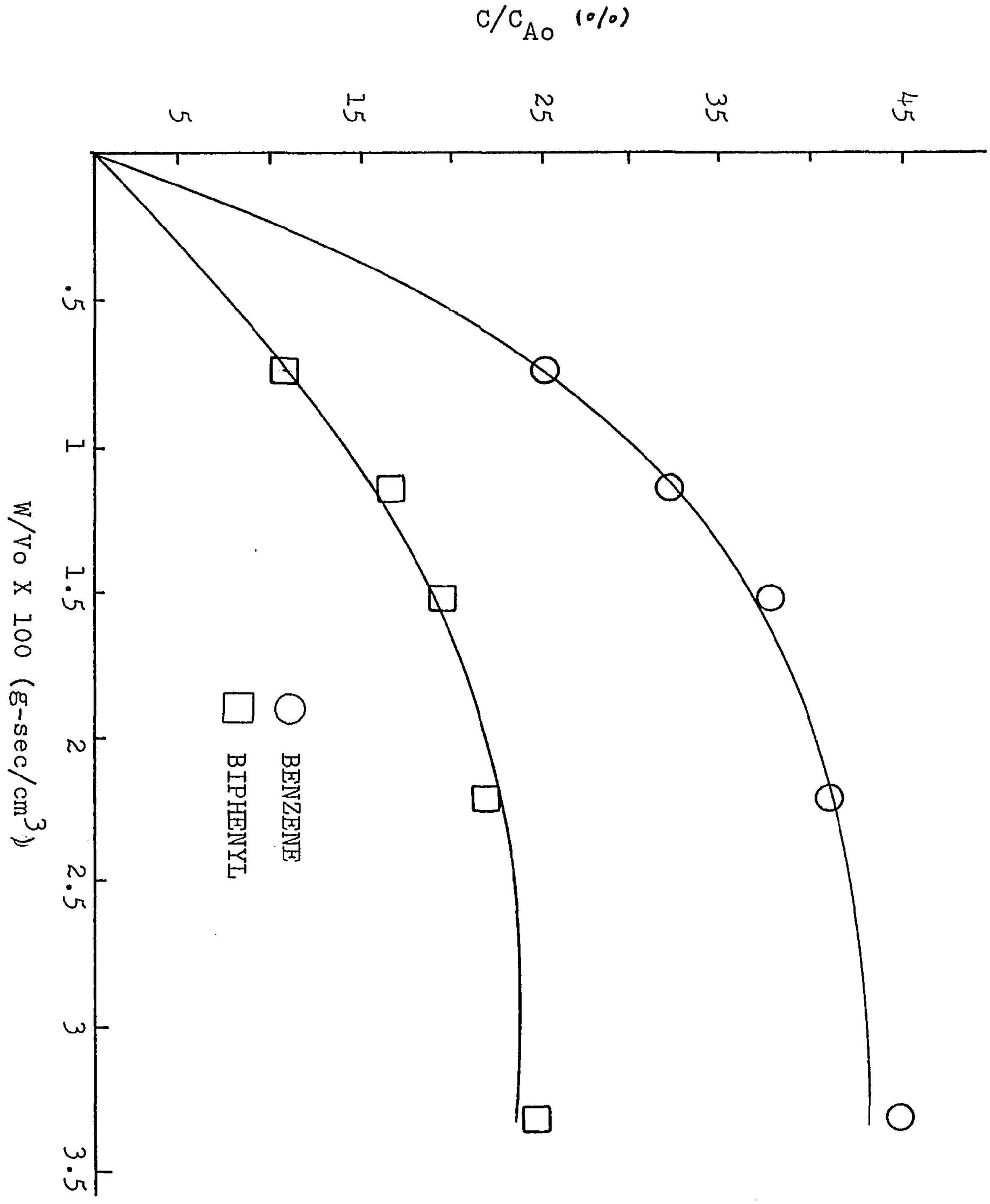
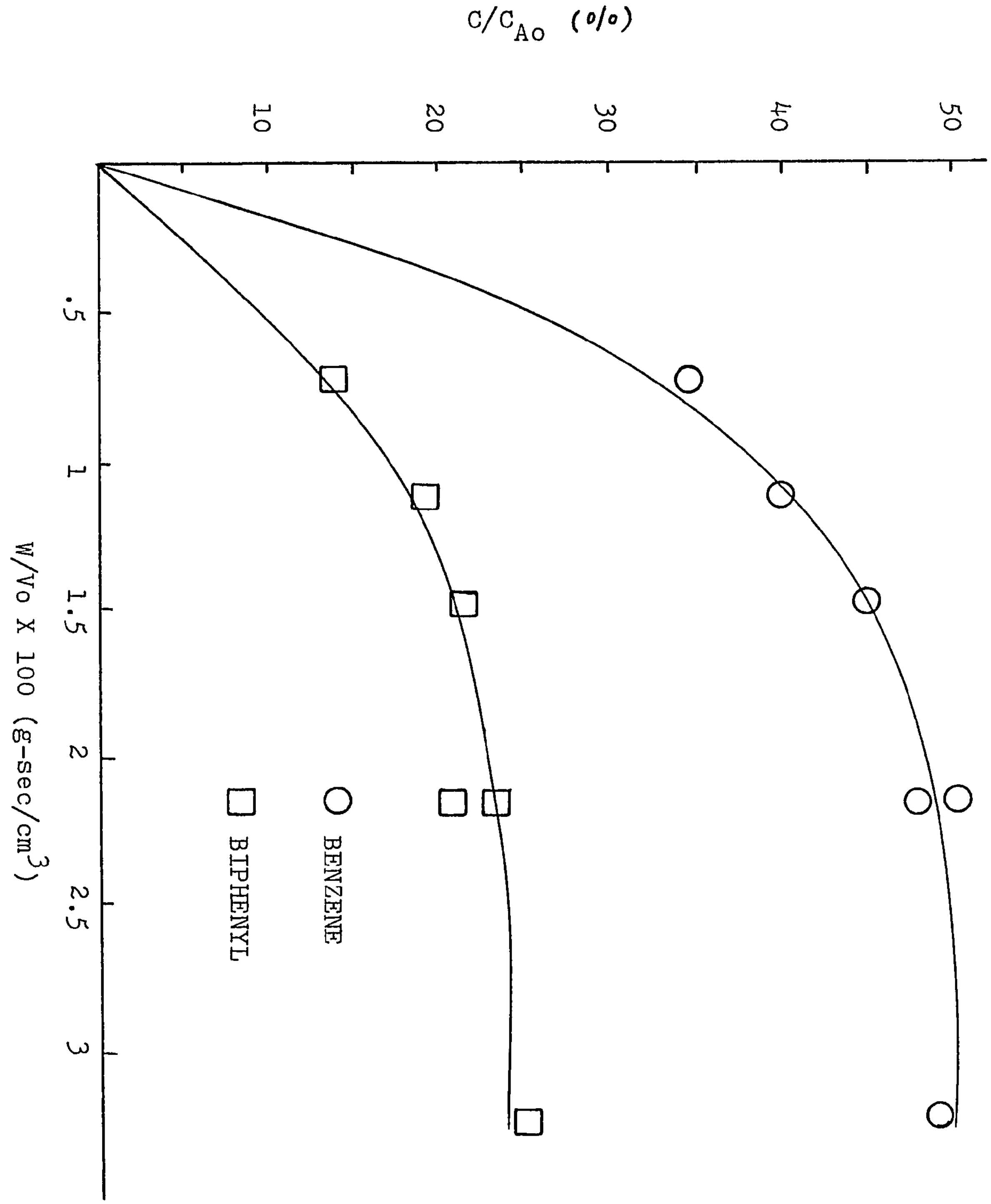


Figure 4-6 Product Distribution Plot Against Residence Time at Temperature 70°C for Reaction of Chlorobenzene with Hydrogen Over Palladium on Alumina Catalyst



$$w/F_{Ao} = \int_0^{x_A} d\ x_A/(-R_A)$$

for an integral reactor, where w is weight of catalyst, F_{Ao} is molar flow rate, x_A is fraction of conversion of reactant A, and $-R_A$ is reaction rate.

Figures 4-7 to 4-10 show the plot of ln(1/(1-X)) vs. w/v_o at 35, 50, 60 and 70°C respectively, where v_o is flow rate (cm^3/sec).

We have observed significant reaction of chlorobenzene in an atmosphere of hydrogen in the low temperature range of 35 to 70°C over palladium catalyst. The products are benzene, biphenyl; formation of which can easily be described by the free radical mechanism. The fact that the reaction occurs so readily at low temperature and low activation energy probably indicates a very stable adduct of the benzene ring system on the catalyst surface. It can not, however, be unambiguously deduced from our results only.

4-5-3 Kinetic Analysis:

We choose the following reaction sequence:

$$A \xrightarrow{k_1} R \qquad \text{(REACTION 1)}$$

$$2\ A \xrightarrow{k_2} S \qquad \text{(REACTION 2)}$$

Figure 4-7 Plot of Ln(1/(1-x)) Vs. Residence Time at Temperature 35°C

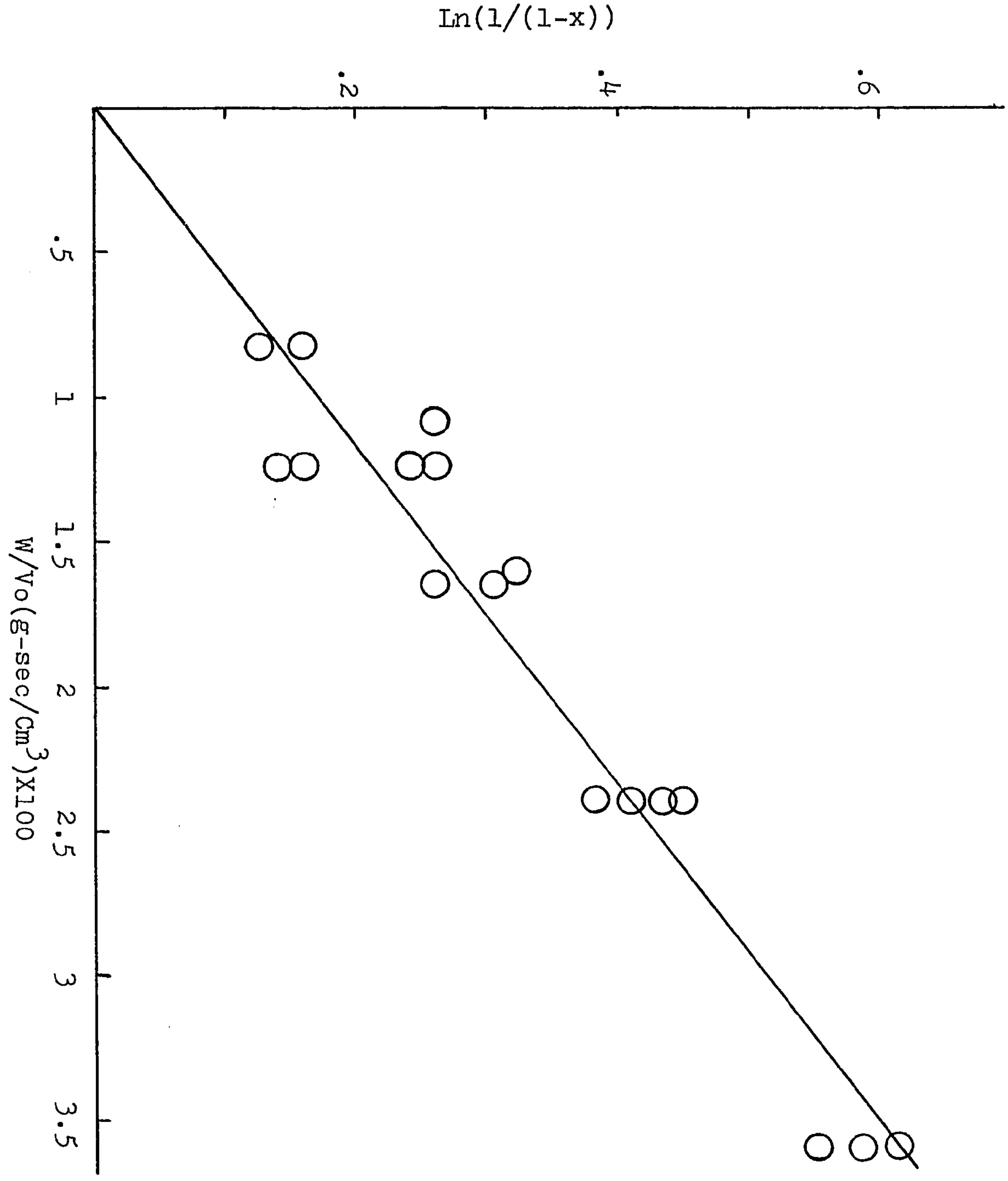


Figure 4-8 Plot of Ln(1/(1-x)) Vs. Residence Time at Temperature 50°C

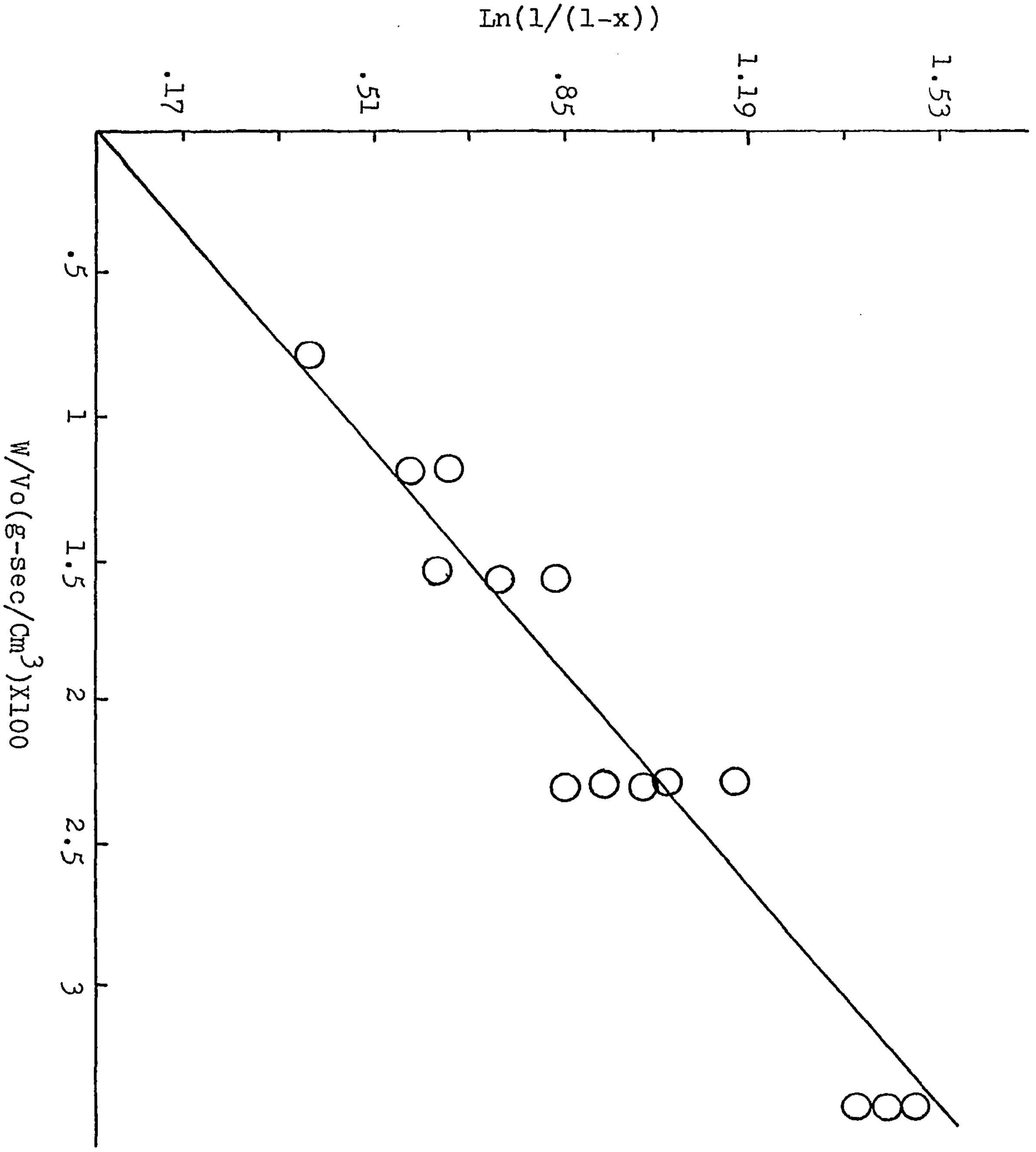


Figure 4-9 Plot of Ln(1/(1-x)) Vs. Residence Time at Temperature 60°C

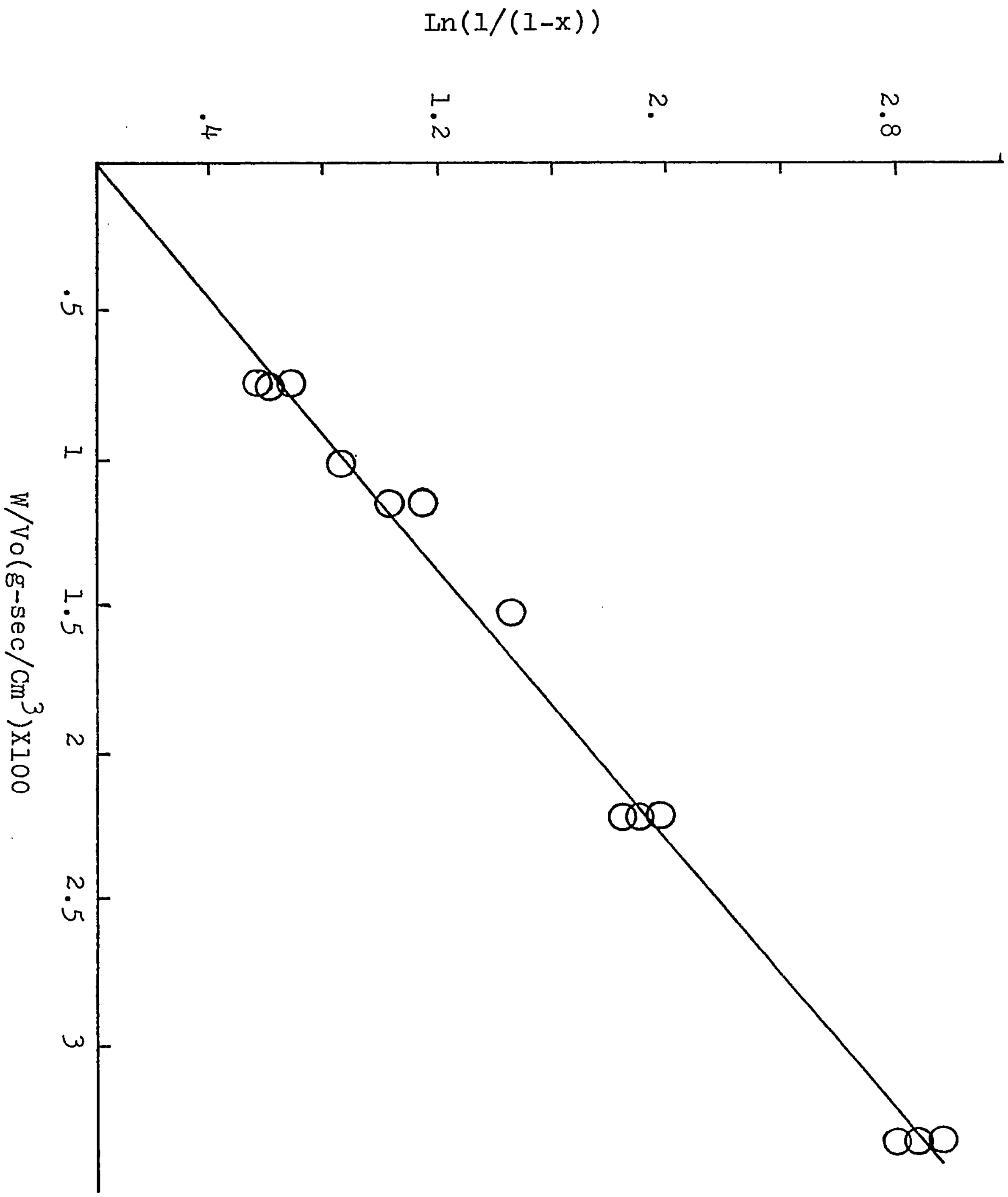
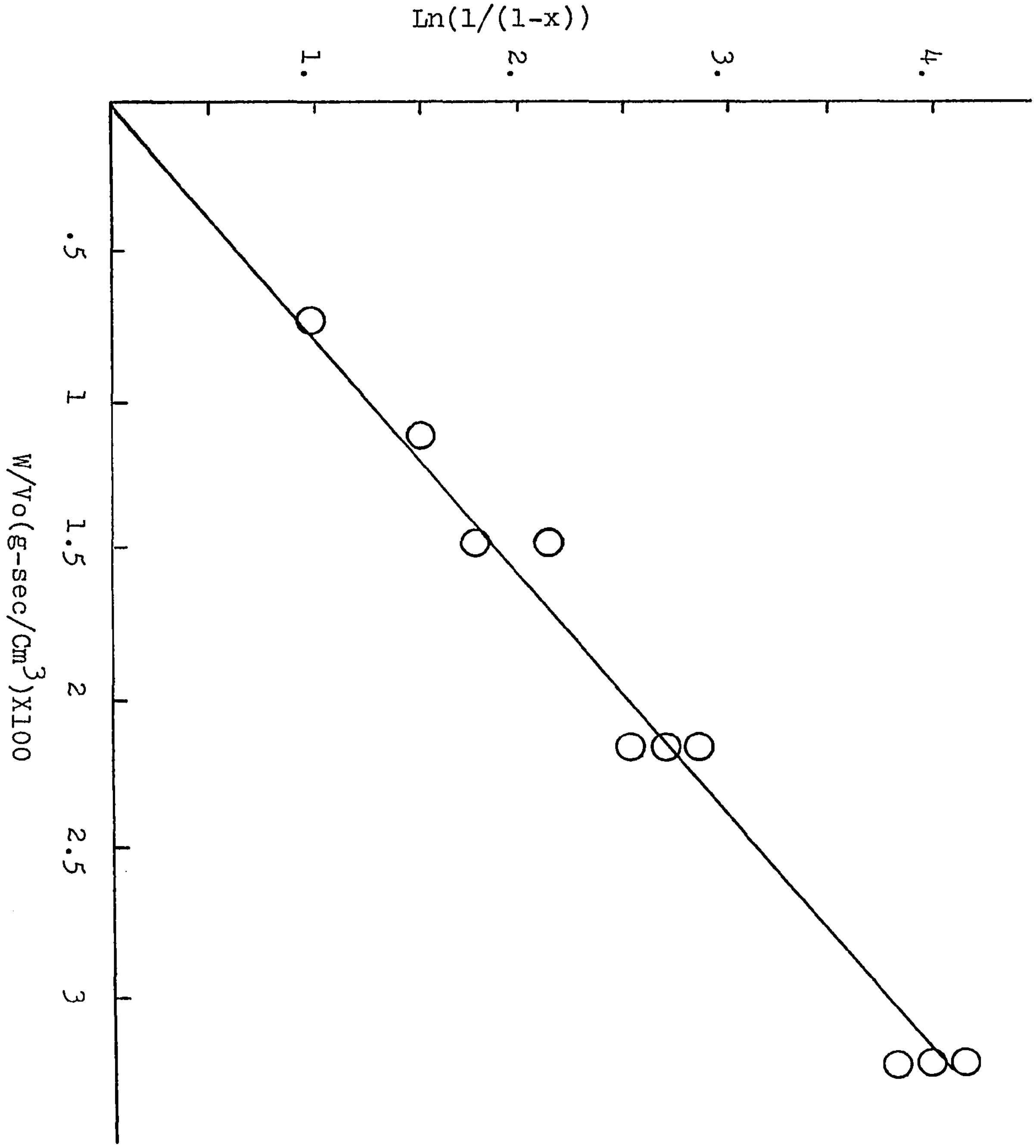


Figure 4-10 Plot of Ln(1/(1-x)) Vs. Residence Time at Temperature 70°C



where A is chlorobenzene, R represents benzene, and S is biphenyl. The relationship between benzene (R) and biphenyl (S) is (if both reactions are first order with respect to A):

$$\frac{C_R - C_{Ro}}{C_s - C_{so}} = \frac{k_1}{k_2}$$

where C_{Ro}= Initial concentration of benzene

C_{so}= Initial concentration of 4-chlorodiphenyl

All of parameters at temperature are given in Table 4-1

TABLE 4-1

Kinetic parameters for reaction of chlorobenzene with hydrogen over palladium on alumina catalyst

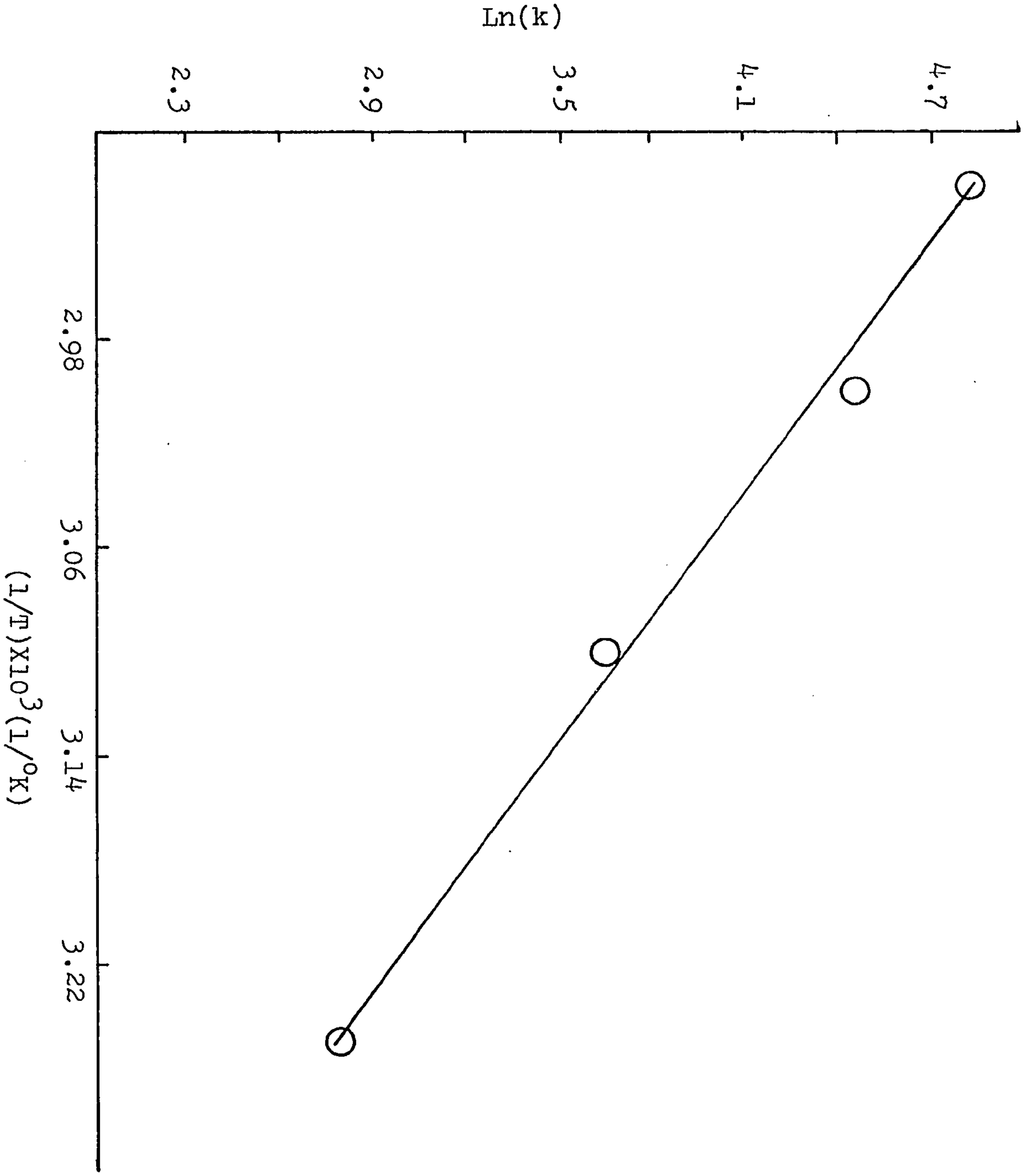
T(°C)	k(cm^3/sec-g)	k_1	k_2
35	16.5	10.9	5.58
50	38.8	25.4	13.4
60	85.7	53.7	32.1
70	124.7	85.5	39.2

Where k is total rate constant (cm^3/sec-g). K_1 and K_2 are the rate constants for reaction 1 and 2 respectively with units identical to that of the total rate constant.

Figure 4-2 shows the loss of activity with time on stream for chlorobenzene reaction with hydrogen over Pd on alumina system at 70°C. The catalyst activity is maintained for about one hour, and then it declines rapidly. The rapid decline in activity of Pd on alumina catalyst might be due to build up of high molecular weight compounds on the surface or some sintering of the active palladium.

Figure 4-11 is a plot of ln k versus reciprocal

Figure 4-11 Arrhenius' Plot for Reaction of Chlorobenzene with Hydrogen Over Pd/Al_2O_3



absolute temperature. The apparent activation energy is 13 Kcal/mole. Heavy product, biphenyl, was observed by GC in the reaction.

4-5-4 Comparison of Homogeneous Vapor Phase and Heterogeneous Catalytic Reaction

It is difficult to get rid of chlorine from chlorobenzene by thermal decomposition in the presence of hydrogen; the observed activation energy is about 61 Kcal/mole according to the experiments of Ritter and Bozzelli (1985). Contrarily, the activation energy is quite low for catalytic reaction by using palladium on Al_2O_3 or on active carbon as observed here. The use of two catalysts also has shown that we can substantially decrease the reaction temperature over that required in homogeneous vapor phase reaction.

Chapter 5 : Discussion and Summary of Four Reactions

Four reactions were studied including

Reaction 1: 1,2-dichloroethane with hydrogen over zeolite catalyst.

Reaction 2: 1,2-dichloroethane with hydrogen over palladium on alumina support.

Reaction 3: Chlorobenzene with hydrogen over palladium on alumina support.

Reaction 4: Chloroform with hydrogen over palladium on alumina support.

Palladium on alumina was used as a catalyst in reaction 2, 3, and 4 because of its effective ability for dechlorinating chlorocarbon substances in liquid phase. The effective dechlorination is quite encouraging for olefinic and aromatic , but not aliphatic chlorocarbons, in gas phase catalytic reactions over palladium catalyst. For olefinic and aromatic chlorocarbons a atable resonance intermediate (see Chapter 3) is formed which decreases the activation energy dramatically. A comparison of the activation energy between thermal non-catalytic decomposition and catalytic reaction by palladium over alumina is listed in Table 5-1.

TABLE 5-1

Activation energy comparison between thermal decomposition and catalytic reactions

Compound	type of bond	Ea-T (Kcal/mole)	Ea-C (Kcal/mole)
Chlorobenzene	C_{cb-cl}	61^*	13
1,2-Dichloroethane	C_{sp^3-cl}	33^*	15
Chloroform	C_{sp^3-cl}	$35\text{-}41^*$ 37.2^{**}	19

Where Ea-T is activation energy for thermal decomposition, Ea-C is activation energy for catalytic reactions over palladium on alumina support, * indicates data obtained from Ritter, Lee, and Mahmood for chlorobenzene, 1,2-dichloroethane, and chloroform respectively, and ** is the data from Semeluk, et. al.(1957).

Zeolite catalysts always suffer rapid deactivation due to carbonaceous deposits growing on the catalyst surface, thus the major emphasis for this first reaction is on the development of deactivation models. Data from the two models we have derived is similar, especially the activation energies. A large difference in A_o factors can be seen, however, even though the intercepts from both Arrhenius' plot are similar (ln A_o for model 1 is 19 and ln A_o for model 2 is 17 see Figure 2-14 and 2-15). Because these values are logs terms. The actual A_o vary by almost a factor of 10. As seen in Figure 2-14 and 2-15. The data appear similar and limited due to difficult in accurate measurement. The slopes could easily have been interpreted to give similar A_o factors, but we elect to fit the data mathmatically by least squates.

In general, the mechanisms of catalytic reaction for chlorocarbons by acidic catalysts, such as acidic zeolite and Al_2O_3, are of the carbonium ion type. Over palladium catalysts negatively charged ion intermediates are postulated for olefinic and aromatic chlorides, while a free radical mechanism is postulated for aliphatic chlorides.

Table 5-2 shows that elimination of chlorine from olefinics by supported transition metals have lower reaction temperatures than that required for aliphatics. It can also be found from table 5-2 that hydrodehalogenation reactions are main reactions when supported transition metal catalysts are used and that dehalogenation reactions are the main reaction when zeolite, alumina modified with alkali-metal chloride, alumina itself, or SiO_2 catalysts are used.

TABLE 5-2
Hydrodehalogenation and/or dehalogenation of some simple halocarbons (literature and this study)

Catalyst(s)	Reactants	Products	Reaction Temperature (°C)	References
Pd/c	chloroform	Methylene Chloride + H_2	100-215°C	(11)

Pd/c	Chloro-Benzene	Benzene	200	(3)
Pt/Al_2O_3	Chloroform + H_2	Methylene Chloride	166-208	(25)
Pt/Al_2O_3	$CCl_4 + H_2$	$CHCl_3$, CH_4	70-180	(42)
Pt/Al_2O_3	$CHCl_3 + H_2$	CH_2Cl_2, CH_4	150-305	(42)
Pt/Al_2O_3	$C_2H_2Cl_2$ $+H_2$	C_2H_5Cl, $C_2H_4Cl_2$	26-120	(61)
Pd/Al_2O_3	12-DCE + H_2	C_2H_5Cl, ethane Ethene	100-245	(68) (this study)
Pd/Al_2O_3	Chloro-benzene	Benzene, Biphenyl	35-70	(68) (this study)
Pt/Al_2O_3	$C_2H_2CL_2$	Ethane, C_2H_3Cl Ethyl chloride 1,2-DCE	$32^{o}C$	(15)
Chrominium	1,1-DCE	C_2H_3Cl	300	(41)
	1,2-DCE	C_2H_4, C_2H_3Cl	300	
	1,1,1-TCE	CCl_2CH_2	300	
	1,1,2-TCE	C_2H_3Cl, CCl_2CH_2	300	
		Cis- and Trans- $C_2H_2Cl_2$	300	
	1,1,2,2-TCE	Cis- and Trans- $C_2H_2Cl_2$, C_2HCl_3	300	
Li/Al_2O_3	1-Bromo-2-Methylpropane	2-Methyl Propene	80-121.5	(33)
$NaCl/Al_2O_3$			91.7-123.4	
KCl/Al_2O_3			65-100	
C_sCl/Al_2O_3			63.5-102.9	
Rh/Al_2O_3	$ClCH{=}CHCH_3$	$CH_3CH_2CH_2Cl$	100	(18)
	5-chloro-1 Hexene	$CH_3(CH_2)_3CHCLCH_3$	52	
Al_2O_3	1,2-DCE	Vinyl Chloride	300	(39)
	1,1-DCE	Vinyl Chloride	300	
	1,1,1-TCE	$CCl_2{=}CH_2$	300	
	1,1,2-TCE	$CCl_2{=}CH_2$,	300	

Ion-Exchanged Sieves 13x, 10x, 4A, 5A	1,1-DCE	$CHCl=CH_2$	300°C	(40)
SiO_2	C_2H_5Cl	-	520-600	(45)
r-Al_2O_3	"	-	370-420	(45)
$CaCl_2$	"	-	360-400	"
REX*	1,2-DCE	C_2H_3Cl, C_2H_5Cl $CHCl_2CH_3$	288	(58)
REX	$CH_2CL_2CH_3$	$CH_2=CHCl$	204	
REX	CCl_3CH_3	$CH_2=CCl_2$	163	
REX	$CH_2=CHCl$	$CH_2=CH_2$, C_2H_5Cl CH_3CHCl_2	260	
X zeolite (containing diffenent cations)	2-Chloro-Butane	1-Butene Isobutene Trans- and Cis-Butene	150-400	(24)
Palladium	C_2H_5Cl + H_2	C_2H_6	99-179	(6)
Platinum	"	"	160-206	"
Nickel	"	C_2H_6 C_2H_4	184-343	"
Palladium	Propyl Chloride + D_2	Deuteropropanes	100	(1)
Pd/c	$CH_2=CHF$ + H_2	CH_3CH_2F, CH_3CH_3	75-350	(65)
Pd/c	CH_3CH_2F + H_2	C_2H_6	100-350	"
Pd/c	$CHF=CHF$ + H_2	C_2H_6 CH_2FCH_2F	150-300	"
Pd/c	$CH_2=CF_2$ + H_2	$C_2H_6^{**}$ CH_3CHF_2	100-350	"
Pd/c	CH_3CHF_2 + H_2	$C_2H_6^{**}$	"	"
Pd/c	CH_3CF_3 + H_2	$C_2H_6^{**}$	100-400	"

*REX = Rare Earth X Catalyst

** Hydrogenolysis product is in trace amounts

1,2-DCE = 1,2-dichloroethane

1,1,2-TCE = 1,1,2-Trichloroethane

1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane

5-1 Discussion of experimental system

5-1-1 The effect of particle size and shape

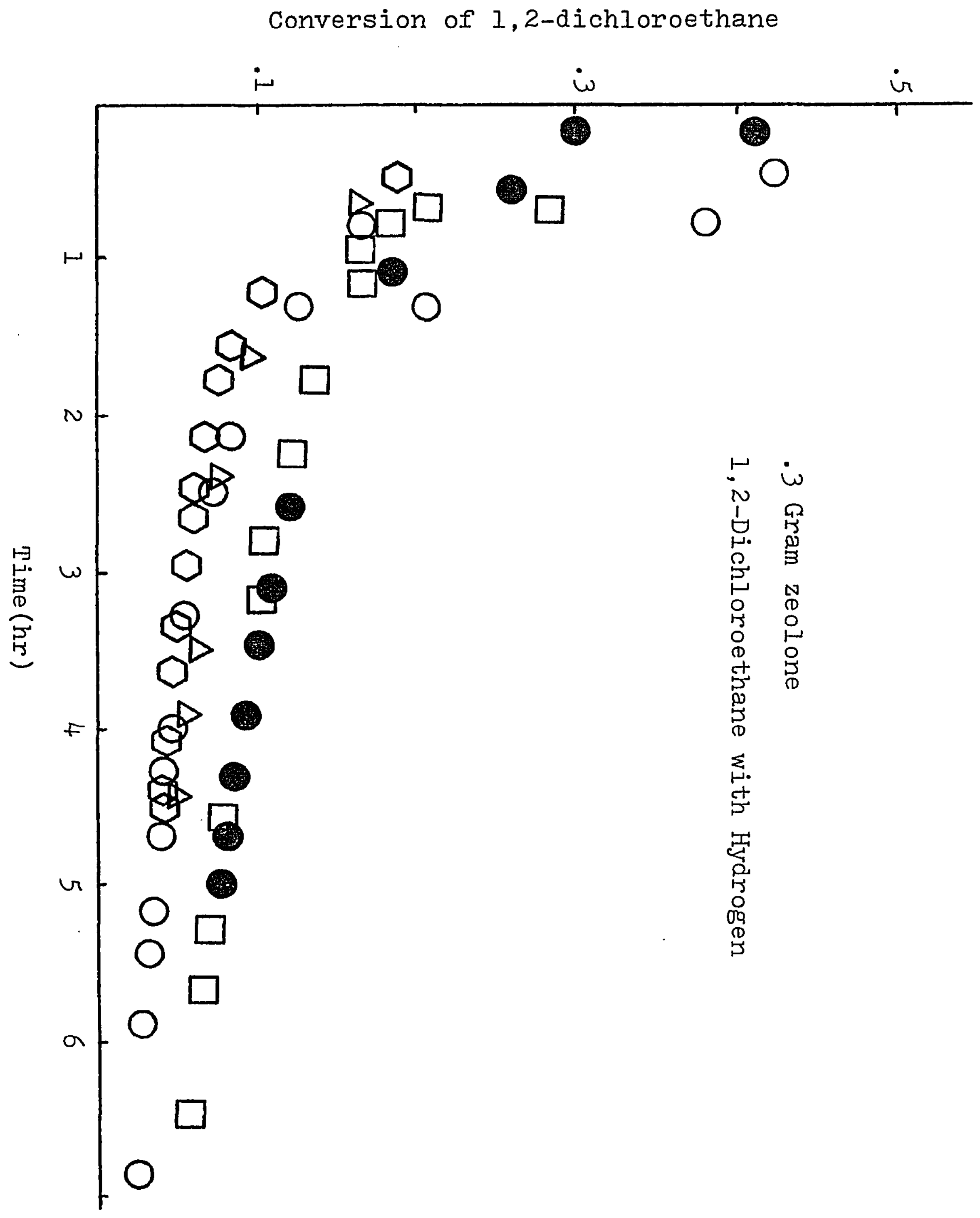
It is easy to understand, from equation 32 in Chapter 2, that the smaller the particle size, the lesser reaction is effected by internal diffusion. When catalysts are in a powder form and the volume of particles is large, pressure drop needs to be considered. This is because the whole system does not be considered to be at constant pressure.

An cylinderical shape of H-Y type of mordenite was initial used. We found that it was very difficult to obtain reproduciable data , even when we kept the reaction conditions completely constant, as shown in Figure 5-1. Finally, we decided to crush the catalysts to smaller size, and the results became consistent and remained constant throughout the four sets of experiments.

5-1-2 Purification of chloroform

Impurity, 2-3 % by weight, was routinely found in the chloroform, even though the manufacturer claimes that the purity of chloroform is 99.9 %. Distillation did not

Figure 5-1 Conversion of 1,2-Dichloroethane Vs. Time



remove the impurity, because of similar boiling points. A simple way to remove this impurity was to pass the chloroform into a column of silica gel and molecular sieve packed as a low pressure (1 atm) liquid chromatograph packed column. Chloroform from the outlet is higher than 99.9 % pure.

LIST OF SYMBOLS

a = Catalyst activity

A = Activity parameter used in equation (1)

A_s = External specific surface of particles (cm^2/g-Catal)

b = K_r/k_d

b1 = $k_d*t/2$

B = k_{do}/k_{d1}

B1 = $k_{d1}*t$

Bim = K_m*R/D_{eff}

C = Amount of carbon used in equation (1)
or = Concentration (mole/c.c)

C_{As} = Concentration of A at r = R

C_o = Reactant concentration at the outer catalyst

C_p = Heat capacity (cal/mole-K)

C_s = Concentration at surface of the catalyst

D_a = $K_w/k_m/A_s$

D_{AB} = Diffusion coefficient (cm^2/sec)

D_{eff} = Effectiveness diffusion coefficient (cm^2/sec)

D_z = Dispersion coefficient (cm^2/sec)

E = Activation energy (Kcal/mole)

f = Defined in equation (41)

k = Reaction rate constant (1/sec)

k_d = deactivation rate constant (1/hr)

k_m = Mass transfer coefficient (cm/sec)

k_r = $k_r'*(H_2)$ (1/hr)

k_r' = Defined in equation (15) (cm^3/hr-mole)

k_w = reaction rate constant (cm^3/g-catal./sec) or (cm^3/g-catal./min.)

k_{do} = Defined in equation (13) (1/hr)

k_{d1} = Defined in equation (12)' (1/hr)

L = Pore length used in equation (11)
or = Bed length (cm)

m = Deactivation order

n = Deactivation order

N_{pe} = Paclet number defined in equation (38)

r = Pore radius (cm)
or = Radial coordinate (cm)

R = Diameter of particles (cm)

R_e = Particle Reynolds number = $dp*G/\mu$

S = Site concentration available at time t

S_o = initial site concentration

S_{cf} = $\mu/\rho/D_{AB}$ = Schmidt number

t = time

T = Absolute temperature (K)

U = Superficial Velocity (cm/sec) or (cm/min)

W = Weight of catalysts (gram)

X = Conversion of reactants

$Xexp$ = Experimental conversion

$Xcal$ = Calculated conversion

z = Length coordinate (cm)

Z = Dimensionless length coordinate

θ = fraction of sites available at any time t

α = The fraction of the catalyst sites

η = effectiveness coefficient

ρ_b = Catalyst bed density ($gram/cm^3$)

Φ = (k/D_{eff})**0.5 * R

τ = Residence time (sec-g-Catal/cm^3)

μ = Viscosity (g/cm-sec)

Δ H = heat of reaction (Kcal/mole)

λ = Thermal conductivity (cal/cm-k-sec)

Φ_s = (R/3)**2 *k/D_{eff}

Appendix

Gauss Newton Nonlinear Regression Method

```
1  REM           ***************************************************
2  REM           *    GAUSS NEWTON NONLINEAR REGRESSION METHOD      *
3  REM           ***************************************************
4  REM    AC = ACTIVITY   G(I,J) IS DERIVATIVE OF F(I)
5  REM   ANPE1 IS PACLET NUMBER.   X(I) IS TIME.  Y(I) IS CONVERSION.
10  DIM L(4),M(40),GTG(40),X(40),G1(5,40),G2(40),G3(5,5),B(5),Y(40),YO(40
     ),E1(40),D1(40),G(40,5),F(50)
15  DIM L(4),M(40),GTG(40),X(40),G1(5,40),G2(40),G3(5,5),B(5),Y(40),YO(40
     ),E1(40),D1(40),G(40,5),F(50),F1(50)
16  REM
17  REM   B(I) IS PARAMETER
20 B(1) = 1.59:B(2) = 3.32:B(3) = 0.67657
25  PRINT " INITIAL TRIAL PARAMETERS ARE"
27  PRINT "B(1)=";B(1);"  B(2)=";B(2);"  B(3)=";B(3)
28  REM   N1 IS DATA POINTS
29 N1 = 26
30  FOR I = 1 TO N1
32  READ X(I): NEXT I
35  FOR I = 1 TO N1
40  READ Y(I): NEXT I
960  REM  MM = NO OF PARAMETERS
980 MM = 3
990  REM
991  REM  S4 IS DERIVATIVE OF ACTIVITY WITH RESPECT TO B(1)
992  REM    S5 IS DERIVATIVE OF ACTIVITY WITH RESPECT TO B(2)
993  REM    S1 IS DERIVATIVE OF A WITH RESPECT TO B(1)
994  REM    S2 IS DERIVATIVE OF A WITH RESPECT TO B(2)
995  REM    S3 IS DERIVATIVE OF A WITH RESPECT TO B(3)
996  REM    S6 IS DERIVATIVE OF R1 WITH RESPECT TO B(1)
997  REM    S7 IS DERIVATIVE OF R1 WITH RESPECT TO B(2)
998  REM    S8 IS DERIVATIVE OF R1 WITH RESPECT TO B(3)
1000  REM
1005 ANPE1 = 2.45:ANPE2 = 2.34:ANPE3 = 2.22
1006 ANPE1 = 2.34
1007  FOR I = 1 TO N1
1008  REM   A IS DEFINED IN CHAPTER 2, EQUATION 2-41
1009 AC =  EXP (B(2) * ( EXP ( - B(1) * X(I)) - 1))
1010 A = (1 + B(3) * AC) ^ 0.5
1012 R1 = (1 + A) ^ 2 *  EXP (ANPE1 / 2 * A) - (1 - A) ^ 2 *  EXP ( - ANP
     E1 / 2 * A)
1013 S4 = B(2) * ( - 1) * X(I) *  EXP ( - B(1) * X(I)) * AC
1014 S5 = AC * ( EXP ( - B(1) * X(I)) - 1)
1015 S1 = 0.5 / A * B(3) * S4:S2 = 0.5 / A * B(3) * S5:S3 = 0.5 / A * AC
1016 R3 = (1 + A) *  EXP (ANPE1 / 2 * A):R4 = (1 - A) *  EXP ( - ANPE1 /
     2 * A):R5 = (1 + A) * ANPE1 / 2:R6 = (1 - A) * ANPE1 / 2
1018 S6 = S1 * R3 * (2 + R5) + R4 * S1 * (2 + R6)
1020 S7 = S2 * R3 * (2 + R5) + R4 * S2 * (2 + R6)
1022 S8 = S3 * R3 * (2 + R5) + R4 * S3 * (2 + R6)
1023  REM      G(I,J) IS DERIVATIVE OF F(I)
1024 G(I,1) = 4 *  EXP (ANPE1 / 2) / Y(I) * (S1 / R1 - S6 / R1 ^ 2 * A)
1026 G(I,2) = 4 *  EXP (ANPE1 / 2) / Y(I) * (S2 / R1 - S7 / R1 ^ 2 * A)
1028 G(I,3) = 1 / Y(I) * 4 *  EXP (ANPE1 / 2) * (S3 / R1 - S8 / R1 ^ 2 *
     A)
1040  NEXT I
1050  FOR IA = 1 TO N1
```

```
1060  FOR J9 = 1 TO MM
1070 G1(J9,IA) = G(IA,J9)
1075  NEXT J9: NEXT IA
1080  FOR IB = 1 TO N1
1082 AC =  EXP (B(2) * ( EXP ( - B(1) * X(IB)) - 1))
1085 A = (1 + B(3) * AC) ^ 0.5
1087 R1 = (1 + A) ^ 2 *  EXP (ANPE1 / 2 * A) - (1 - A) ^ 2 *  EXP ( - ANP
     E1 / 2 * A)
1088 F1(IB) = 1 - 4 * A *  EXP (ANPE1 / 2) / R1
1089 F(IB) = 1 - 1 / Y(IB) + 4 * A *  EXP (ANPE1 / 2) / R1 / Y(IB)
1090 E1(IB) =  - F(IB)
1100  NEXT IB
1110  FOR JA = 1 TO MM
1120 G2(JA) = 0.
1130  FOR K3 = 1 TO N1
1140 G2(JA) = G2(JA) + G1(JA,K3) * E1(K3)
1150  NEXT K3: NEXT JA
1160  FOR IC = 1 TO MM
1170  FOR JB = 1 TO MM
1180 G3(IC,JB) = 0.
1190  FOR K4 = 1 TO N1
1200 G3(IC,JB) = G3(IC,JB) + G1(IC,K4) * G(K4,JB)
1210  NEXT K4: NEXT JB: NEXT IC
1220 I = 1
1230  FOR K5 = 1 TO MM
1240  FOR JC = 1 TO MM
1250 GTG(I) = G3(K5,JC)
1260 I = I + 1
1270  NEXT JC: NEXT K5
1280  GOSUB 5000
1290 I = 1
1300  FOR K = 1 TO MM
1310  FOR J = 1 TO MM
1320 G3(K,J) = GTG(I)
1330 I = I + 1
1340  NEXT J: NEXT K
1350  FOR I = 1 TO MM
1360  FOR J = 1 TO MM
1370 D1(I) = 0.
1380  FOR K = 1 TO MM
1390 D1(I) = D1(I) + G3(I,K) * G2(K)
1400  NEXT K: NEXT J: NEXT I
1410  FOR I = 1 TO MM
1420 B(I) = B(I) + D1(I)
1430  NEXT I
1440  PRINT B(1),B(2),B(3)
1502  FOR I = 1 TO MM
1503  IF ( ABS (D1(I)) - .000001) > 0 THEN 1510
1504  IF (I - MM) = 0 THEN 1530
1505  NEXT I
1510 O = O + 1
1520  IF (O - 50) <  = 0 THEN 1007
1530  PRINT "B(1)=";B(1);"  B(2)=";B(2);"B(3)=";B(3)
```

```
1535  FOR I = 1 TO N1
1540  PRINT "XEXP("I")=";Y(I);"  XCAL("I")=";F1(I);"  ERROR %="; - F(I)
1545  PRINT : NEXT I
1580  DATA  .0988,.2292,.2428,.372,.3883,.5147,.5481,.6769,.7111,.8189,.9
     031,1.005,1.0478,1.2008,1.2114,1.3536
1582  DATA  1.4097,1.466,1.5744,1.7347,1.9258,2.0664
1585  DATA  .18,.13,.12,.094,.087,.075,.064,.054,.057,.048,.043,.036,.039
     ,.033,.024,.028,.024,.026,.022,.021,.019,.02
1600  END
4000  REM      ***************************************************
4010  REM      *  SUBROUTINE MINV OBTAINED FROM IBM 1130          *
4020  REM      *  SCIENTIFIC SUBROUTINE PACKAGE, PROGRAMMERS      *
4030  REM      *  MANUAL                                          *
4040  REM      ***************************************************
5000 N = 3
5030 D = 1.
5035  PRINT "N=";N
5040 NK =  - N
5050  FOR K1 = 1 TO N
5060 NK = NK + N
5070 L(K1) = K1
5080 M(K1) = K1
5090 KK = NK + K1
5100 BIGA = GTG(KK)
5110  FOR J1 = K1 TO N
5130 IZ = N * (J1 - 1)
5140  FOR I1 = K1 TO N
5150 IJ = IZ + I1
5160  IF ( ABS (BIGA) -  ABS (GTG(IJ))) >  = 0 THEN 5200
5170 BIGA = GTG(IJ)
5180 L(K1) = I1
5190 M(K1) = J1
5200  IF (I1 - N) > 0 THEN 5215
5210  NEXT I1
5215  NEXT J1
5220 J2 = L(K1)
5230  IF (J2 - K1) <  = 0 THEN  GOTO 5330
5250 KI = K1 - N
5260  FOR I2 = 1 TO N
5270 KI = KI + N
5280 HOLD =  - GTG(KI)
5290 JI = KI - K1 + J2
5300 GTG(KI) = GTG(JI)
5310 GTG(JI) = HOLD
5320  NEXT I2
5330 I = M(K1)
5340  IF (I - K1) <  = 0 THEN  GOTO 5440
5360 JP = N * (I - 1)
5370  FOR J3 = 1 TO N
5380 JK = NK + J3
5390 JI = JP + J3
5400 HOLD =  - GTG(JK)
5410 GTG(JK) = GTG(JI)
5420 GTG(JI) = HOLD
5430  NEXT J3
```

```
5440  IF (BIGA) <  > 0 THEN  GOTO 5470
5450 D = 0.
5460  RETURN
5470  FOR I4 = 1 TO N
5480  IF (I4 - K1) = 0 THEN 5505
5490 IK = NK + I4
5500 GTG(IK) = GTG(IK) / ( - BIGA)
5505  NEXT I4
5510  FOR I5 = 1 TO N
5520 IK = NK + I5
5530 IJ = I5 - N
5540  FOR J5 = 1 TO N
5550 IJ = IJ + N
5570  IF (I5 - K1) = 0 THEN 5610
5580  IF (J5 - K1) = 0 THEN 5610
5590 KJ = IJ - I5 + K1
5600 GTG(IJ) = GTG(IK) * GTG(KJ) + GTG(IJ)
5610  IF (J5 - N) > 0 THEN 5615
5613  NEXT J5
5615  NEXT I5
5620 KJ = K1 - N
5630  FOR J6 = 1 TO N
5640 KJ = KJ + N
5650  IF (J6 - K1) = 0 THEN 5680
5670 GTG(KJ) = GTG(KJ) / BIGA
5680  NEXT J6
5690 D = D * BIGA
5700 GTG(KK) = 1. / BIGA
5710  NEXT K1
5720 K = N
5730 K = K - 1
5740  IF (K) <  = 0 THEN 5960
5750 I = L(K)
5760  IF (I - K) <  = 0 THEN 5850
5770 JQ = N * (K - 1)
5780 JR = N * (I - 1)
5790  FOR J7 = 1 TO N
5800 JK = JQ + J7
5810 HOLD = GTG(JK)
5820 JI = JR + J7
5830 GTG(JK) =  - GTG(JI)
5840 GTG(JI) = HOLD: NEXT J7
5850 J = M(K)
5860  IF (J - K) <  = 0 THEN 5730
5870 KI = K - N
5880  FOR I8 = 1 TO N
5890 KI = KI + N
5900 HOLD = GTG(KI)
5910 JI = KI - K + J
5920 GTG(KI) =  - GTG(JI)
```

```
5930 GTG(JI) = HOLD
5940  NEXT IB
5950  GOTO 5730
5960  RETURN
```

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