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Hydrodechlorination reactions of trichloroethylene and 1,1 1, trichloroethane over alumina supported palladium catalysts, and, trichloroethylene over nickel catalyst

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ABSTRACT

Title of Thesis : Hydrodechlorination Reactions of,
Trichloroethylene and 1,1,1 Trichloroethane on Alumina Supported
Palladium catalysts and Trichloroethylene on Nickel Catalysts

Atul R. Shah, Master of Science, 1987

Thesis Directed by: Dr. Joseph W. Bozzelli
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N. J. I. T.

The primary objective of this study was to evaluate the viability for conversion of chlorocarbon wastes solvents into useful hydrocarbons and HCl by catalytic reduction. The second objective was to investigate the pathways for these hydrodechlorination reactions over the chosen alumina supported Palladium and nickel catalysts, as well as determine selectivities, product distribution, and deactivation mechanism.

Reactions of trichloroethylene with hydrogen over alumina supported palladium catalyst was studied in temperature range 40°C to 57°C at one atmosphere total pressure. The major products observed were ethane and (cis) 1,2 dichloroethylene with trace products chloroethylene, chloroethane and (trans) 1,2 dichloroethylene. At the increased temperature, increased conversion to useful hydrocarbon ethane with decrease in conversion to lower

chlorine content hydrocarbons was observed. The activity of catalyst decreased 40 % after one hour of reaction. The activation energy was found to be 12.1 kcal/mole for hydrodechlorination of trichloroethylene.

Hydrodechlorination of 1,1,1 trichloroethane with hydrogen over alumina supported palladium catalyst was studied in temperature range of 57°C to 77°C at one atmosphere total pressure. A free radical mechanism involving formation of three intermediate and concerted addition of hydrogen to the intermediate was proposed as the mechanism for the formation of ethane as a terminal product. The activation energy was found to be 12.75 kcal/mole for reactions of 1,1,1 trichloroethane with hydrogen.

Hydrodechlorination of trichloroethylene with hydrogen over nickel catalyst was studied in the temperature range of 165 to 189°C at one atmosphere total pressure. Higher conversion (95 %) to low molecular weight hydrocarbons methane, ethylene, ethane and propyne was observed along with traces of chloroethane. In the temperature range studied, selectivity is 65 % to ethane and at higher temperatures, increased conversion to methane was observed. The activation energy was found to be 7 kcal/mole for hydrodechlorination over nickel catalysts.

HYDRODECHLORINATION REACTIONS OF TRICHLOROETHYLENE AND 1,1,1 TRICHLOROETHANE OVER ALUMINA SUPPORTED PALLADIUM CATALYSTS, AND, TRICHLOROETHYLENE OVER NICKEL CATALYST

by

Atul R. Shah

Thesis Submitted to the Faculty of Graduate School of the
New Jersey Institute Of Technology
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degree of Master of Science - Chemical Engineering
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APPROVAL SHEET

Title of Thesis : Hydrodechlorination Reactions of Trichloroethylene and 1,1,1 Trichloroethane over Alumina Supported Palladium Catalysts and Trichloroethylene over Nickel Catalysts

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For love and inspiration I shall be eternally grateful to my parents.

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Chapter - 1 Catalytic Hydrodechlorination Reactions

1.1 Introduction:

Chlorinated hydrocarbons have been extensively used in industries either as raw material for production of other chemicals, such as chlorobenzene, nitrochlorobenzene or as a solvents, such as trichloroethylene and 1,1,1 trichloroethane, for cleaning metal parts; these processes in turn produce significant amount of chlorinated hydrocarbon wastes especially the solvent use where there is no end product for the chemical. The disposal of these chlorinated hydrocarbon wastes has generated much interest in recent years since these chlorinated compounds are often carcinogenic<8> and disposal requires compliance with TSCA and RCRA environmental laws. The possible treatment of such hazardous waste to more environmentally acceptable useful hydrocarbons, thus make possible reutilize the bulk of the material appears desirable.

Environmentalists and environmental engineers are still searching for alternate solutions to waste disposal problems<29>. One popular current method of disposal that has been extensively used is storage in land fills for toxic wastes. Land filling is now receiving strong opposition due to possible future contamination of ground water from seepage of toxic waste material. Several alternate techniques are under development to solve this growing problem of disposal, such as incineration, biodegradation, hydrodechlorination<11>, where toxic materials are completely destroyed or converted into environmentally safe products.

At present, incineration at high temperature in the presence of excess oxygen has become one viable economical method for complete destruction of wastes in to CO_2 and H_2O<22>. However, incinerators produce trace amounts of several undesirable and thermally stable combustion products, such as partially oxygenated carbon-chlorides (Dioxins) and chlorinated oxides. These end products are sometimes more toxic than the starting material. If the incinerator is not operated at near optimum conditions, considerable amounts of these highly toxic products can be produced.

Thermal reactions of chlorinated hydrocarbons in hydrogen atmosphere can be used as an alternative conversion route to oxygen rich incineration<5,29>. One advantage of thermal hydrodechlorination over the oxygen rich incineration is, the production of potentially useful hydrocarbons and the stable chlorinated compound HCl which can be easily be either neutralized or recycled. The major disadvantage of thermal hydrodechlorination is that complete conversion requires reaction temperature in the order of 1000-1200°C, and hence is energy intensive. Consequently, it can not be applied to large volume of low concentration effluent streams from an economic point of view.

Non thermal methods such as biological treatments using microbes have been developed which can decompose many hazardous chemicals including PCB and pentachlorophenol. The disadvantage in this case is the very slow rate of biodegradation reaction. Catalytic hydrodechlorination of chlorinated wastes in a hydrogen atmosphere has been shown as a promising alternative to thermal reaction in case of low concentration effluent streams<10,26,33,36>. The use of a catalyst enables one to carry out the reactions at significantly lower temperature than that required for thermal reductions. In addition to use of lower concentrations of reactant hydrogen, the use of hydrogen rich environment favors the formation of HCl, useful hydrocarbons and less chlorinated hydrocarbons. HCl produced can easily be neutralized or scrubbed and hydrocarbons produced can be used as a chemical feed stock, fuel, or recycled.

The objective of the current study is to examine the catalytic hydrodechlorination reactions of trichloroethylene and 1,1,1 trichloroethane over alumina supported palladium and NiO catalysts. It is hoped that this study will yield information on selectivity, reactivity, and deactivation characteristics of the catalyst for hydrodechlorination reactions. The kinetic parameter and product distribution data will, in addition, provide information on the choice of catalysts, desired operating temperatures, and rate of reaction.

1.2 Literature Survey:

Halocarbons are hazardous and toxic in nature and removal of halogen is necessary to convert them into less toxic species. Three different research techniques have been employed to convert this toxic wastes into useful fuels and also to recover halocarbons of lower halogen content, they are (1) Hydrogenation

(2) Dehydrohalogenation

(3) Hydrodehalogenation.

Hydrogenation of chloromethanes has been studied by Barneveld and Ponec (1984) on evaporated metal film of Ni, Co, Cu, Fe, Rh, Pd and some alloys Ni-Cu, Ni-Pd. They observed that metals active in Fischer-Tropsch synthesis produce higher hydrocarbons both in absence and in presence of CO. They observed reactions of chloromethanes at $483^{\circ}K$ and 110 kPa total pressure over Ni, Cu and Co metal films. Copper catalyst converts small part of CH_2Cl_2 into methane and a reaction of CH_3Cl into methane was observed for Ni and Co. Witt et al. (1981) studied heterogeneous catalytic hydrogenolysis of six flourocarbons, $CH_2=CHF$, CH_3CH_2F, $CHF=CHF$, $CH_2=CF_2$, CH_3CHF_2, and CH_3CF_3 over carbon supported palladium surfaces. They found that C-F hydrogenolysis took place more readily for one F atom attached to one carbon atom and more difficult for two or more F attached to one carbon atom. The apparent activation energy values range from 12 kcal/mole for CH_3CH_2F to 26 kcal/mole for CH_3CHF_2, and CH_3CF_3.

G. Ham and W. Coker (1964) studied the hydrogenation of 1,3-dichloropropene over Rh, Pd, Pt, and Platinum oxide. The major products using Pd, Pt and Platinum oxides were propene and hydrogen chloride where as Rh showed higher yields of 1,3-dichloropropene and propyl chloride. Rhodium on alumina catalysts is a superior catalyst for the hydrogenation of a vinylic or allylic halogen substituted olefins to haloalkanes, but under hydrogenation conditions used, hydrogenolysis of the chloroalkanes did not occur. The yield of chloroalkanes, as well as the rate of hydrogenation, was affected by the catalyst support. Horner, Schlater and Kamerer (1959) found that when using Raney Ni in alkali methanol (liquid phase), primary and sec-monochlorides didn't react, but that vinylic or allylic chloride would undergo hydrogenolysis as the double bond was reduced. Alkyl bromides or iodides underwent hydrogenolysis as compared to none for chlorides. The ease of reaction order for dehalogenation, RX to RH, is RI > RBr > RCl.

Baltzly and Phillips (1946) studied dehalogenation of halogen substituted compound over Pd on charcoal. They found that saturated aliphatic bromides, such as, isobutyl bromide, t-butyl bromide, and cyclohexyl bromide, did not undergo hydrogenolysis but aromatic halides, such as bromobenzene, allyl chloride, and benzyl chloride, were, however, readily dehalogenated. Kindler et al. (1953) studied the selective hydrogenation of the double bond in 2-allyl-4-

chlorophenol over palladium catalyst. Dehalogenation of the starting material or product was major side reaction. They found that solvent affected the yield of chloride ion. The following chloride ion yields were reported: methanol, 6.2%; ethanol, 8.6%, isopropyl alcohol, 3.6%; benzene, 0%; cyclohexane, 0%.

Lacher and co-workers (1956) carried out hydrogenation and hydrogenolysis of various C_1-C_3 fluorocarbons on palladium on carbon catalyst. The major fidings are: (i) The lower members of a homologus series are more difficult to hydrogenate than the members of higher molecular weight. (ii) The hydrogenolysis of the C-Cl bonds occur more readily than the hydrogenation of the C=C bonds, which in turn is more easily accomplished than the hydrogenolysis of the C-F bonds. (iii) The relative inertness of the C-F bonds persists in fluoroolefins as well as in fluorochloro-olefins.

Besprozvannyi, Kononov, and Kharlamov (1965) investigated carbon tetrachloride hydrogenation in n-heptane solvent in the pressure range of 4 to 20 atm and a temperature range 80 to 110°C over 0.04 wt% palladium on pumice. Mechanisms involving the formation of both hydrogen and chloroform radicals were proposed to account for the formation of both $CHCl_3$ and C_2Cl_6.

I. Mochida, Y. Yoneda (1968) have studied elimination reaction of HCl from 1,1,2-Trichloroethane on solid bases, solid acids, and alumina. They found elimination reaction proceeded with different selectivity on solid bases, solid acids, and alumina. The product distributions were 1,1-dichloroethylene > trans-1,2-dichloroethylene > cis-1,2-dichloroethylene on solid bases, and cis > trans > 1,1 on solid acids, and cis > 1,1 > trans on alumina. They also studied elimination reaction of 1,1,2-trichloroethane on ion exchanged molecular sieves and found that it has higher catalytic activity and the molecular sieve with a higher 1,1-dichloroethylene to 1,2-dichloroethylene ratio had a higher trans/cis ratio.

A. Lycourghiotis and N. Katsanos (1975) have studied the dehydrohalogenation of 1-bromo,2-methyl propane over alumina modified with alkali metal chlorides. The main product of the reaction was 2-methyl propene. Small amounts of water adsorbed on the catalyst surface increased its activity. Mochida et al., also studied the same reaction on ion exchanged molecular sieve and found that they have higher catalytic activities.

P. Venuto, E. Givens and coworker (1966) have studied dehydrohalogenation of two carbon haloalkanes in the temperature range of 65-370°C over a rare earth X Zeolite catalyst. They observed , the following order of decreasing temperature for appreciable reaction is: CH_2Cl-CH_2Cl > C_2H_5Cl > $CHCl_2CH_3$ > CCl_3-CH_3.

H. Noller and coworker (1965) studied HCl elimination reaction from 2,3-dichlorobutane on $CaCl_2$, CaO and Al_2O_3 in temperature range from 150-370°C using microcatalytic or pulse technique. The observed products were cis- and trans-2-chloro-2-butene, 2-chloro-1-butene, 1,3-butadiene, 1-butyne, and 2-butyne.

Thermal hydrodechlorination of chloroform and trichloroethylene with hydrogen in the temperature range 550 to 1000^oC using tubular flow reactor were studied by Burhan et. al. (1985). No chlorinated hydrocarbons, products or reactants, were observed above 850^oC. The major products at this temperature were C_2H_2, C_2H_4, CH_4, HCl, and benzene. The activation energy were 35.3 and 35.0 kcal/mole in gas phase for conversion of chloroform and trichloroform respectively. In the study of hydrodechlorination on aliphatic chlorides, Yang and Bozzelli (1986) studied the reaction of 1,2 dichloroethane, with hydrogen over H-Y mordenite zeolite, in the temperature range 350^oC to 450^oC and found the major product vinyl chloride and that catalyst suffered severe deactivation. They also studied reactions of 1,2 dichloroethane, chlorobenzene, chloroform with hydrogen over alumina supported palladium catalyst, which did not deactivate severely.

Dodsan and Rase (1978) studied the hydrodechlorination of chloroform over three catalysts namely: Pd on charcoal, Pt-Re/Al_2O_3 and Pt/Al_2O_3 in the temperature range 100 to 300^oC. At 188^oC ,1 atm pressure and 3:1 H_2:$CHCl_3$ mole ratio, selectivity to methylene chloride for Pd/carbon, Pt/Al_2O_3, and Pt-Re/Al_2O_3 are 75 %, 90%, and 100 % respectively. They found that Palladium deactivated rapidly and Pt/Al_2O_3 was the most active catalyst. A. Weiss and K. Krieger (1971) conducted a detailed study on the mechanism and chemistry of dichloroethylene with hydrogen reaction over 0.5% Pt on alumina catalyst. They showed that both dichloroethylene and vinyl chloride are simultaneously hydrogenated and hydrodechlorinated to give dichloroethane, chloroethane and ethane as terminal products in which vinyl chloride is produced as intermediate. Hickok (1957) reacted methylene chloride and molecular hydrogen over palladium in a flow system in temperature range 80-395^oC. At low temperatures 170^oC the hydrogenation products observed were methyl chloride and methane. Methyl chloride was present in large quantities. At 287^oC, methane appeared in large quantities.

Improved selectivity and activity of the hydrodechlorination reaction of chloroform on specially treated Pt/Al_2O_3 was observed by C. Noelke and H. Rase (1979). They found that in a temperature range of 166-208^oC and one atmospheric pressure, $CHCl_3$ is readily converted to methylene chloride with good selectivity.

Chapter-2 Hydrodechlorination of Trichloroethylene and 1,1,1 Trichloroethane over Pd/Al_2O_3 catalyst.

2-1. INTRODUCTION:

Transition metals are commonly placed on a variety of supports such as: SiO_2, Al_2O_3<31>. This is done not only to disperse the metal component, thereby increasing the number of surface metal sites available for catalysis, but also to stabilize these small metal crystallites after they are formed. A catalysts ability for hydrogenation reaction depends on amount of hydrogen adsorbed on surface. Graham (1868) observed that Pd adsorbs 930 times its own volume of hydrogen at room temperature and the active surface complex of hydrogen adsorbed contains atomic hydrogen. The work of Y. Yang and J. Bozzelli (1986) on hydrodechlorination reaction using Pd/Al_2O_3 suggest that reaction can be carried out at significantly lower temperature with higher selectivity to non chloro-hydrocarbon products. In this study we used alumina supported palladium catalyst in order to better understand reactivity and selectivity for hydrodechlorination reactions of trichloroethylene and 1,1,1 trichloroethane.

2-2. Literature Survey:

2.2.1 Pd/Al_2O_3 catalyst:

The work of Vannice et al. (1975) on catalytic synthesis of hydrocarbons from H_2/CO mixtures over group VIII metals suggests that increasing the acidity of support for Pd catalyst results in an increase in methane turnover number. They observed, Pd catalyst activity depended on the acidity of the support chosen i.e. more acidic the support the higher the specific activity for methanation reaction. They compared SiO_2 support with Al_2O_3 support and observed increased methanation reaction with alumina catalyst. G. C. Bond and P. B. Wells (1962) studied the hydrogenation reaction of unsaturated hydrocarbons over Pd, Rh, Ni, Pt, Fe supported catalyst. They observed a selectivity of unity for ethylene hydrogenation over Pd/Al_2O_3 catalyst. Palladium is characterized by its ability to catalyze very efficiently the processes of olefin exchange and isomerization while giving absolutely minimal hydrogen exchange.

Z. Czarny and J. Oszczudlowski (1984) have studied dehydrochlorination of 1,2 dichloroethane over different catalytic surfaces. They observed that activity and selectivity of alumina/metal chloride and silica gel/metal chloride or oxide catalysts depended on the donor-acceptor properties of their surfaces. The stronger the acceptor properties the more active the catalyst for dehydrochlorination reaction. They found alumina to be the most active catalyst for dehydrochlorination of 1,2 dichloroethane.

2.2.2 Hydrodechlorination Reaction:

Some aliphatic and olefinic chlorides have been hydrodehalogenated by various methods to produce lower Cl content compounds. Yang and Bozzelli (1986) studied reaction of 1,2 dichloroethane with hydrogen over palladium on alumina catalyst in the temperature range 100 to 245 °C. They proposed free radical mechanism to interpret formation of ethane, ethene and ethyl chloride. It was interesting to note that with increase in temperature, conversion for ethane and ethene increased while it decreased for ethyl chloride. The activation energy they observed was 15 kcal/mole. They reported a decrease in catalytic activity after one hour of reaction time and after 13.5 hours of regeneration at 245°C temperature in hydrogen atmosphere, only 68 % of the original activity was recovered.

Yang and Bozzelli also reported reaction of chloroform with hydrogen over the above Pd/Al_2O_3 catalyst in temperature range 60 to 150°C. A Free radical mechanism was again proposed for formation of methylene chloride and methane. The activation energy obtained was 19 kcal/mole.

In another study Yang and Bozzelli studied hydrodechlorination of the aromatic hydrocarbon chlorobenzene with hydrogen over the Pd/Al_2O_3 catalyst in remarkably low temperature range 35 to 70°C. An adsorbed resonance mechanism was proposed for the formation of major products benzene, biphenyl and HCl. The observed activation energy was 13 kcal/mole.

Chen and Bozzelli (1987) studied reaction of trichloroethylene with hydrogen over Rh/SiO_2 catalyst in temperature range 90 to 130°C. The major products were methane, ethylene, ethane, dichloroethylene, dichloroethane with the observed the activation energy of 13 kcal/mole. They also reported reaction of 1,2 dichloroethane over Rh/SiO_2 catalyst. The major products were methane, ethylene, ethane, and chloroethane. At increased temperature increased selectivity was observed for ethane. Total fractional conversion decreased from 40 % to 10 % after 3 hrs on stream for reaction of 1,2-dichloroethane over Rh/SiO_2 catalysts.

2-3. EXPERIMENTAL

2.3.1 Apparatus And Procedure:

A schematic diagram of the apparatus used is as shown in the Fig. 2-1. Two impingers connected in series and kept in ice bath at 0^oC were used to insure the saturation of reagent vapor. Saturated vapors of trichloroethylene and 1,1,1 trichloroethane were carried by hydrogen gas which was also used as a reagent. Hydrogen flow was monitored by a gas Rotameter. The reactor incorporated a 3 mm length of Pd/Al_2O_3 catalyst ,obtained from Strem Chemicals, in a 7 mm ID by 38 cm in length Pyrex glass tube that extended in a single zone electric furnace oven, 21 cm long. Teflon tubing connection were used before and after the reactor and were heated to avoid condensation of reactant which may have high boiling points. The catalyst is in the form of powder (surface area 95-115 m^2/gm). 0.1 gram of catalyst was used for each experimental run and the catalyst bed 3 mm in length is supported on either side by 5 mm thick glass wool plugs. The catalysts were reduced in the hydrogen atmosphere for two hours at 360^oC and then cooled to the reaction temperature in the hydrogen atmosphere prior to experiment. Thermocouples (chromel-alumel) were used to measure the temperature at the catalyst bed.

Sampling of the reaction products was carried out with a six port sampling valve shown in Fig. 2-2. In "Load" position, sample is collected in 0.5 ml sampling loop by

Fig. 2-1

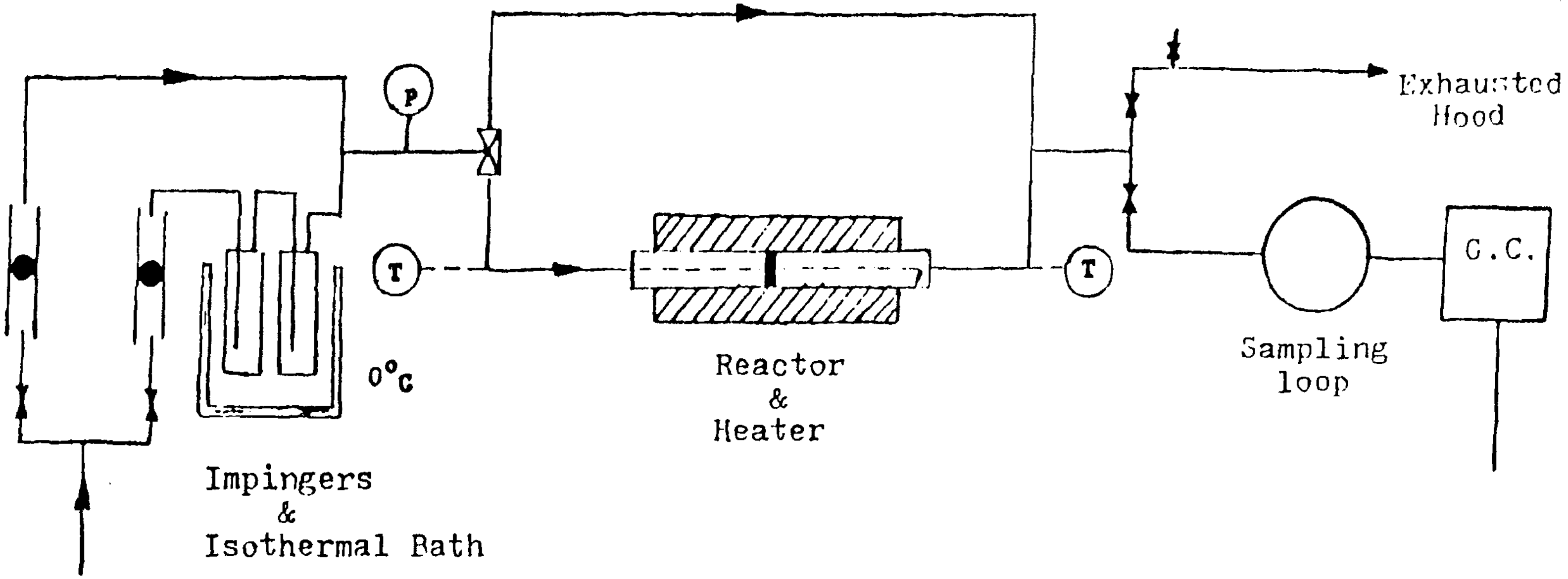
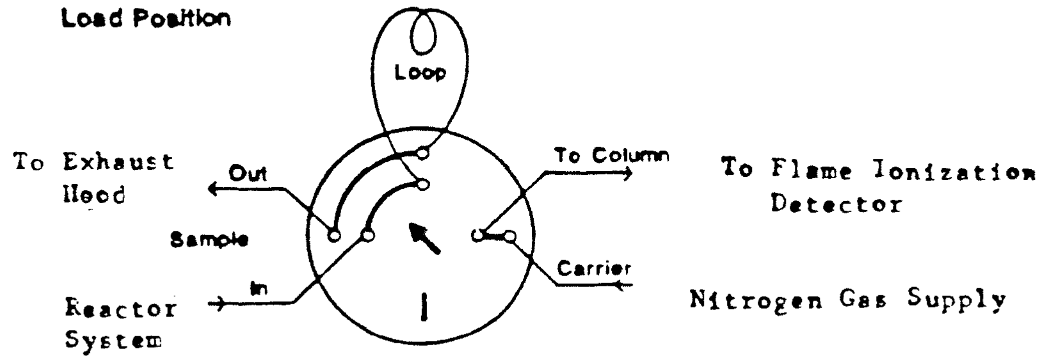


Figure Schematic Diagram of Reactor System



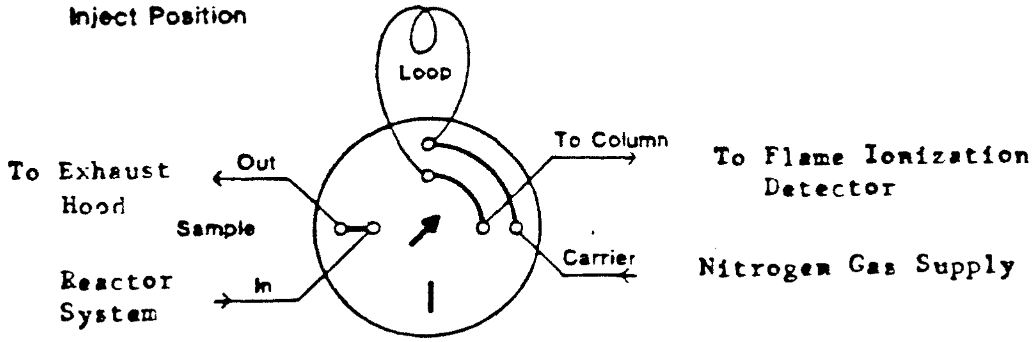


Fig. 2-2 Six Port Sampling Valve Configuration

applying vacuum with loop pressure always one atmosphere and is then carried by nitrogen GC carrier gas to chromatographic column in "Inject" position.

The hydrodechlorination reaction is extremely exothermic and to avoid temperature gradients in either the reactor or catalyst bed, all the experimental runs were limited to conversions in the range 0 to 10 % .

2.3.2 PRODUCT ANALYSIS

The reactor effluent was analyzed through an online Varian 1200 model gas chromatograph equipped with flame ionization detector and 1/8 inche O.D. by 3.6 meter long column packed with Poropak Q (60-80 mesh). The hydrogen and air flow rate to FID were 30 cm^3/min and 250 cm^3/min respectively. Nitrogen was used as GC carrier gas, at a flow rate of 25 ml/min. The temperature program used , to effect good separation, was 50°C to 190°C at a programming rate of 12°C/min. Chromatographic analysis were based on calibrations using known chemical standards of trichloroethylene, chloroethylene, chloroethane, (cis) and (trans) 1,2-dichloroethylene, and standard gas mixtures of ethane, 16.81, acetylene, 15.13, propylene, 16.82, N-butane, 16.32, ethylene, 16.82, propane, 16.81, propyne, 16.81, and methane, 16.37 ppm by volume obtained from Scott Speciality Gases. But the column was unable to effect separation of acetylene and ethylene. A Varian 4270 model integrator/recorder was connected to GC to facilitate quantitative analysis of the reactor effluent. A GC/MS spectrometer was used to confirm the identification of the products. The equipment used was a Carlo Erba Strumentizione Fractovap 4160 series GC interfaced with a Kratos MS 25 double focus magnetic sector Mass Spectrometer and used an OV 101 capillary column, 30 meter x 0.22 mm ID.

2.3.3 MATERIALS

Catalyst - Pd(0.5 %) on Alumina was obtained from Strem Chemical , Newburyport, MA 01950. Catalog # 46-1930

Gases- Hydrogen and Nitrogen obtained from Liquid Carbonic, Chicago, IL. were of commercial grade.

Reagent- Both Trichloroethylene (99.9 %) and 1,1,1 Trichloroethane (98 %) pure were obtained from Fisher Scientific Company, Fair Lawn, NJ.

2-4 Results And Discussion:

2.4.1. Trichloroethylene/ H_2 / Pd/Al_2O_3

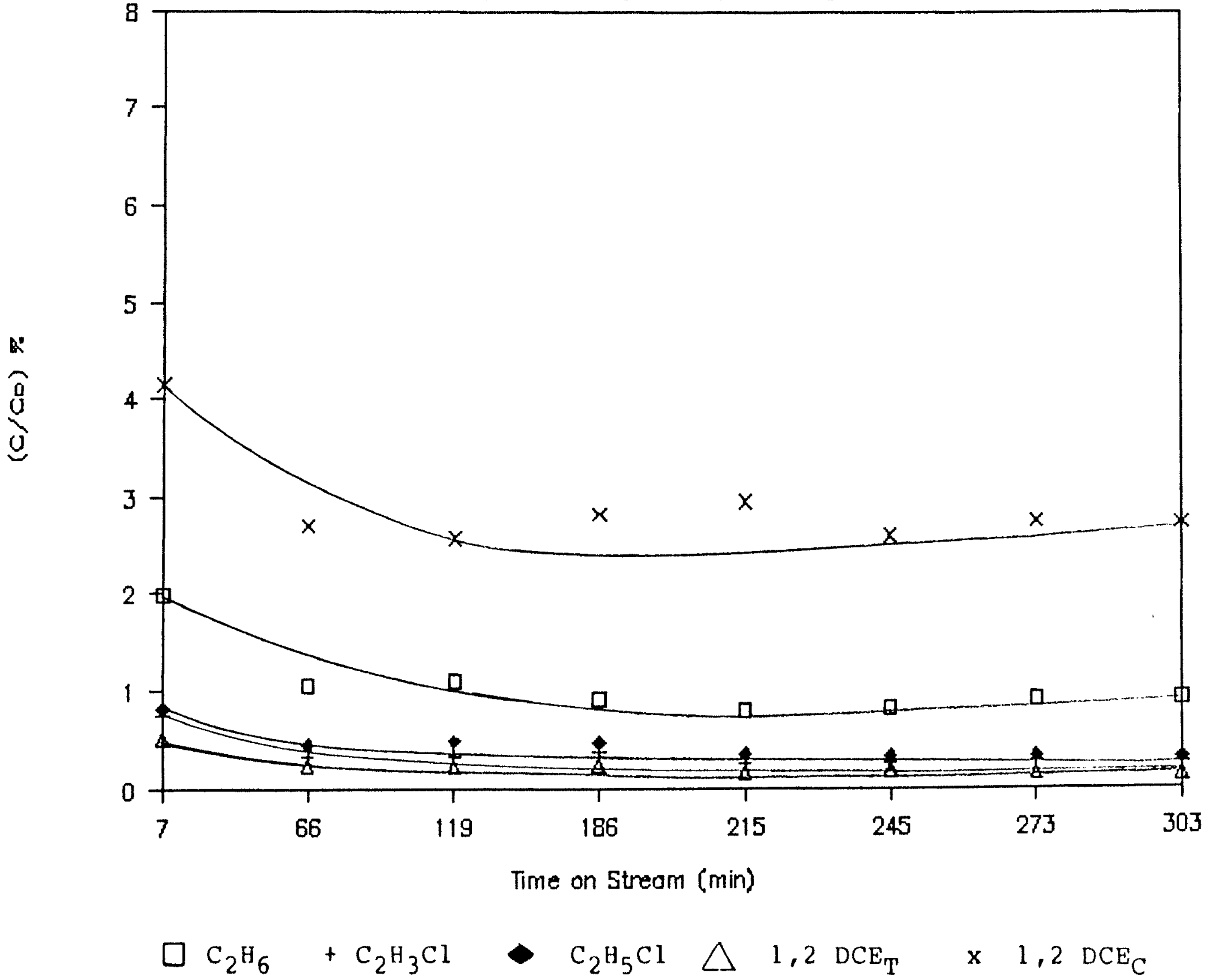
Hydrodechlorination of trichloroethylene over alumina supported catalyst was studied at temperatures of up to 100° C at one atmospheric pressure in hydrogen atmosphere. The main products of the reaction were found to be ethane (25 %) and (cis) 1,2 dichloroethylene (55 %) whereas trace products were chloroethylene (6 %), chloroethane (9 %), and (trans) 1,2 dichloroethylene (5 %).

Sinfelt and Yates (1967), discussed the order of activities for the noble metals of group VIII as a function of percentage d character. They indicate that in hydrogenolysis, activity increases with increasing percentage d characters. Since rhodium catalyst have showed higher percentage d character compared to palladium, they would be expected to be more active for hydrogenolysis. The reaction of trichloroethyelene and hydrogen over Rh/SiO_2 was initiated at temperatue 90°C<10>. Alumina supported palladium catalyst showed higher reactivity at lower temperature then Rh/SiO_2 catalyst, but this may be due to the support effect since SiO_2 is neutral whereas alumina support is acidic. The fractional conversion with respect to time on stream at 50°C is shown in the Fig. 2-3. It shows that in the first hour of reaction time there is a decrease in conversion to useful hydrocarbons with increase in conversion to lower chlorine number chlorocarbons. The 40 % decrease in total conversion during first hour of

Fig. 2-3

Product Distribution for Rxn. TCE + H2

Over Pd/Al2O3 Catalyst, Temp= 50 Deg. C



reaction can also be seen from Fig. 2-4. This is probably deactivation of catalyst and may be due to the adsorption of HCl formed during the reaction, with the subsequent equilibrium established leading to the longer term stable product distribution.

The selectivity, which is defined as a ratio of product conversion to total conversion is shown as a function of time on stream in Fig. 2-5. Alumina supported palladium catalyst showed higher selectivity for C_2 hydrocarbons. At higher temperature hydrodechlorination reaction is favored by higher selectivity to nonchlorinated hydrocarbon. Example of this is, at 40^{o}C temperature, selectivity is 83 % for chlorinated hydrocarbon with (ethane, 17 %) and at 57 ^{o}C temperature, selectivity of 71 % is observed for lower chlorine number chlorocarbon with 29 % for useful hydrocarbon ethane, as seen from Fig. 2-6 and Table 2-1 of " Selectivities as a Function of Temperature".

2.4.1.1 Effect of Residence Time

Selectivity of different products at different residence time and with time on stream is given in Table 2-2. It shows change in selectivity with time on stream at different residence time for 57^{o}C temperature. Fig. 2-7, 2-8 and Table 2-3 demonstrate the effect of residence time on selectivity for hydrodechlorination of trichloroethylene, at different temperatures. The total conversion increases with increases in residence time. Selectivity for ethane increases 15 % and that for chloroethylene, chloroethane,

Fig. 2-4

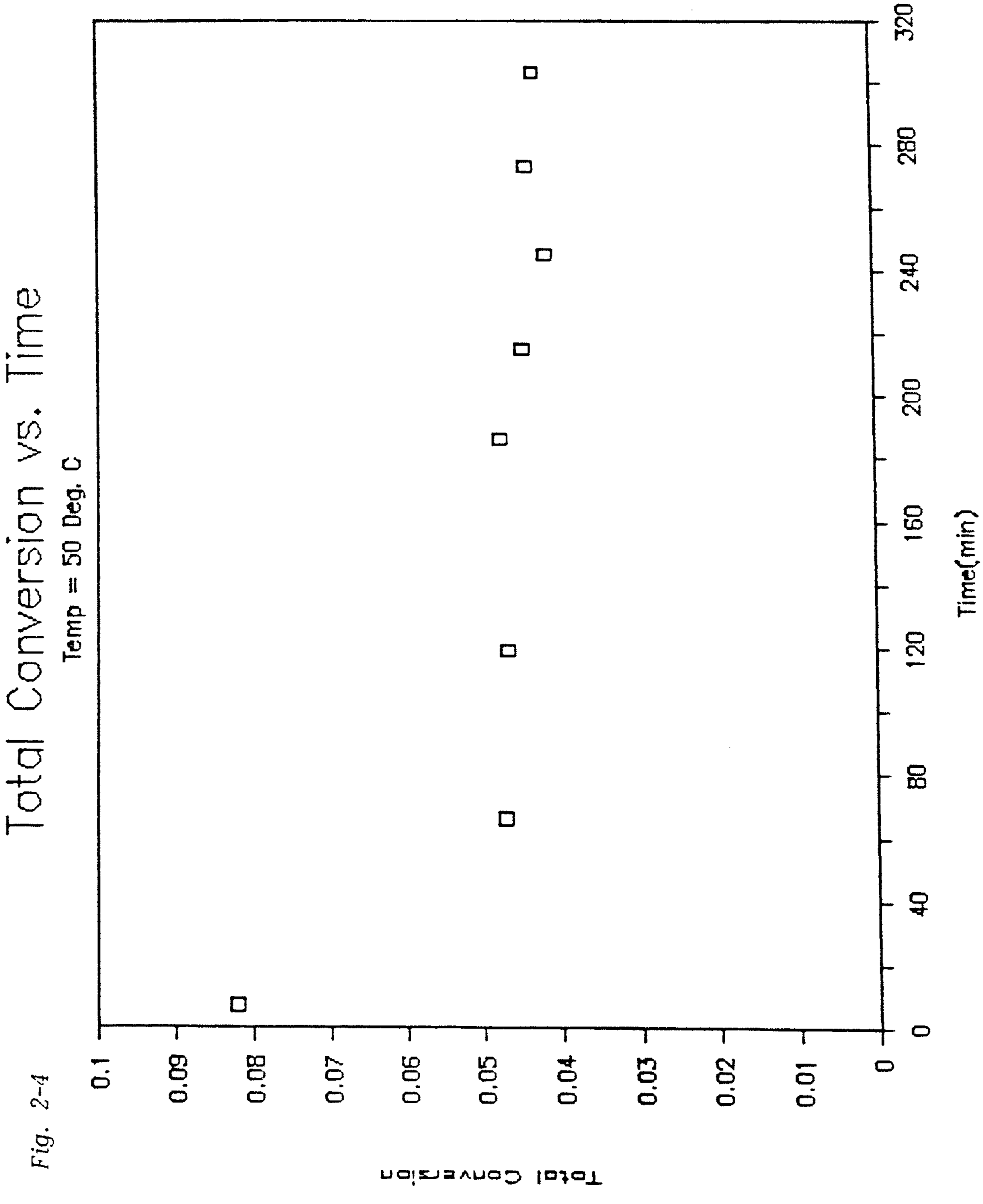

Total Conversion vs. Time
Temp = 50 Deg. C
Total Conversion
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Time(min)
0
40
80
120
160
200
240
280
320

Fig. 2-5

Selectivity vs. Time for Rxn. TCE + H2

over Pd/Al2O3 catalyst, Temp= 50 Deg. C

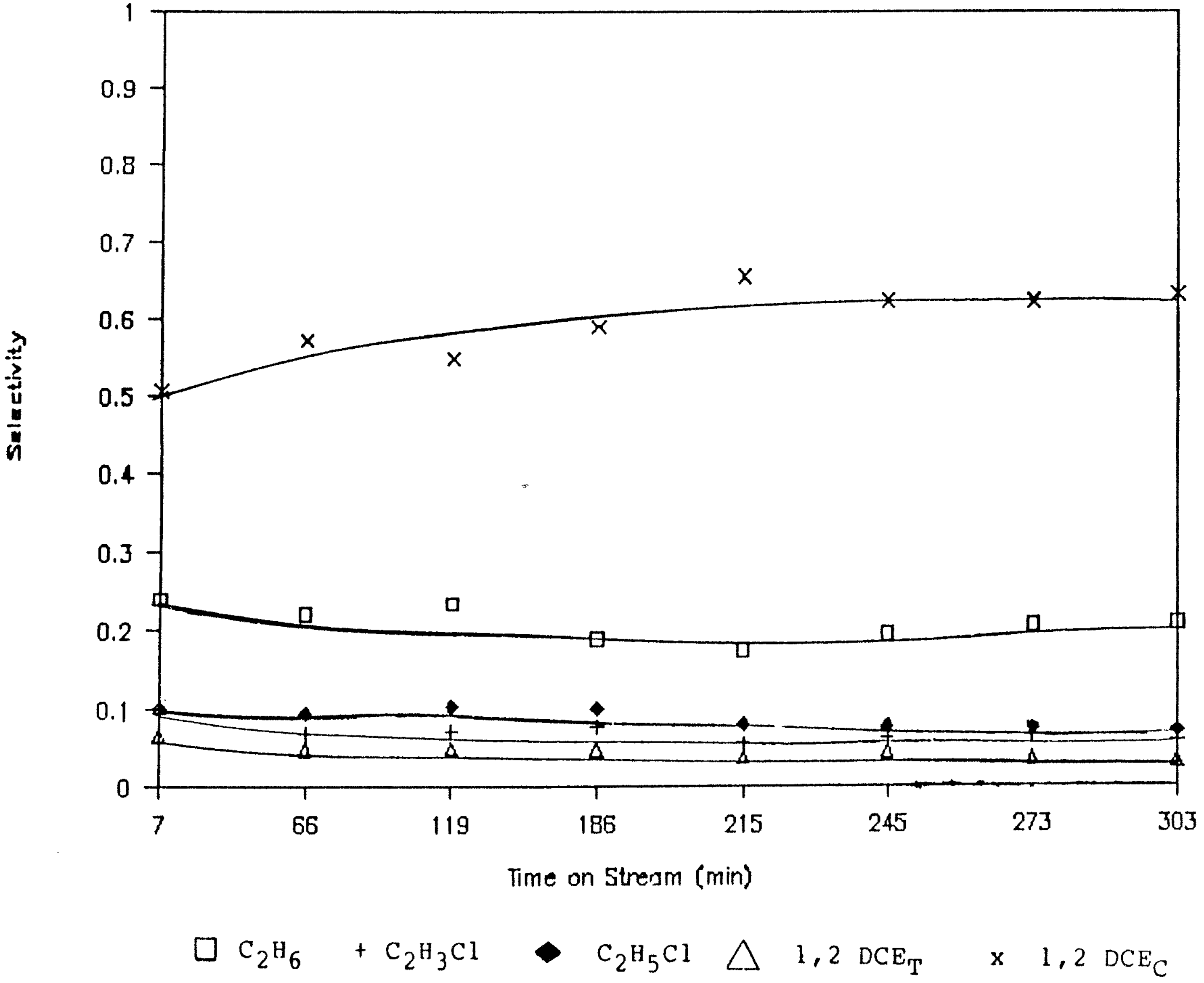


Table 2-1 Effect of Temperature on Trichloroethylene Hydrodechlorination Selectivity

Catalyst	Pd/Al2O3 (0.5 wt%)		
Dispersion (%)			
Temperature Deg. C	40	50	57
selectivity (%)			
C2H6	16.91	21.72	28.89
C2H3Cl	2.79	6.068	5.69
C2H5Cl	13.2	13.07	5.71
C2H2Cl2(trans)	1.91	4.19	2.83
C2H2Cl2(cis)	64.13	52.46	57.28

Fig. 2-6

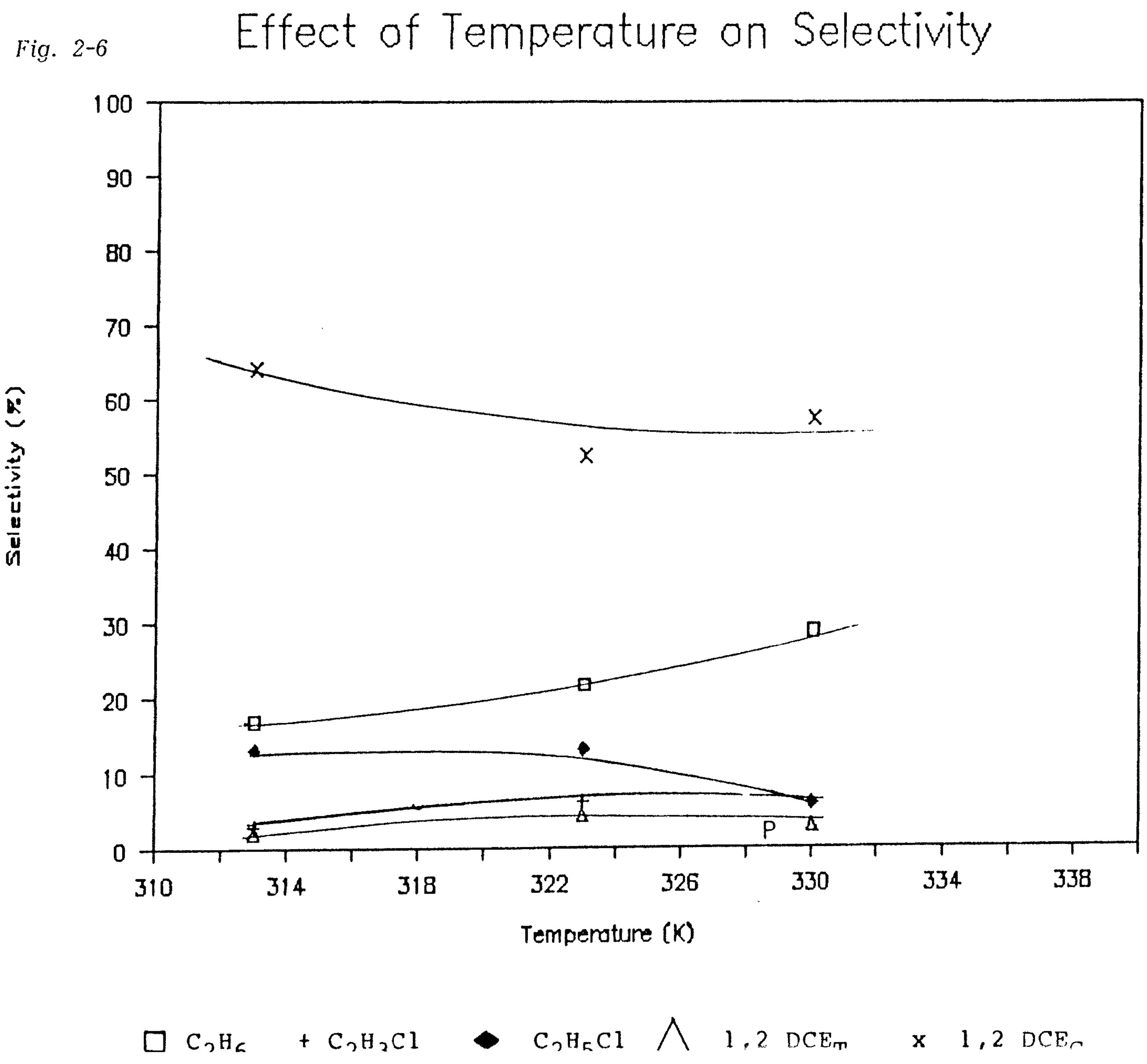

Effect of Temperature on Selectivity
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
310
314
318
322
326
330
334
338
Temperature (K)
P
C_2H_6
+ C_2H_3Cl
C_2H_5Cl
1,2 DCE_m
x 1,2 DCE

Table 2-2 Selectivity of Hydrodechlorination of Trichloroethylene at Different Residence Time

Time On Stream (min)	Selectivity(%)				
	C2H6	C2H3Cl	C2H5Cl	C2H2Cl2 (Trans)	C2H2Cl2 (cis)
W/Vo = 1.792*E-5 (Kg.Hr/Lit)					
42.00	44.11	4.81	3.01	2.00	46.07
75.00	42.85	5.11	3.00	2.13	46.91
102.00	43.86	4.47	3.00	2.17	46.50
130.00	44.83	4.56	2.97	2.08	45.57
168.00	44.99	4.71	3.11	2.19	44.99
196.00	45.23	4.52	2.88	2.14	45.23
223.00	44.54	4.45	2.83	2.08	46.10
251.00	43.32	4.58	2.92	2.07	47.10
281.00	43.94	4.48	2.85	2.03	46.70
W/Vo = 9.578*E-6 (Kg.Hr/Lit)					
3.00	39.61	5.90	5.12	2.49	46.87
31.00	35.11	5.74	5.13	2.57	51.45
61.00	35.41	4.61	4.78	2.38	52.82
91.00	35.89	4.62	4.28	2.31	52.88
151.00	33.37	5.03	4.82	2.44	54.34
181.00	33.61	5.16	4.87	2.60	53.75
213.00	33.57	5.18	4.84	2.57	53.83
255.00	33.65	4.96	4.55	2.55	54.29
283.00	34.46	4.80	4.45	2.38	53.89
W/Vo = 3.779*E-6 (Kg.Hr/Lit)					
4.00	29.37	7.48	9.93	4.38	48.83
65.00	26.72	6.16	7.33	2.98	56.79
96.00	28.23	6.10	7.51	3.06	55.09
124.00	29.28	6.08	7.15	2.93	54.54
154.00	30.19	5.34	6.34	2.67	55.50
198.00	29.97	5.21	6.00	2.81	56.01
231.00	29.00	5.55	5.86	2.63	56.95
259.00	28.87	5.39	5.71	2.75	57.28

Table 2-3 Selectivity of Hydrodechlorination of Trichloroethylene at Different Residence Time and at Different Temperature

(a) at 40 Deg. C.

ResidenceTime(Kg-Hr/Lit)	1.792*E-5	9.578*E-6	3.779*E-6
Total Conversion	2.66	2.1	1.53
Selectivity (%)			
C_2H_6	18.6	16.2	14.4
C_2H_3Cl	7.6	4.04	2.75
C_2H_5Cl	10.46	12.3	14.95
1,2 $C_2H_2Cl_2$(trans)	8.28	4.68	2.3
1,2 $C_2H_2Cl_2$(cis)	55.04	62.75	65.8

Tabel 2-3 Selectivity of Hydrodechlorination of Trichloroethylene at Different Residence Time and Different Temperature

(b) at 57 Deg. C.

ResidenceTime(Kg-Hr/Lit)	1.792*E-5	9.578*E-6	3.779*E-6
Total Conversion	7.53	5.46	4.74
Selectivity (%)			
C_2H_6	43.93	33.89	28.93
C_2H_3Cl	4.5	4.98	5.38
C_2H_5Cl	2.86	4.67	5.86
1,2 $C_2H_2Cl_2$(trans)	2.06	2.52	2.73
1,2 $C_2H_2Cl_2$(cis)	46.63	53.9	56.75

Fig. 2-7

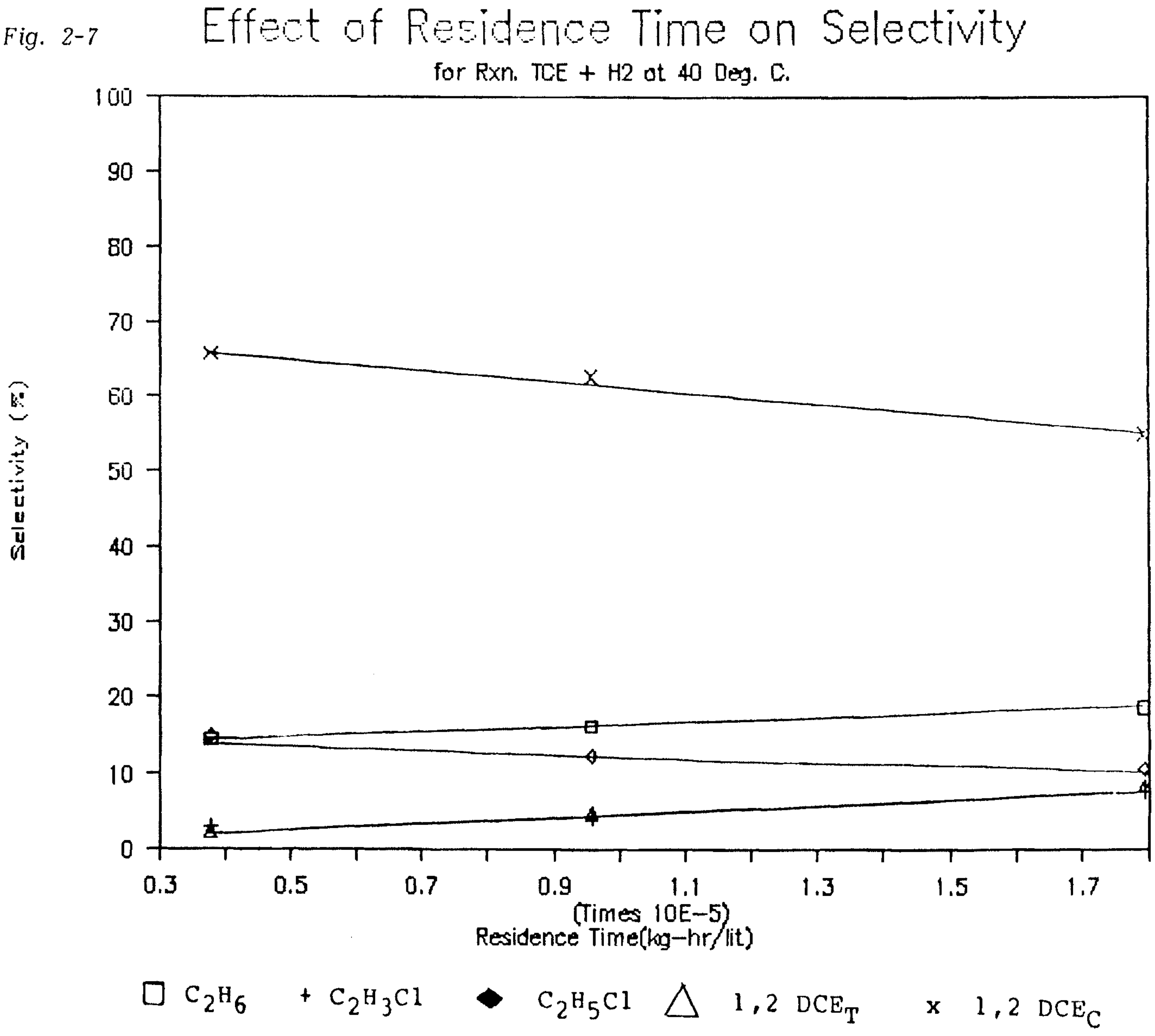
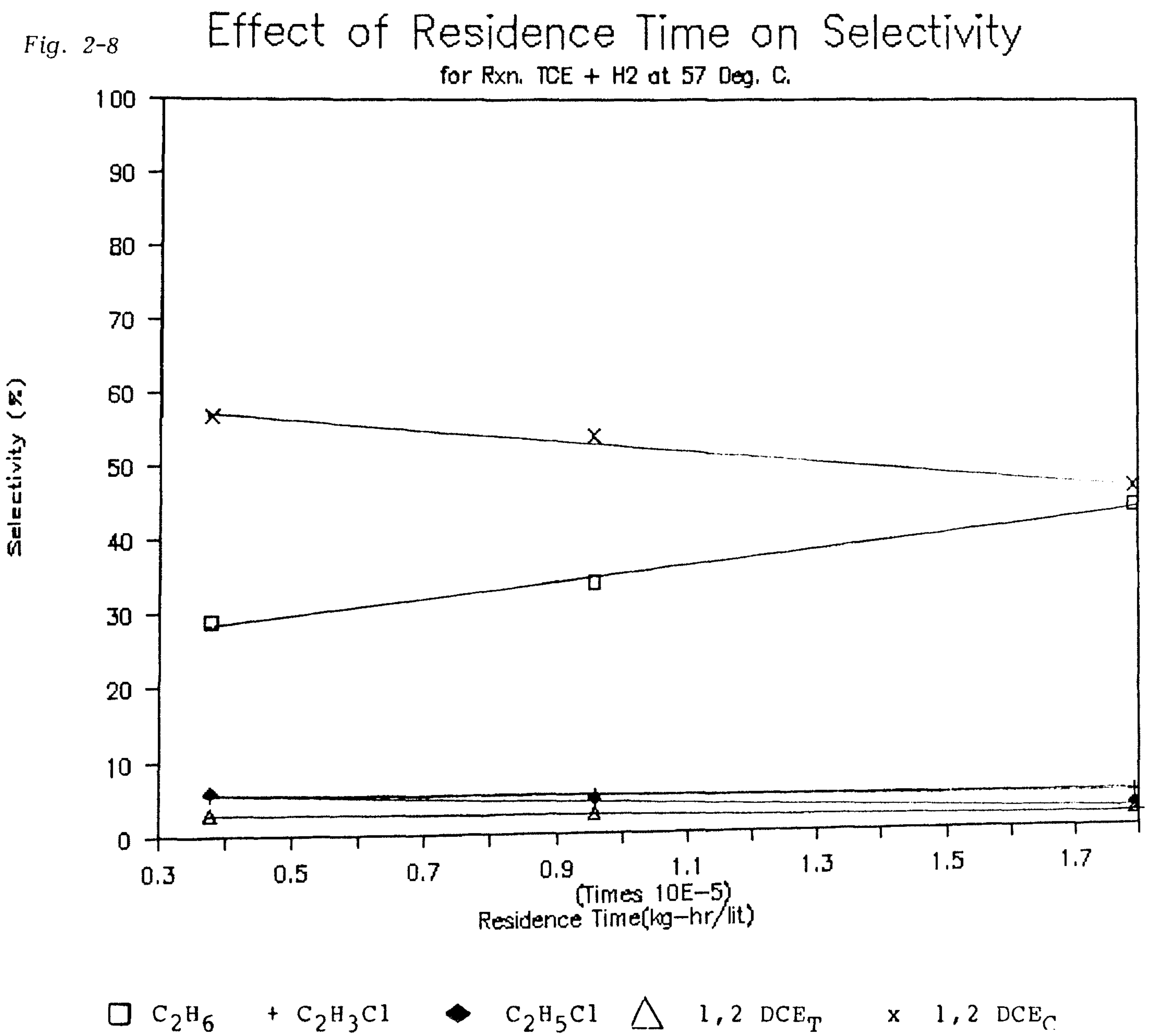

Effect of Residence Time on Selectivity
for Rxn. TCE + H2 at 40 Deg. C.
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
(Times 10E-5)
Residence Time(kg-hr/lit)
□ C_2H_6
+ C_2H_3Cl
◆ C_2H_5Cl
△ 1,2 DCE_T
x 1,2 DCE_C

Fig. 2-8


Effect of Residence Time on Selectivity
for Rxn. TCE + H2 at 57 Deg. C.
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
(Times 10E-5)
Residence Time(kg-hr/lit)
□ C_2H_6
+ C_2H_3Cl
◆ C_2H_5Cl
△ 1,2 DCE_T
x 1,2 DCE_C

(cis) 1,2-dichloroethylene decrease with increase in residence time, which shows that lower chlorinated hydrocarbon are intermediate products. On increased contact time these intermediates further hydrodechlorinate to produce ethane.

2.4.1.2 Reaction Kinetics

In this study hydrogen was used to carry the reagent vapor into reactor and was in excess. The reaction was carried out at one atmosphere total pressure with partial pressure of reagent employed was 20 torr for trichloroethylene at all temperatures studies. Since hydrogen is used in excess, it is reasonable to assume that the reaction proceeds by pesudo first order rate law. By using the integral method to fit data, we obtain the performance equation<20>.

$$\ln (1/(1-x)) = t * k ,$$

where x is the conversion of trichloroethylene, k is rate constant , and t is defined as W/V_o. W is the weight of the catalyst and V_o is the volumetric flow rate. Figure 2-9 and Table 2-4 show kinetic parameters and indicates rate constants (pesudo first order) at different tempratures for hydrodechlorination of trichloroethylene.

The Arrhenius plot is shown in Figure 2-10, and yields an apparent activation energy of 12.1 kcal/mole for hydrodechlorination of trichloroethylene. The straight line in Arrhenius plot supports the assumption and that there is no diffusion limitation.

Table 2-4 Kinetic Parameter for Reaction Trichloroethylene with Hydrogen over Pd/Al_2O_3 Catalyst.

T(^{o}C)	k (liter/kg-hr)
40	737
50	1500
57	2075

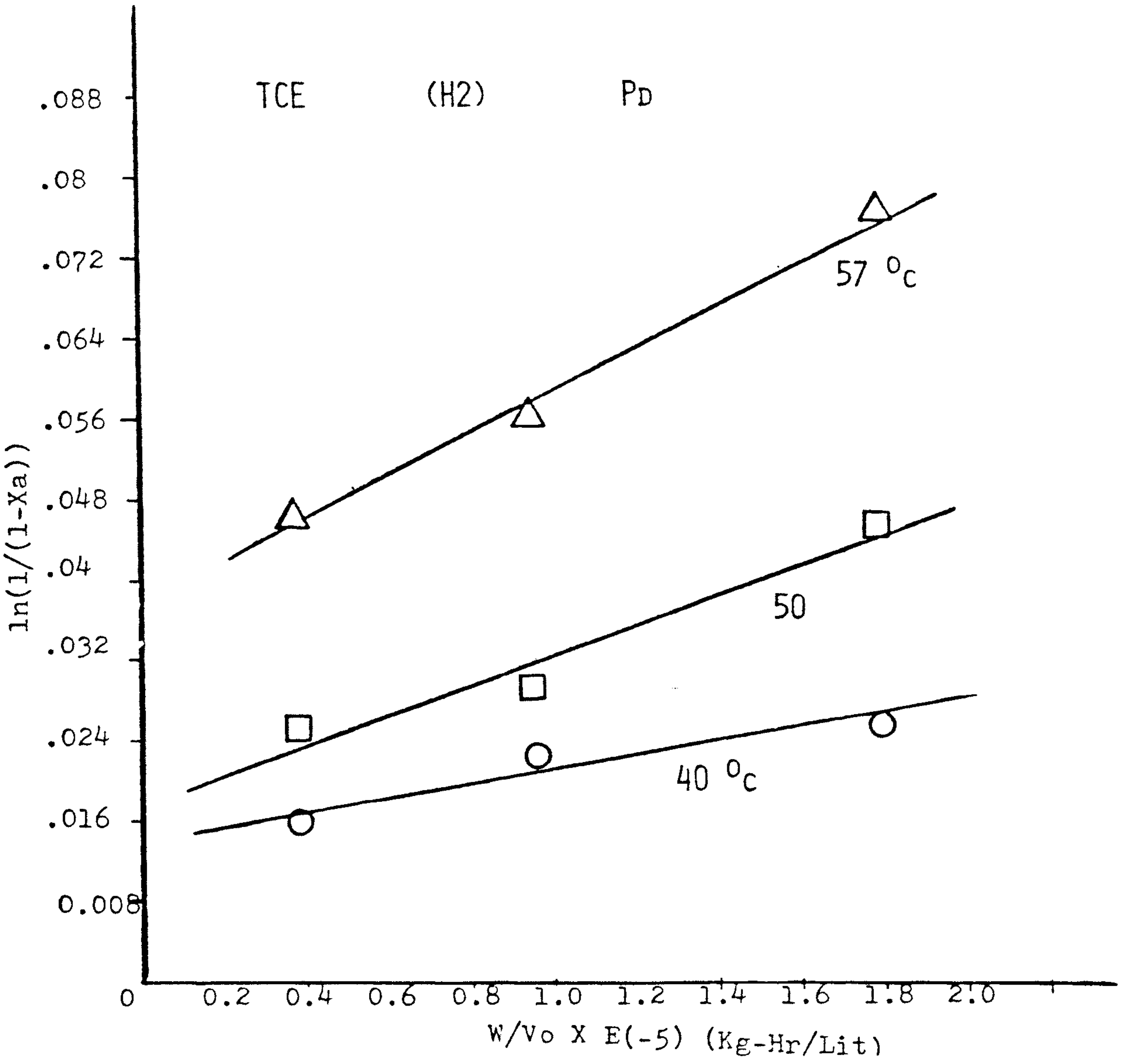


Fig. 2-9 Plot of ln(1/(1-x)) Vs. Residence Time

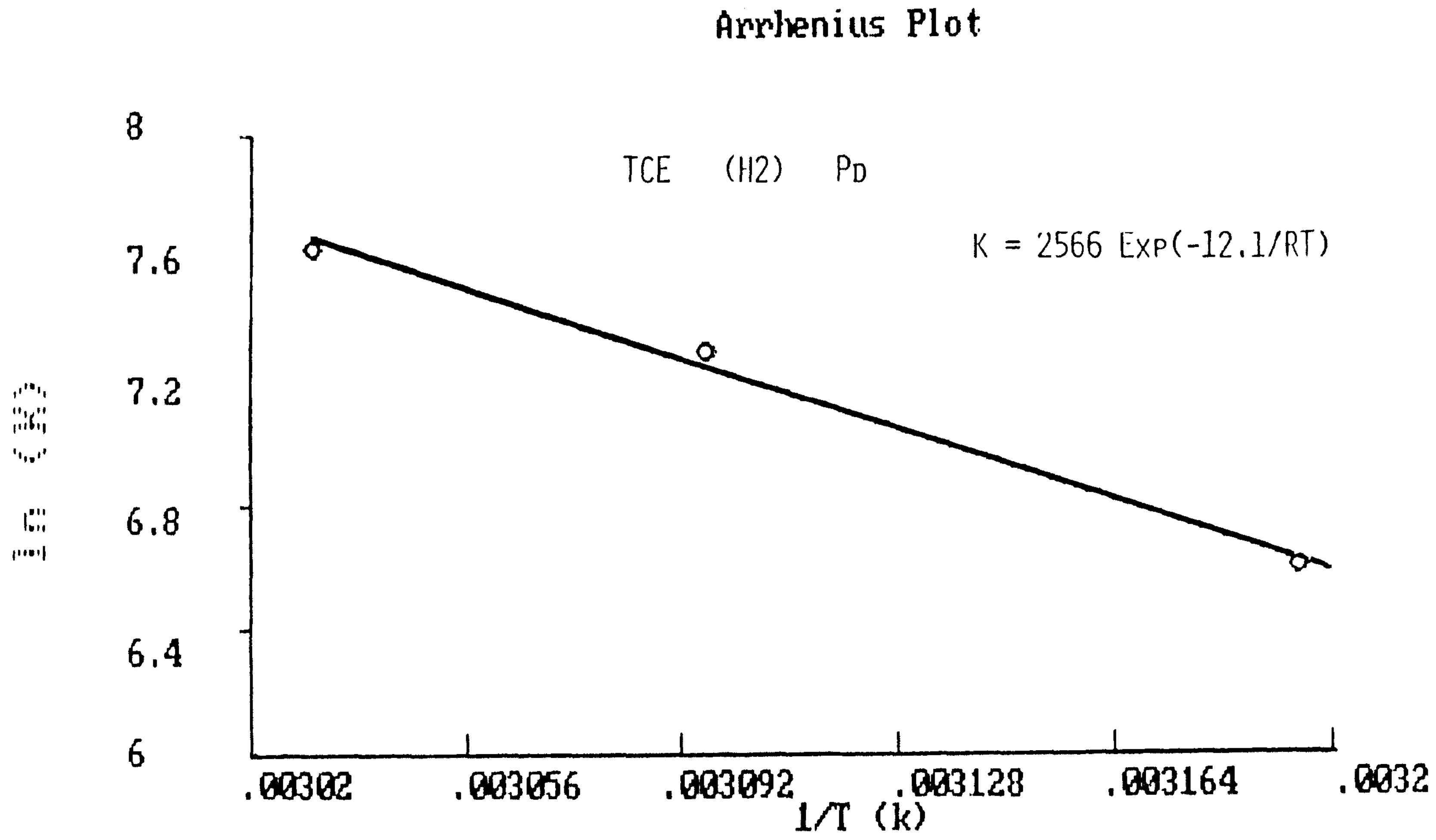


Fig. 2-10 Arrhenius Plot for Rxn. TCE + H_2 over Pd/Al_2O_3

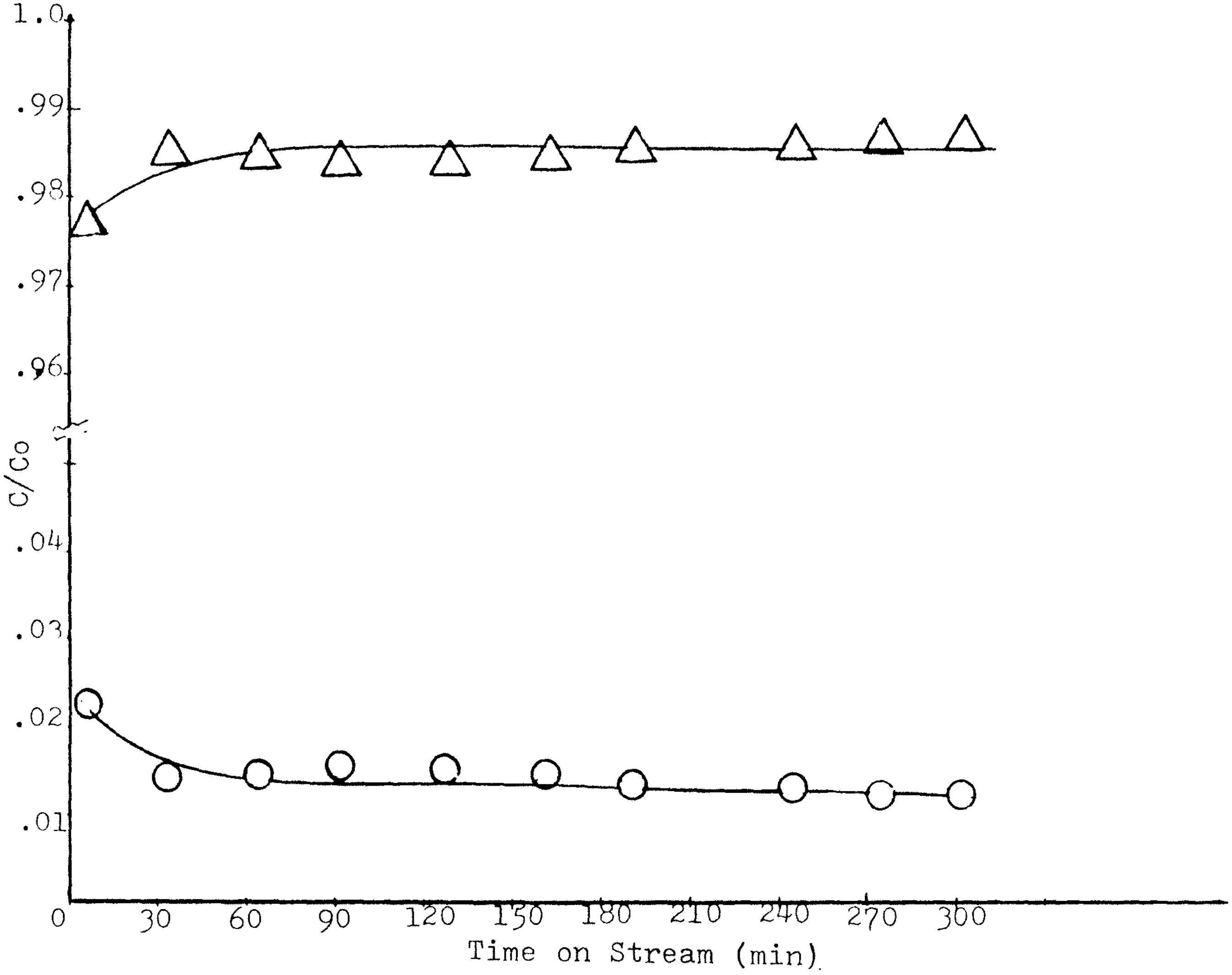
2.4.2 1,1,1 Trichloroethane/H_2/ Pd/Al_2O_3:

Hydrodechlorination reaction of 1,1,1 trichloroethane was studied in hydrogen atmosphere over alumina supported palladium (0.5 %) catalyst (surface area, 95-115 m^2/gm) in the temperature range 57 to 77°C. The only product observed was ethane, no chlorinated hydrocarbons were observed in the temperature range studied. The typical product distribution for the reaction as a function of time on stream is shown in the Fig. 2-11. The total conversion decreased 20 % after one hour of reaction time with decrease in conversion to ethane indicating a catalytic activity decrease during the first hour of reaction time with constant activity afterwards as seen in reaction of trichloroethylene could be due to the formation of chloride on metal surface and/or the carbon deposition from trichloroethylene.

Yang et al. (1986) observed the deactivation of Pd/Al_2O_3 catalyst for hydrodechlorination reaction of aliphatic chlorinated hydrocarbons. The 25 % decline in activity (first hour) might be due to the adsorption of HCl produced during the reaction, on the surface of catalyst and/or sintering of the catalyst. They regenerated catalyst activity by reduction in hydrogen atmosphere at 245°C and they found that catalyst recovered to only 56% initial activity. The loss in activity may be due to the sintering of the catalyst.

Since there is only one product, selectivity of

Fig. 2-11 Product Distribution for Rxn. 1,1,1 TCE H2 over Pd/Al203, Temp 57 Deg. C



Pd/Al_2O_3 catalyst for this reaction is unity. At increased temperature there is increased conversion to ethane. At higher temperatures other hydrocarbon like methane, ethylene and butane are observed at level below 4 %.

2.4.2.1 Reaction Kinetics:

Again hydrogen is in excess, since reaction is carried out in hydrogen atmosphere. The reaction was carried out at one atmosphere total pressure with 35 torr partial pressure of 1,1,1 trichloroethane. An integral method was used to evaluate the data (first order reaction) with respect to 1,1,1 trichloroethane.

The performance equation is<20>

$$\ln(1/(1-x)) = t * k,$$

where x is conversion of 1,1,1 trichloroethane, k is rate constant and t is defined as W/V_o, where W is weight of the catalyst and V_o is volumetric flow rate of reactant. The reaction occured by pesudo first order with respect to 1,1,1 trichloroethane as seen from Fig. 2-12 with kinetic parameters for this reaction as given in Table 2-5.

An Arrhenius plot shown in Fig. 2-13, which yields an activation energy of 12.75 kcal/mole for 1,1,1 trichloroethylene hydrodechlorination.

Table 2-5 Kinetic Parameter for Reaction 1,1,1 Trichloroethane with Hydrogen over Pd/Al_2O_3 catalyst.

T(^oC)	k(lit/kg-hr)
57	696
68	1100
77	2566

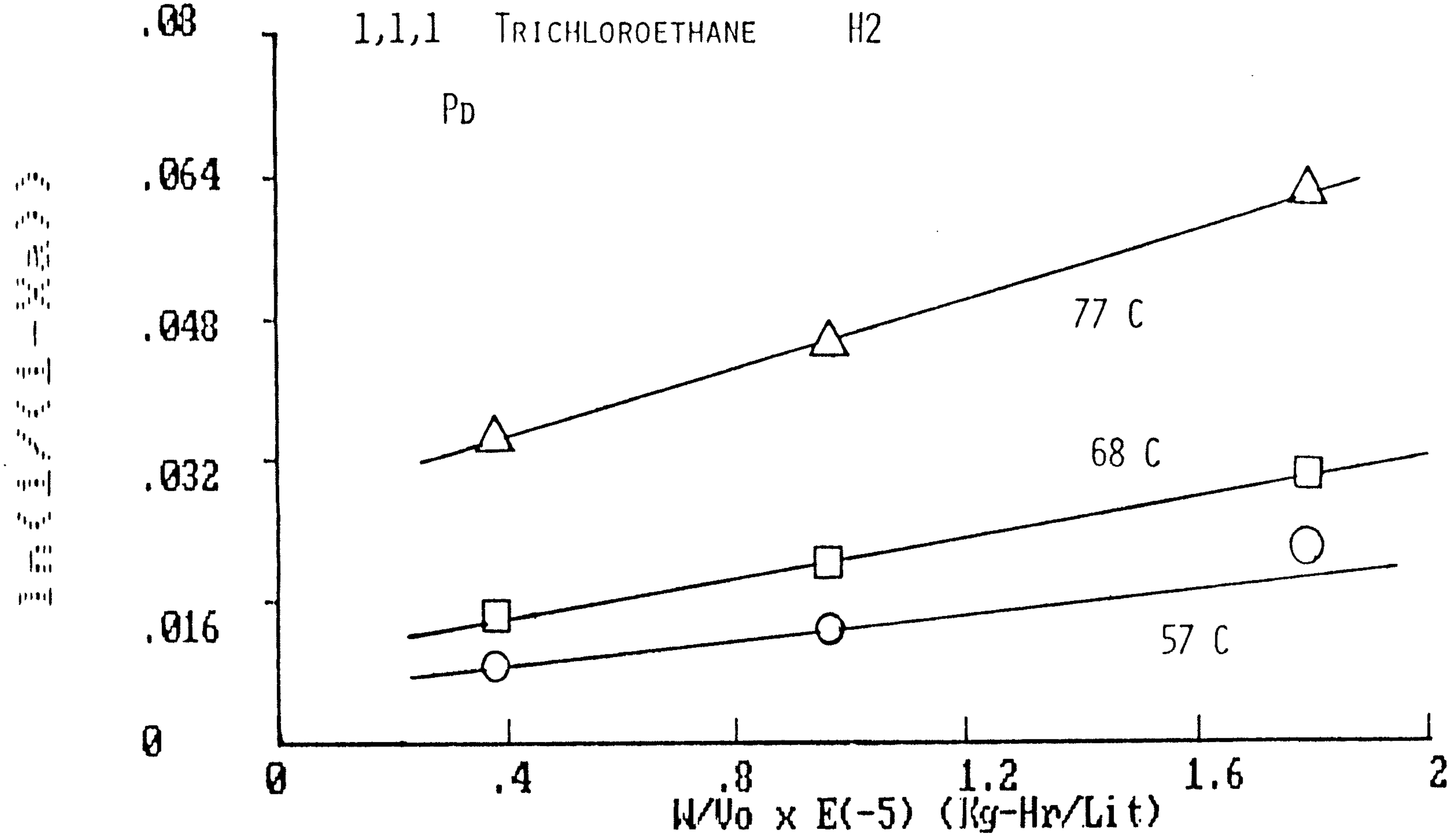


Fig. 2-12 Plot of ln(1/(1-x)) Vs. Residence Time

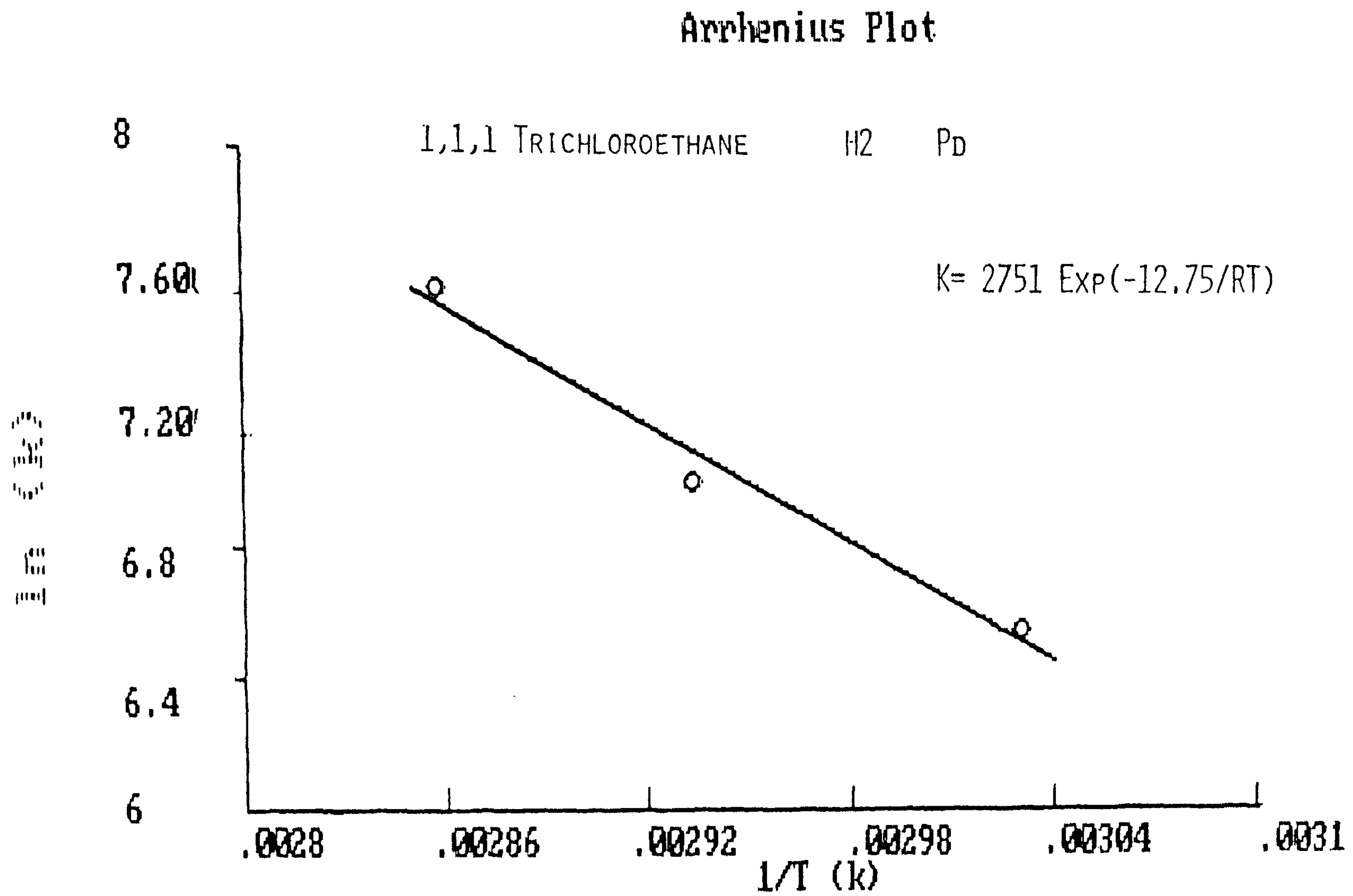


Fig. 2-13 Arrhenius Plot for Rxn. 1,1,1 TCE + H2 over Pd/Al_2O_3

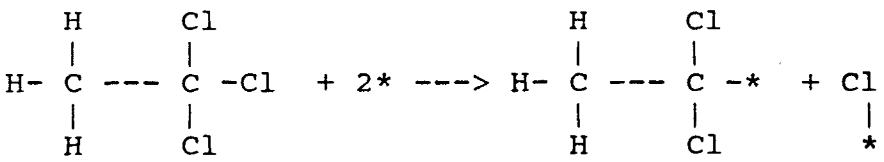
2.4.2.2 Mechanism

In the study of hydrodechlorination reaction on aliphatic hydrocarbons 1,2 dichloroethane (DCE) and chloroform (CF), Yang and Bozzelli (1986) proposed a free radical mechanism involving disociative adsorption on Pd/Al_2O_3 catalyst towards the formation of products, chloroethane, ethylene and ethane from DCE, and, methylene chloride and methane from CF . The adsorption of chlorinated hydrocarbons occurs through partial or complete fission of the C-Cl bond. Weiss et al. (1971) proposed a free radical mechanism involving disociative adsorption of CCl_4 on platinum surface followed by sequential and concerted addition of hydrogen to CCl_3* free radical to form products chloroform and methane. We propose, the reaction follows similar steps.

Graham (1868) observed that adsorbed hydrogen dissociate readily into atoms on palladium catalyst surface:

$$H_2 \quad \underset{\longleftarrow}{\overset{Pd}{\longrightarrow}} \quad H* + H*$$

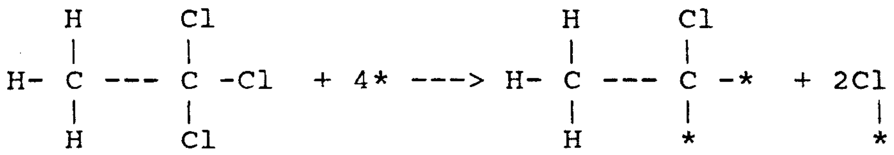
1,1,1 Trichloroethane must then undergo dissociative adsorption and three possible intermediates are produced.



$$\begin{array}{ccccccccccccc} & H & & Cl & & & & & H & & Cl & & \\ & | & & | & & & & & | & & | & & \\ H- & C & --- & C & -Cl & + 2* & \longrightarrow & H- & C & --- & C & -* & + \; Cl \\ & | & & | & & & & & | & & | & & \;\; | \\ & H & & Cl & & & & & H & & Cl & & \;\; * \end{array}$$

(I)

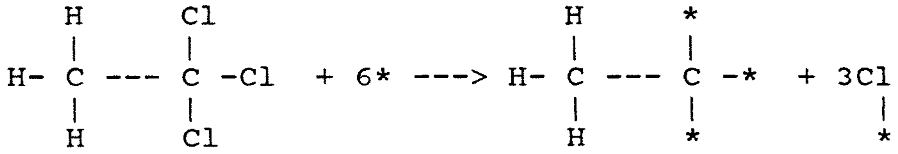
or



$$\mathrm{H-\overset{H}{\underset{H}{C}}---\overset{Cl}{\underset{Cl}{C}}-Cl} \;+\; 4* \;\text{--->}\; \mathrm{H-\overset{H}{\underset{H}{C}}---\overset{Cl}{\underset{*}{C}}-*} \;+\; 2\underset{*}{\mathrm{Cl}}$$

(II)

or



$$\mathrm{H-\overset{H}{\underset{H}{C}}---\overset{Cl}{\underset{Cl}{C}}-Cl} \;+\; 6* \;\text{--->}\; \mathrm{H-\overset{H}{\underset{H}{C}}---\overset{*}{\underset{*}{C}}-*} \;+\; 3\underset{*}{\mathrm{Cl}}$$

(III)

Intermediate (I) is then attacked by concerted hydrogen radical addition to give ethane as terminal product.

$$CH_3\text{-}CCl_2{*} \quad + 2\ H{*} \text{ ---> } CH_3\text{-}CHCl{*} + HCl{*} \qquad \text{(i)}$$

$$CH_3\text{-}CHCl{*} \quad + 2H{*} \text{ ---> } CH_3\text{-}CH_2{*} + HCl{*} \qquad \text{(ii)}$$

$$CH_3\text{-}CH_2{*} \quad + H{*} \text{ ---> } CH_3\text{-}CH_3 \qquad \text{(iii)}$$

Similarly intermediate (II) and (III) undergo concerted addition of hydrogen to give ethane as a terminal product:

$$CH_3\text{-}CCl{*} \quad + 2H{*} \text{ ---> } CH3\text{-}CH{*} + HCl{*} \qquad \text{(iv)}$$

$$CH_3\text{-}CH{*} \quad + 2H{*} \text{ ---> } CH_3\text{-}CH_3 \qquad \text{(V)}$$

and

$$CH_3\text{-}C{*} \quad + 3H{*} \text{ ---> } CH_3\text{-}CH_3 \qquad \text{(vi)}$$

It is unlikely that desorption are involved, since we did not find intermediate products that results from gas phase reaction with hydrogen,

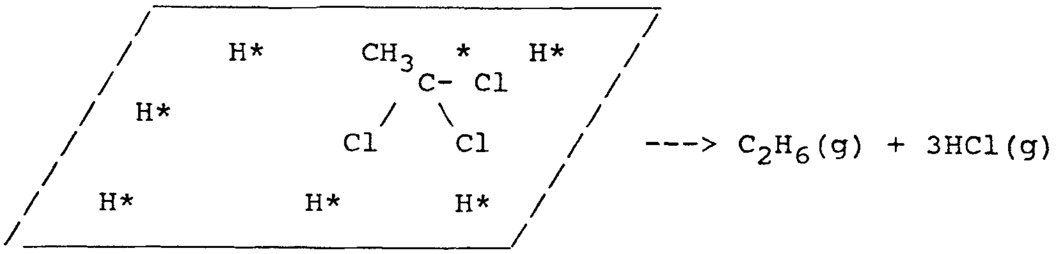
$$CH_3\text{-}CHCl^* + H_2 \longrightarrow CH_3CH_2Cl + H^* \qquad \text{(Vii)}$$

or

$$CH_3\text{-}CCl_2^* + H_2 \longrightarrow CH_3CHCl_2 + H^* \qquad \text{(Viii)}$$

These reaction (vapor phase abstraction of H_2) would, however, have a 10-12 kcal activation energy and may not occur rapidly enough under our conditions.

Since desorption of intermediates and their subsequent readsorption most probably does not occur, the reaction sequenece for intermediate (I), (II), (III) may be regarded as a single step concerted or multistep reaction:



G. Somorjai et al. (1985) observed the formation of ethylidyne on the surfaces of Rh and Pt during ethylene hydrogenation.

Chapter-3 Hydrodechlorination Reaction of Trichloroethylene over Nickel catalyst

3.1 INTRODUCTION:

Supported catalysts of platinum, palladium, and Rhodium exhibit high reactivity for hydrodechlorination reactions, are expensive for practical high volume and low reagent purity use in the conversion of halocarbon wastes. The relatively high cost and lack of domestic supplies for noble metals has spurred considerable effort towards the development of non noble metal catalyst systems. Nickel catalyst have shown high catalytic activity for hydrogenation of carbon oxides. As a methanation catalyst, nickel is preminent. It is relatively inexpensive and is very active when present in forms that have high surface areas<13>.

There has been relatively little work reported on reactions of chlorinated hydrocarbons with hydrogen over nickel catalysts. In this study we investigated catalytic activity and selectivity of a nickel catalyst on reaction of trichloroethylene with hydrogen; in an attempt to develop relatively inexpensive catalyst for conversion of halocarbon wastes into non chlorinated useful products and HCl.

3.2 Literature Survey:

3.2.1 Catalyst:

The activity of transition metal films Ni, Rh, Fe, W, and Ta for ethylene hydrogenation reactions has been studied by O. Beeck (1950). He found that rate of hydrogenation of ethylene over the porous transition metal films depends on the heat of adsorption of ethylene. He also noted that plots of d-character of metallic single bond versus either the heat of adsorption of ethylene, or the rate of hydrogenation show smooth curve; indicating greater the d-character; the lower the heat of adsorption and the higher the rates. Beeck et al. (1950) have also showed that chemical properties (electronic configurations) and the resultant physical properties (crystal parameters) of the catalyst surface influence the rate of reaction. This is illustrated for nickel catalyst by showing that the (110) plane is very active as a catalyst for this reaction. The (110) plane oriented nickel films have at least five times the specific activity of unoriented films for hydrogenation of ethylene. A study on rate and product of reaction from oriented and unoriented nickel films for reactions of hydrogen (gas phase) with preadsorbed ethylene shows that 20 % of the residue can be reacted in 1 hr, the products being about 90 % saturated polymer (C_4-C_{10}) and 10 % ethane at 23°C. The reaction rates and products are identical for both type of film. No other studies on hydrogenation activity for olefinic hydrocarbon on nickel has been reported.

3.2.2 Hydrodechlorination Reactions:

W. Van Barneveld and V. Ponec (1984) studied reactions of chlorinated methane molecules in mixtures with hydrogen alone, or with H_2 and CO , on metals with varying activities and selectivities in the Fischer-Tropsch synthesis Ni, Co, Cu, Fe, Rh, Pd and on some alloys Ni-Cu, Ni-Pd. They found that metals active in the Ficher-Tropsch synthesis produce higher hydrocarbons in the absence and in presence of CO. They reported on specific reactions of CH_3Cl, CH_2Cl_2, $CHCl_3$ with hydrogen at 483°K and standard conditions. The reactions ran upto high conversions of chloromethanes added. The conversion of CH_3Cl into CH_4 has been observed on Ni and Co, which indicated that prevailing adsorption mode arises from C-Cl bond fission. They also studied the reaction of CH_2Cl_2/H_2 over $NiCl_2$ catalyst for the reason that possibly Ni ions and not Ni metal atoms could have been the catalysts for hydrocarbon chain growth. $NiCl_2$ appeared to be completely inactive with CH_2Cl_2, under standard conditions, indicating that Ni metal is not converted to metal chloride. This was also confirmed using X-ray diffraction after the contact of Ni metal with chloromethane/hydrogen mixtures. They observed very low (< 1%) selectivities of Ni-Cu and Ni-Pd alloys compared with Ni.

The catalytic hydrogenolysis of ethylchloride and ethylbromide has been studied on evaporated metal films of palladium, platinum, nickel and in less detail on films of iron, tungsten and rhodium by Campbell and Kemball (1961). The main reaction was the formation of ethane and hydrogen halides but ethylene was also observed over nickel and iron. The reactions of ethyl chloride and ethyl bromide with hydrogen over Ni films (100 cm^2) were studied over a temperature range of 184 to 343°C. The main products were ethylene and ethane. Formation of methane was reported at 343°C. The initial rate of production of methane was 0.09% / min per 100 cm^2 apparent area of catalyst. The hydrogenation of ethylene to ethane was inhibited very strongly by hydrogen chloride or ethyl chloride. The activation energies were 13 and 26 kcal/mole for reaction of ethyl chloride and ethyl bromide with hydrogen over Ni catalyst respectively.

3.3 Experimental:

3.3.1 Apparatus and Procedure:

A schematic diagram of the apparatus used and experimental procedures are essentially the same as in the reactions of trichloroethylene and 1,1,1 trichloroethane over alumina supported catalyst discussed in chapter 2. The catalyst used in this study is in the form of fine green NiO powder. 0.4 gram of nickel oxide, obtained from Strem Chemicals, catalyst was diluted with 0.5 gram of glass port (60-80 mesh), obtained from F & M Scientific Corp., in order to reduce the pressure drop at the catalyst bed, with length of catalyst bed 1.3 cm. The catalyst bed was supported on either side by 5 mm glass wool plugs. The NiO powder/ glass beads catalysts were reduced in the hydrogen atmosphere for two hours at 350°C and then cooled to the reaction temperature in hydrogen atmosphere prior to experiment. Thermocouples (chromel-allumel) were used to measure the temperature at both ends of the catalyst bed. Sampling of the reaction products were carried out as discussed in chapter 2.

The hydrodechlorination reaction is exothermic and to avoid temperature gradients in either the reactor or catalyst bed, all experiments were confined conversion to below 10 %.

3.3.2 Product Analysis:

The reactor effluent was analyzed through an online Varian 1200 model gas chromatograph equipped with flame ionization detector and 1/8 inche O.D. by 3.6 meter long column packed with poropak Q. Nitrogen gas was used as carrier gas; at a flow rate of 25 ml/min. The temperature program used to effect good separation was 50 to 190°C at a programming rate of 12°C/min. The column was unable to effect good separation of acetylene and ethylene. A GC/MS spectrometer was used to confirm the identification of products. This included a Carlo Erba Strumentizione Fractovap 4160 series GC interfaced with a Kratos MS 25 double focus magnetic sector Mass spectrometer and with a OV 101 capillary column 30 meters x 0.22 mm I.D..

3.3.3 Materials:

Catalyst - NiO was obtained from Strem Chemicals,
NewburyPort, MA 01950. Catalog # 93-2832

Glass Ports - ST-135, 60-80 mesh

F & M Scientific Corp., Avondale, PA.
(presently Hewlett-Packard)

Reagent - Trichloroethylene (99.9 %) was obtained from
Fisher Scientific Company, Fair Lawn, NJ.

3.4 Results And Discussion:

The reaction of trichloroethylene with hydrogen at one atmosphere total pressure over the nickel catalysts was studied in temperature range 165 to 190°C. The major observed products were, methane, ethane, ethylene and traces of propyne and chloroethane. It was interesting to find higher conversions (95 %) to useful hydrocarbons with only 5 % less chlorinated hydrocarbons. The reaction proceeds at higher temperature compared to palladium on alumina catalyst discussed in chapter 2. The typical product distribution at 189°C is shown in the Fig. 3-1. It shows ethylene production decreased with reaction time corresponding to increased ethane and methane, indicating, that ethylene produced is in an adsorbed state on catalysts surface with successive hydrogenation to ethane and methane. A stable product distribution was observed after 1.5 hr time on stream with ethane as a major product. Deactivation of the nickel catalyst did not occur during the course of reaction.

Selectivities of nickel catalyst for hydrodechlorination of trichloroethylene at different residence time and time on stream is as given in Table 3-1. The observed change in selectivity with time on stream at 189°C are shown in Fig. 3-2. Selectivity of 65 % was observed for ethane and less than 5 % for ethyl chloride. Table 3-2 gives selectivities of products as a function of temperature and this effect of temperature on selectivity is demonstrated by Fig. 3-3. Increasing the temperature from

Fig. 3-1

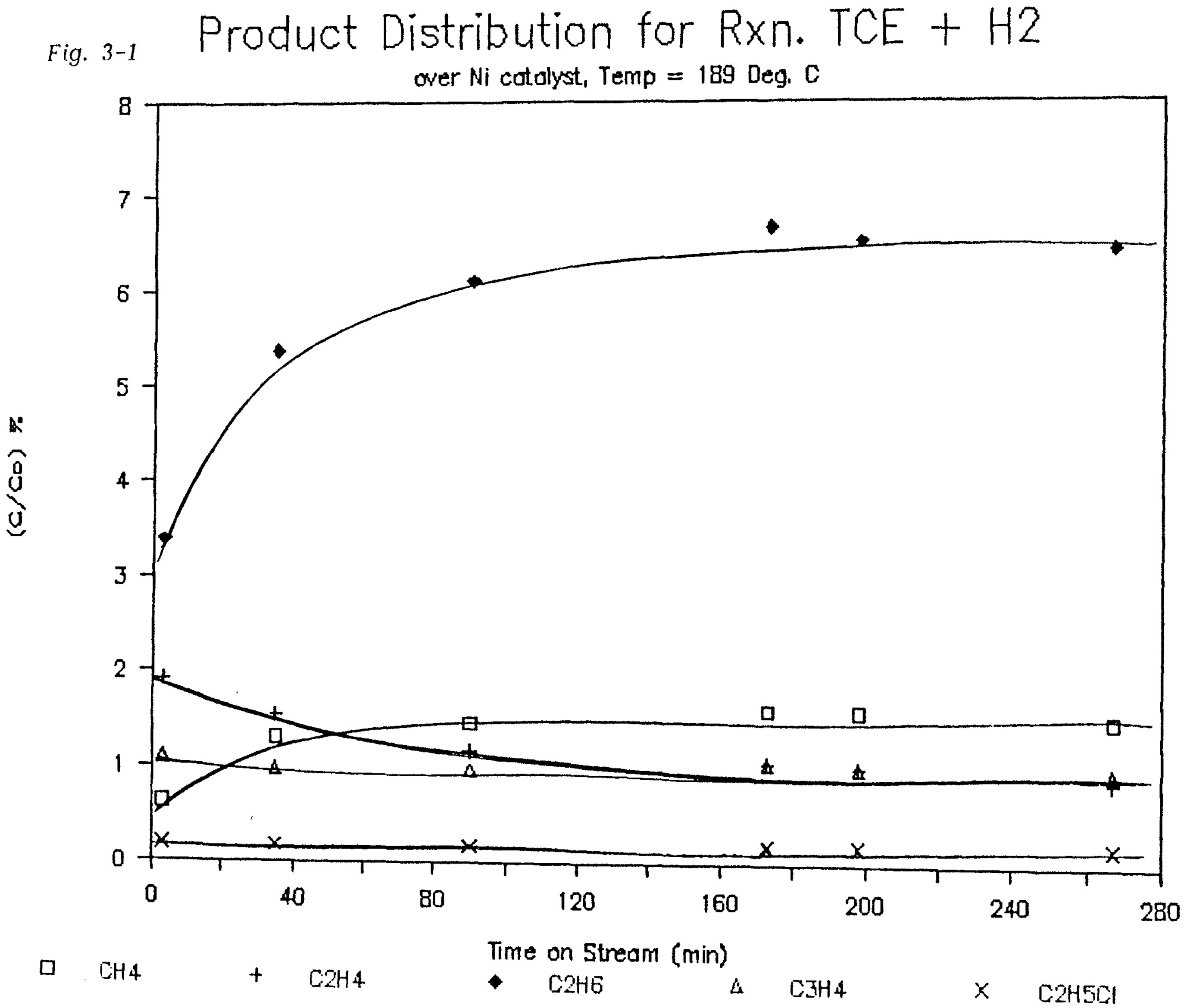

Product Distribution for Rxn. TCE + H2
over Ni catalyst, Temp = 189 Deg. C
(C/Co) %
8
7
6
5
4
3
2
1
0
0
40
80
120
160
200
240
280
Time on Stream (min)
□ CH4
+ C2H4
◆ C2H6
Δ C3H4
× C2H5Cl

Table 3-1 Selectivity for Hydrodechlorination of Trichloroethylene over Ni catalyst at 189 Deg. C.

Time On Stream (min)	Selectivity (%)				
	CH4	C2H4	C2H6	C3H4	C2H5Cl
W/Vo = 7.168*E-05 (kg-hr/lit)					
3.00	8.56	26.65	47.09	15.12	2.59
35.00	13.90	16.42	57.46	10.46	1.76
90.00	14.78	11.84	61.94	9.74	1.70
173.00	15.16	9.93	63.32	9.88	1.71
198.00	15.43	9.71	63.43	9.66	1.77
267.00	15.06	8.74	64.74	9.61	1.85
W/Vo = 3.831*E-05 (kg-hr/lit)					
4.00	7.61	29.09	44.76	14.46	4.08
35.00	13.94	21.65	51.90	10.38	2.13
65.00	14.32	16.91	56.61	10.05	2.11
96.00	14.50	15.21	58.16	10.06	2.06
127.00	14.86	13.99	59.11	10.02	2.01
200.00	14.78	12.15	60.86	10.13	2.08
261.00	15.11	11.28	61.51	9.98	2.11
W/Vo = 2.2909*E-05 (kg-hr/lit)					
6.00	8.17	38.06	38.66	12.34	2.77
32.00	13.71	26.49	48.65	9.07	2.08
60.00	14.43	23.18	51.77	8.69	1.93
91.00	15.08	21.22	53.23	8.61	1.87
136.00	15.44	19.44	54.86	8.40	1.87
163.00	15.28	18.49	55.75	8.60	1.89
192.00	14.95	17.86	56.80	8.46	1.92
220.00	15.62	17.19	56.77	8.49	1.93
248.00	15.57	16.84	56.94	8.73	1.92
275.00	15.42	16.27	57.79	8.55	1.96

Fig. 3-2

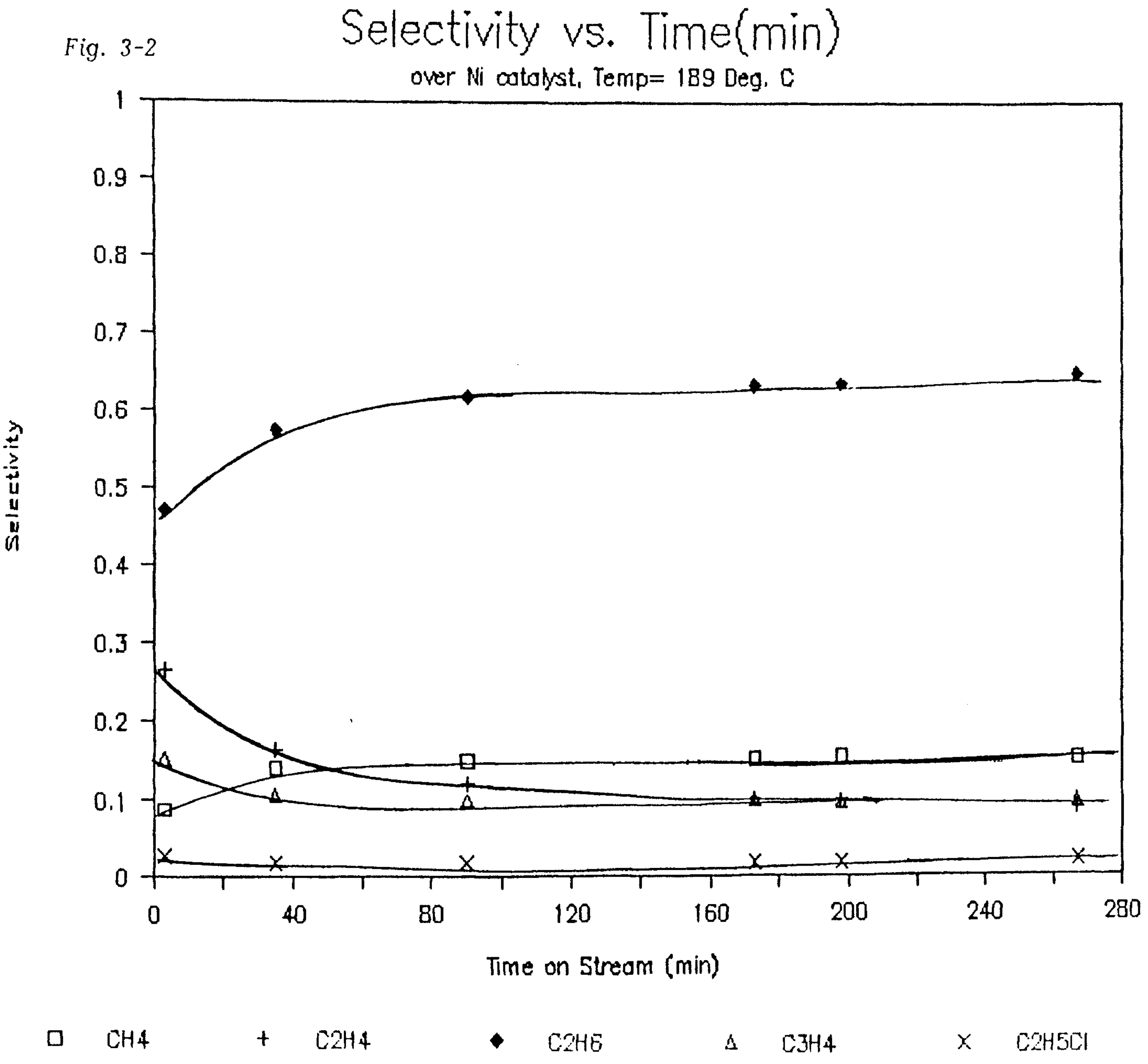
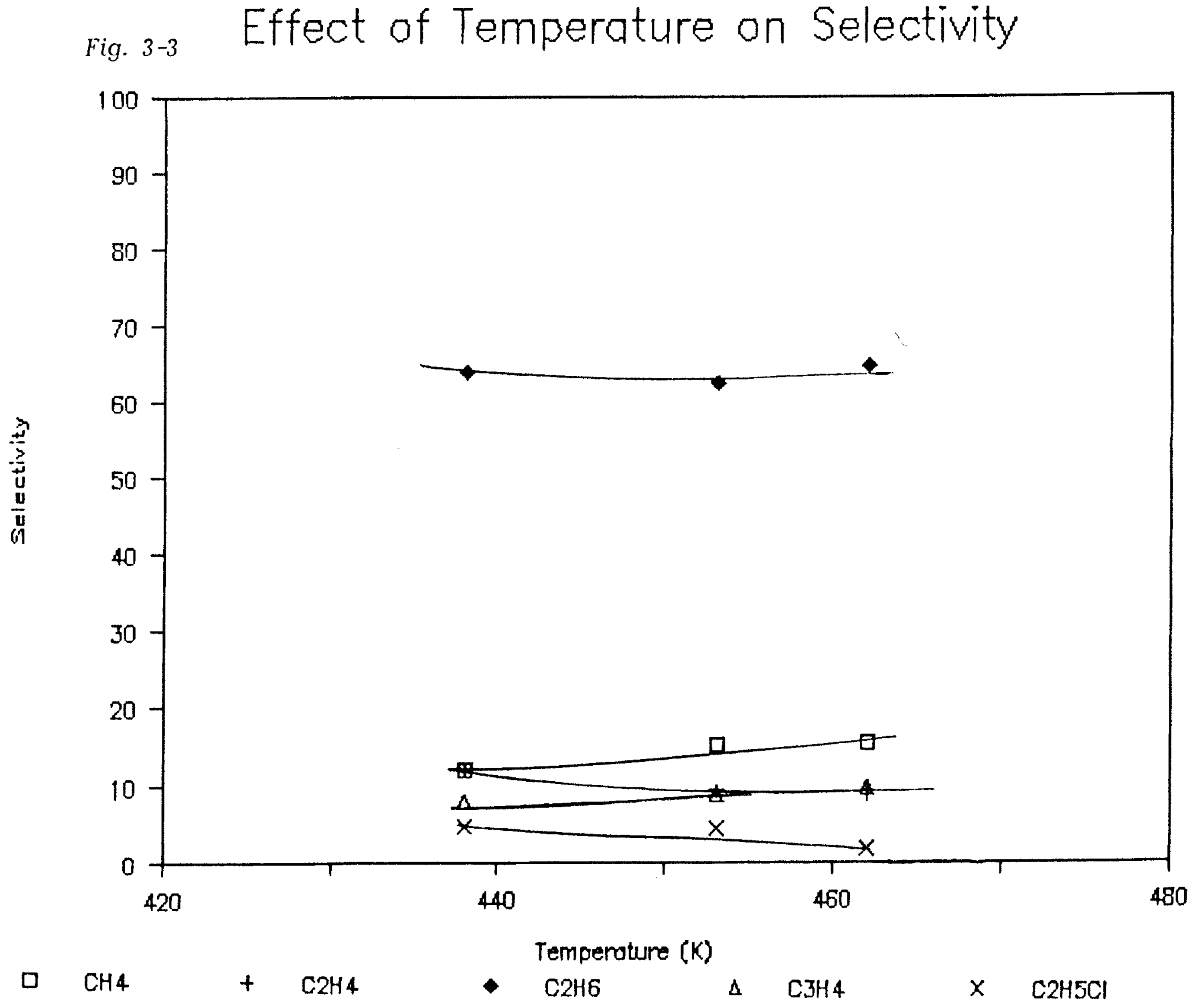

Selectivity vs. Time(min)
over Ni catalyst, Temp= 189 Deg. C
Selectivity
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
40
80
120
160
200
240
280
Time on Stream (min)
□ CH4
+ C2H4
◆ C2H6
Δ C3H4
X C2H5Cl

Table 3-2 Selectivity of Hydrodechlorination of Trichloroethylene at Different Temperature

Catalyst	Ni		
Total Conversion	4.98	6.78	9.95
Temperature (Deg. C)	438	453	462
CH4	11.85	15.06	15.42
C2H4	11.78	9.15	8.74
C2H6	63.75	62.28	64.75
C3H4	7.87	8.63	9.61
C2H5Cl	4.64	4.22	1.76

Fig. 3-3


Effect of Temperature on Selectivity
Selectivity
100
90
80
70
60
50
40
30
20
10
0
420
440
460
480
Temperature (K)
□ CH4
+ C2H4
◆ C2H6
Δ C3H4
× C2H5Cl

165 to 189°C, decreased selectivity for ethyl chloride favoring production of hydrocarbon at higher temperature. Selectivity of ethylene decreases 30 % with increase in selectivity for methane as temperature is increased from 165 to 189°C. Selectivity of ethane is not effected in the temperature range studied. A less detailed study at 320°C showed a selectivity of 50 % for methane, which exceeded that for ethane 25 %.

3.4.1 Effect of Residence Time:

The effect of residence time on total conversion and selectivity is given in Table 3-3. It shows the change in selectivity of products with residence time at 165, 180, 189°C. The decrease in total conversion with decrease in residence time was observed. Selectivity at different residence time and at different temperature is shown in Figures 3-4, 3-5, and 3-6. Selectivity for methane, propyne and ethyl chloride are unaffected by residence time. Increasing the residence time from 0.0825 to 0.258 (kg-sec/lit), decreased selectivity of ethylene 9 %, with increase in selectivity for ethane; suggesting ethylene is a intermediate product which is further hydrogenated to ethane at increased residence time.

3.4.2 Reaction Kinetics:

In this study hydrogen used to carry the reagent vapor into reactor and was in excess. The reaction was carried out at one atmosphere total pressure and partial pressure of trichloroethylene was 20 torr for all temperatures studies.

Table 3-3 Selectivity of Hydrodechlorination of Trichloroethylene over nickel catalyst at different residence time and temperature

(a) at 165 Deg. C

Residence Time(kg-hr/lit)	7.168E-5	3.8314E-5	2.2909E-5
Total Conversion	4.98	4.7	3.48
Selectivity (%)			
CH4	12	13.73	12.2
C2H4	11.78	17.89	18.81
C2H6	63.54	59.29	57.7
C3H4	7.35	6.58	7.56
C2H5Cl	4.64	2.5	3.72

Fig. 3-4 Effect of Residence Time on Selectivity

Rxn. TCE + H2 over Ni catalyst at T=165

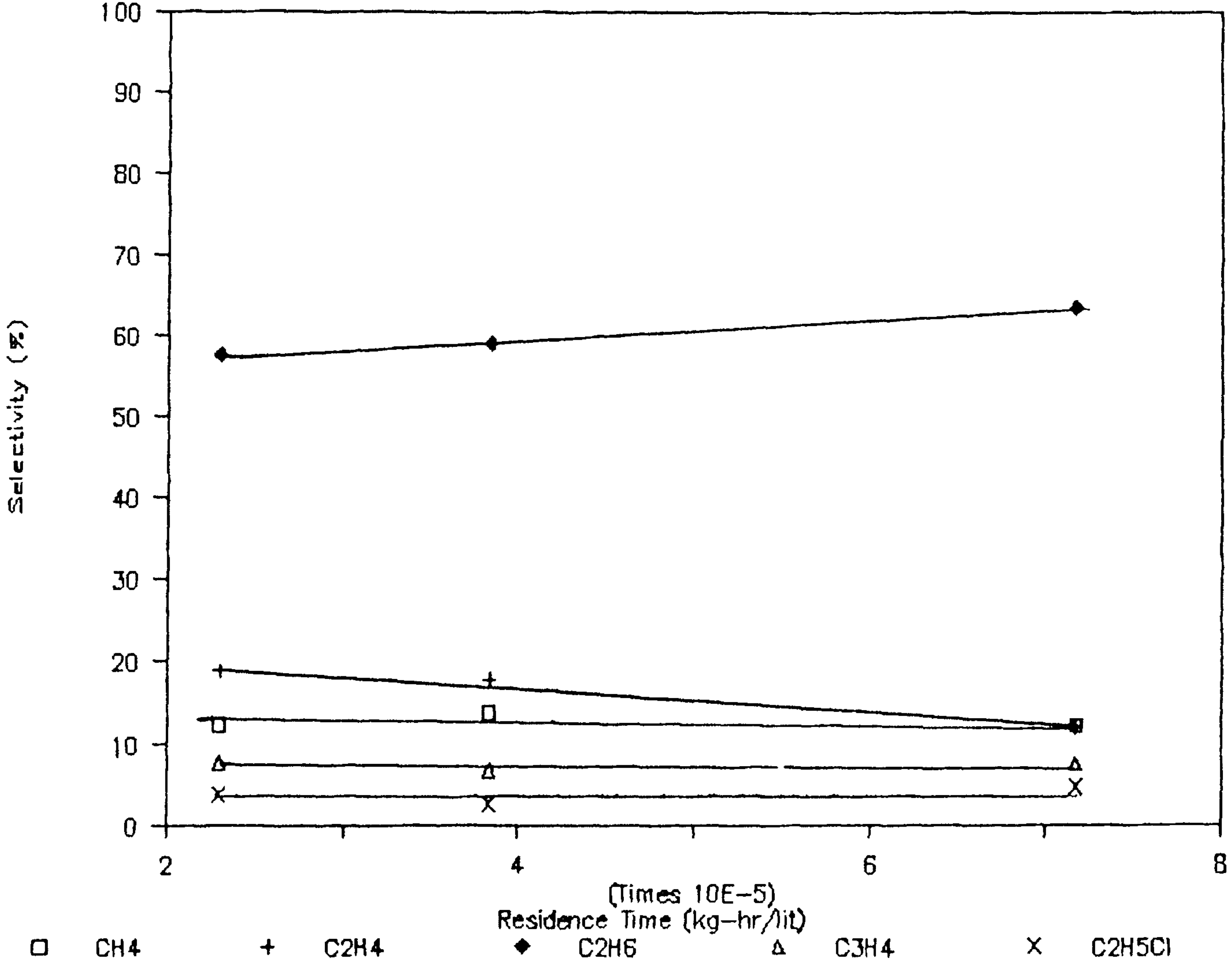


Table 3-3 Selectivity of Hydrodechlorination of Trichloroethylene over nickel catalyst at Different Residence Time and Temperature

(b) at 180 Deg. C

Residence Time(kg-hr/lit)	7.168E-5	3.8314E-5	2.2909E-5
Total Conversion	6.78	5.68	4.93
Selectivity (%)			
CH4	15.67	15.16	14.96
C2H4	9.15	12.29	15.19
C2H6	62.28	61.35	57.26
C3H4	8.63	8.11	8.7
C2H5Cl	4.22	3.08	3.59

Fig. 3-5

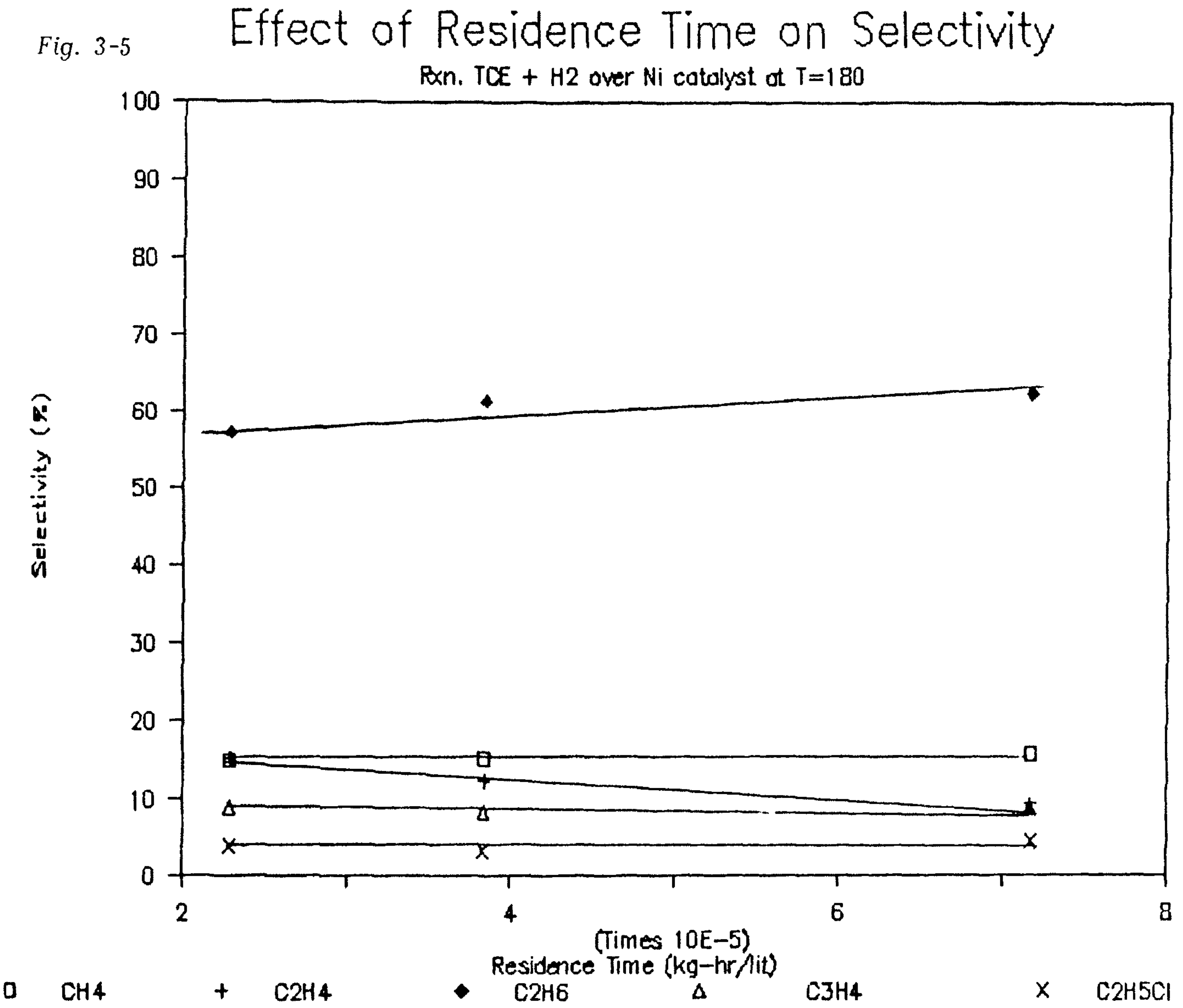
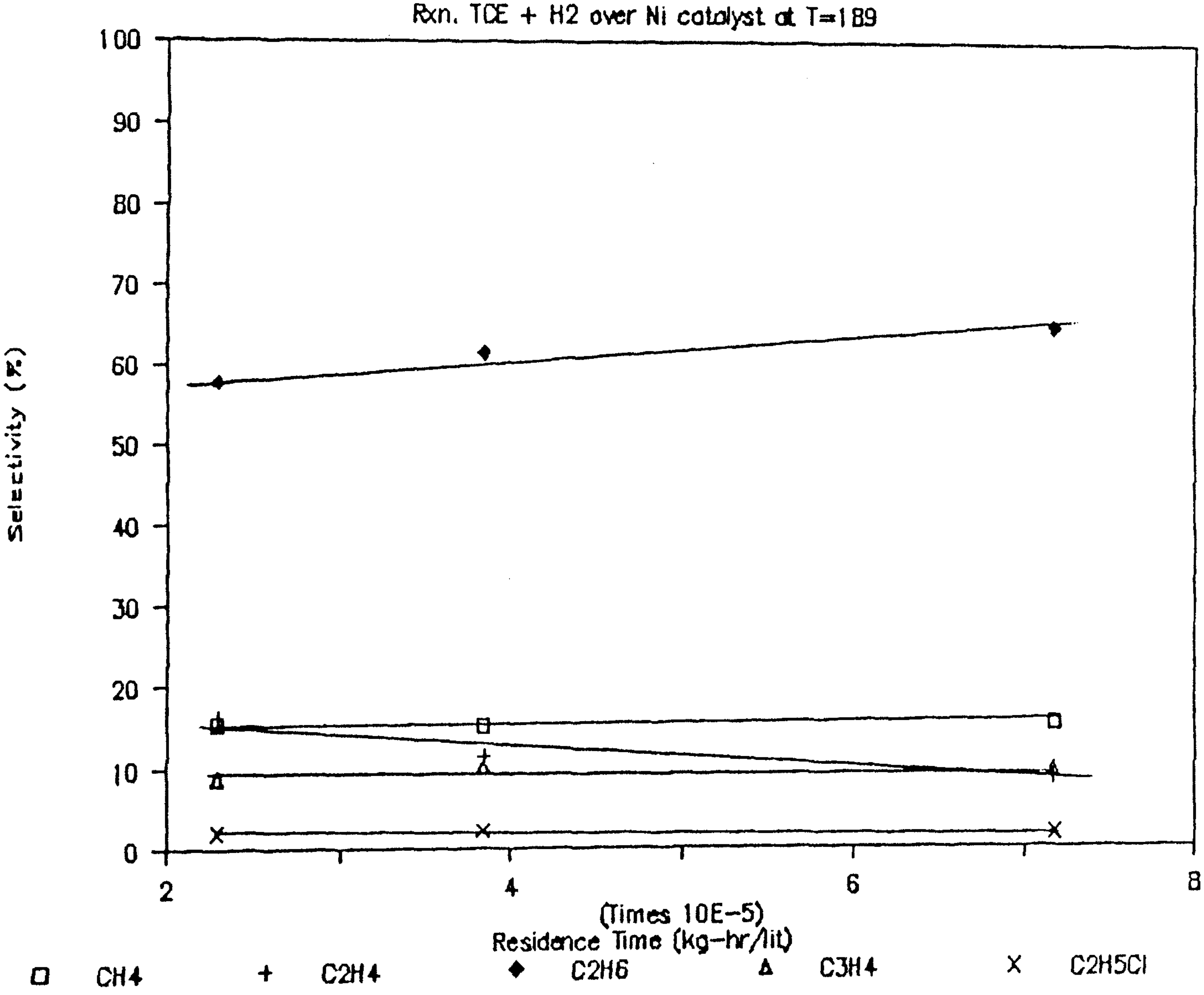

Effect of Residence Time on Selectivity
Rxn. TCE + H2 over Ni catalyst at T=180
Selectivity (%)
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
(Times 10E-5)
Residence Time (kg-hr/lit)
□ CH4
+ C2H4
◆ C2H6
Δ C3H4
X C2H5Cl

Table 3-3 Selectivity of Hydrodechlorination of Trichloroethylene over nickel catalyst at Different Residence Time and Temperature

(c) at 189 Deg. C

Residence Time(kg-hr/lit)	7.168E-5	3.8314E-5	2.2909E-5
Total Conversion	9.95	9.1	8.42
Selectivity (%)			
CH4	15.42	15.11	15.42
C2H4	8.74	11.28	16.27
C2H6	64.74	61.51	57.79
C3H4	9.61	9.98	8.66
C2H5Cl	1.76	2.09	1.94

Fig. 3-6 Effect of Residence Time on Selectivity



An integral method was used to evaluate data under assumption of first order reaction with respect to trichloroethylene.

The performance equation is<20>:

$$\ln(1/(1-x)) = t * k,$$

where x is conversion of trichloroethylene, k is rate constant and t is defined as W/V^{o}, where W is weight of the catalyst and V^{o} is volumetric flow rate of reactant. Fig. 3-7 show kinetic parameters obtained for this reaction and indicates the reaction followed pesudo first order theory with rate constants in Table 3-4.

The Arrhenius plot is as shown in fig. 3-8, and yields an activation energy of 7.0 kcal/mole for the hydrodechlorination of trichloroethylene over nickel catalysts.

Table 3-4 Kinetic parameters for reaction trichloroethylene with hydrogen over Ni catalyst.

T(^{o}C)	k(lit/kg-hr)
165	353
180	481
189	546

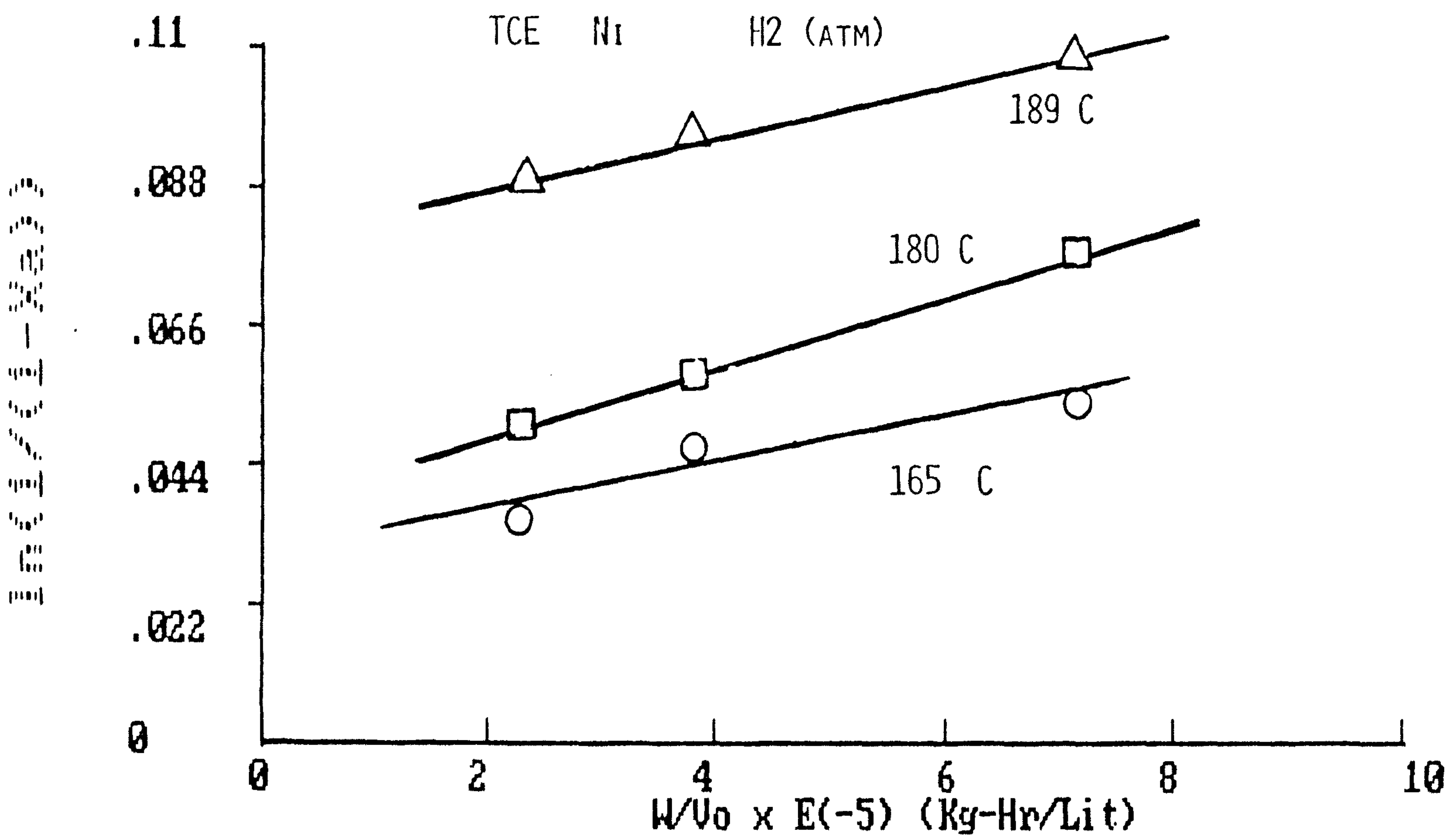


Fig. 3-7 Plot of ln(1/(1-x)) vs. Residence Time

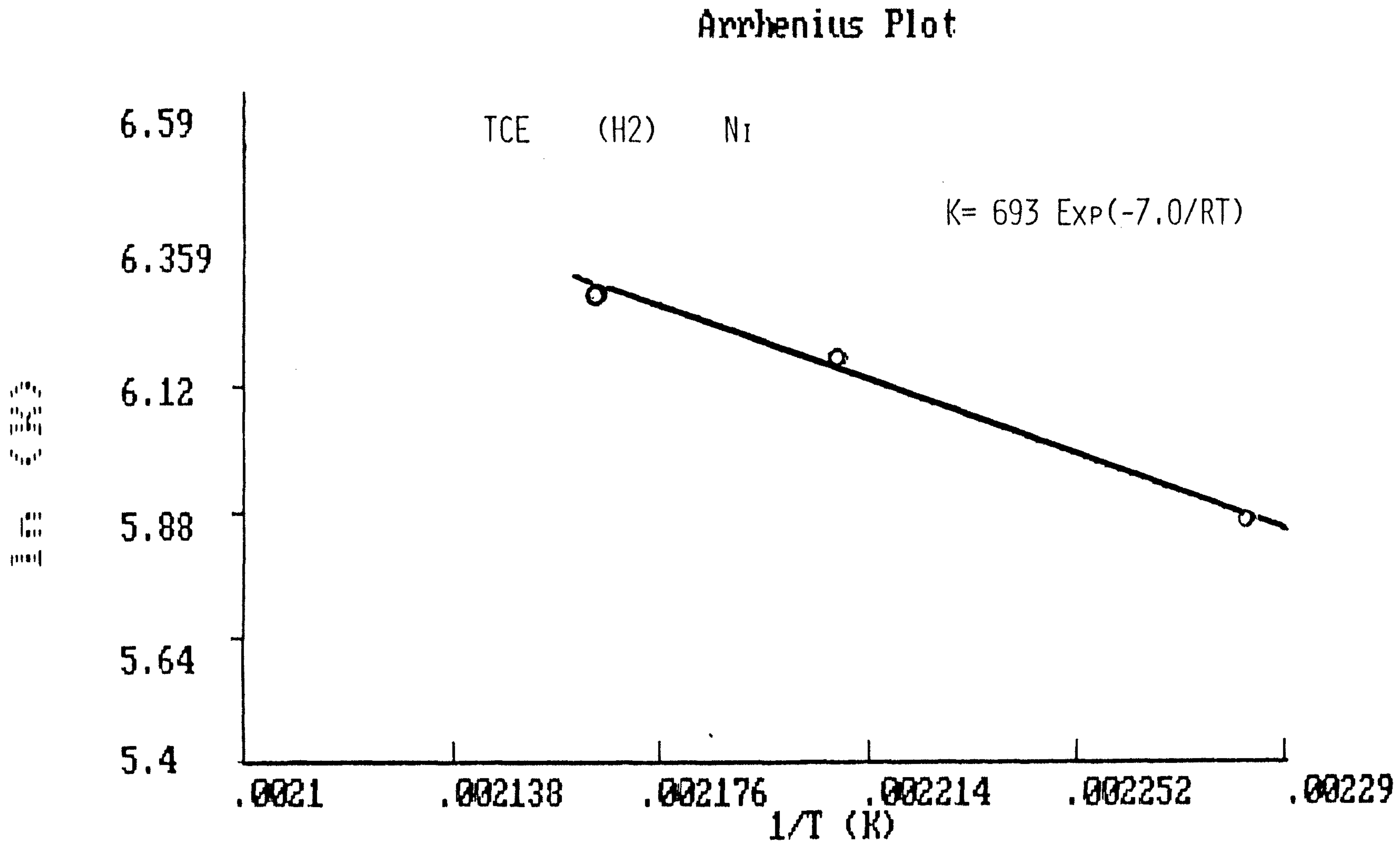


Fig. 3-8 Arrhenius Plot for Rxn. TCE + H_2 over Nickel

REFERENCES

1. Barneveld, V.and Ponec, V., " Reactions of CH_xCl_{x-4} with Hydrogen: Relation to the Fischer-Tropsch Synthesis of Hydrocarbons", J. of Cata., 88, 382, 1984.
2. Bond,G. C., " Catalysis by Metals ", Academic Press, New york, 1962.
3. Baltzly,R. and Phillips, A. , Journal of Amer. Chem. Soc., 68, 261, 1946.
4. Besprozvannyi, M. A., Kononov, N. F., and Kharhmov, V. V., IZV, Akad. Nawk. SSSR, Ser. Khim, 1345, 1965.
5. Burhan, M., Master of Science Thesis, New Jersey Inst. of Technology, 1985.
6. Beeck, O., Proc. Roy. Soc. A., 118-128, 1950.
7. Campbell, J. S. and Kemball, C.,"Catalytic Fission of Carbon-Halogen Bonds: Part 1-Reactions of Ethyl Chloride and Ethyl Bromide with Hydrogen Over Evaporated Metal Films", Trans. Faraday Society, 57, 809, 1961.
8. Chemical Engineering News, 56, 7 (July 24, 1978).
9. Czarny,Z., and Oszczudlowski, J.," Influence of The Chemical Composition of The Catalyst on The Dehydrochlorination of 1,2 Dichloroethane", React. Kinet. Catal. Lett., Vol. 25, Nos. 3-4, 195, 1984.
10. Chen, Y. M., " Hydrodechlorination Reactions on Silica Supported Rhodium catalysts ", Masters of Science Thesis, (New Jersey Institute of Technology, 1987).
11. Cheremisinoff, P. N., Pollution Engineering, Feb., pp.

42-49, 1987.

12. Dodson, D. A., and Rase, F. H., " Methylene Chloride from Chloroform by Hydrochlorination", Ind. Eng. Chem. Prod. Res. Dev., Vol. 17, No. 3, 1978.

13. Emmett, P., " Catalysis ", Vol. IV, 473, 1956.

14. Graham, T., Proc. Roy Soc., 36, 63 (1868).

15. Ham, G. E. and Coker, W. P.," Selective Hydrogenation of Haloalkenes to Haloalkanes", J. of Org. Chem., 29, 194, 1964.

16. Horner, L., Schlafer, L., and Kammerer, Ber., 92, 1700, (1959)

17. Hickok, R. L., Ph.D. Dissertation, Dept. of Chemistry, University of Colorado, 1957.

18. Kindler, K., Oelschlager, H., and Henrich, P., Ber., 86, 167, 1953.

19. Lycourghiotis, A., Katsanos, N., and Hadzistelios, I., " Catalytic Dehydrodehalogenation on Alumina Modified with Alkali Metal Chlorides", J. of Catalysis, 36, 385, 1975.

20. Levenspiel, O., Chemical Reaction Engineering , 2nd Edn., John Wiley, New York, 1972

21. Lacher, J. R., Kianpour, A., Oetting, F., and Park, J., Trans. Faraday Soc., 52, 1500, 1956.

22. Manson, L. and Unget, S., " Hazardous Material Incinerator Design Criteria, USEPA 600/2-79-198 NTIS PB 80 -131964 (1979).

23. Mochida, I., Take, J., Saito, Y. and Yoneda, Y.,

" Linear Free Energy Relationship in Hetrogeneous Catalysis. VI. Catalytic Elimination Reaction of Hydrogen Chloride from Chloroethanes on Solid Acids and Bases", J. of Organic Chemistry, 32, 3894, 1967.

24. Mochida,I. and Yoneda, Y., " Elimination Reaction of Hydrogen Chloride from 1,1,2-Trichloroethane on Ion Exchanged Molecular Seives", J. of Org. Chem., 33, No. 5, May 1968.

25. Mochida,I. and Yoneda, Y., " Dehydrodechlorination and Dechlorination of Chloroethanes on Chromia Catalysts ", J. of Org. Chem., 33, No. 5, May 1968.

26. Noelke,C. J. and Rase, H. F., " Improved Hydrodechlorination Catalysis: Chloroform Over Platinum-Alumina with Special Treatment.", Ind. Eng. Chem. Prod. Res. Dev., Vol. 18, No. 4, 1979.

27. Noller, H., Hantshce, H., and Andreu, P., " On The Mechanism of Contact Eliminations : IX. HCl Elimination from Gaseous 2,3-Dichlorobutane on $CaCl_2$, CaO, and Al_2O_3 ", J. of Catalysis, 4, 354, 1965.

28. Noller, H. and Kladnig, W., " Elimination Reactions of 1-Chlorobutane and 2-Chlorobutane Over X and A Zeolites Containing Different Cations", J. of Catal., 29, 385, 1973.

29. Ritter,E., Master of Science Thesis, (New Jersey Institute of Technology, 1986)

30. Sinfelt,J. and Yates, D., " Catalytic Hydrogenation of Ethane over the Noble Metals of Group VIII", J. of

Catalysis, 8, 82, 1967.

31. Somorjai, G. A., J. Phys. Chem, 89, 1598, 1985.

32. Venuto, P. B., Givens, E. N., Hamilton, L. A. and Landis, P. S., " Organic Reactions Catalyzed by Crystalline Aluminosilicates: V. Dehydrodehalogenation and Related Reactions", J. of Catalysis, 6, 253, 1966.

33. Vannice, M. A., " The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures Over the Group VIII metals.", Journal of Catalysis, 40, 129, 1975.

34. Weiss, A. H. and Krieger, K. A., " Hydrodechlorination Kinetics And Reaction Mechnanisms.", J. of Catalysis, 6, 167, 1966.

35. Witt,D. S., Wu, E., Loh, K., Tang, Y., " Heterogeneous Hydrogenolysis of Some Fluorocarbons", J. Of Catalysis, 71, 270, 1981.

36. Weiss, A., Gambhir, B. and Leon, R.," Hydrodechlorination of Carbon Tetrachloride", J. of Cata., 22, 245, 1971.

37. Yang,Y. D., " Reactions of Chlorocarbon Species with Hydrogen over Palladium on Alumina and Zeolite Catalysts " (Ph. D. Thesis, New Jersey Institute of Technology, 1986).