

KINETICS OF THE REACTION OF
CHLOROMETHYL METHYL ETHER WITH
2-METHYL-1-BUTENE

By

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

The reaction of chloromethyl methyl ether with olefins was investigated. Kinetics of the reaction between chloromethyl methyl ether and 2-methyl-1-butene in the presence of diethyl ether was determined. A Lewis acid, titanium tetrachloride, was used as a catalyst in all experiments. The product γ -chloroethers were isolated and characterized by infrared spectra.

When an aliphatic ether was initially present, the reaction was second order overall, first order in each reactant. When the aliphatic ether was not initially present the apparent order with respect to chloromethyl methyl ether increased as the reaction proceeded. It is proposed that the product γ -chloroether competes with the chloromethyl methyl ether for coordination with the catalyst. The aliphatic ether added to the starting mixture has this same effect and reduces the apparent autoinhibition of the reaction by the product.

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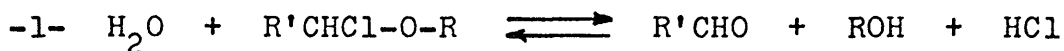
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INTRODUCTION

The study of α -haloethers dates back to 1839, when Malaguti isolated α -chloroethyl ethyl ether from the chlorination of diethyl ether(1). Since that time many people have studied the reactions of the α -haloethers. Two excellent review articles summarize most of the literature through 1966(1, 2).

α -Haloethers have steadily increased in their importance to the chemical industry. They are highly reactive and have been used as chloromethylating agents. They are used in the preparation of ion exchange resins(3) and to increase chain lengths of organic compounds. There are drawbacks to their use. They react vigorously with water to decompose by the reaction:

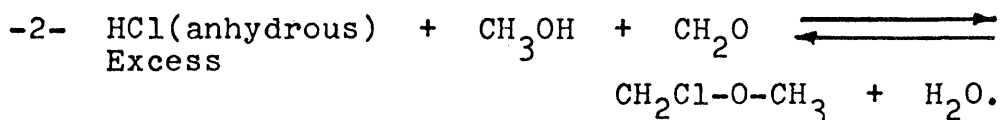


R = hydrocarbons of C₆ or less,

R' = H, or hydrocarbons of C₆ or less.

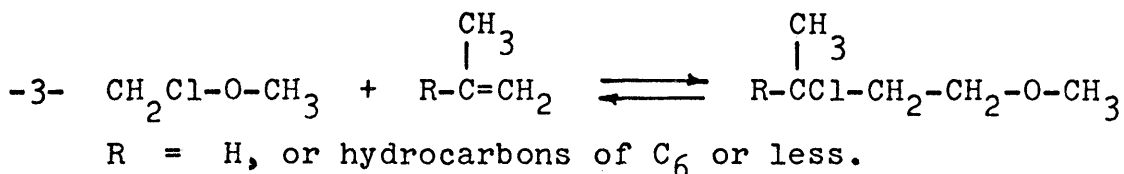
There is also a health hazard, since they have been proved to be carcinogens(4, 5). Thus special handling of α -haloethers is necessary.

α -Haloethers can be produced inexpensively by the reverse of reaction-1-. Chloromethyl methyl ether (CME) can be produced by the reaction:



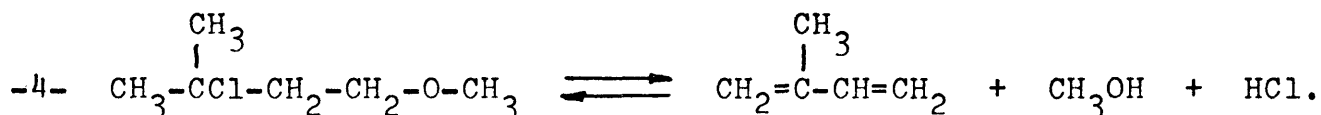
The organic phase is then separated from the concentrated HCl phase. The reaction must be cooled to decrease acetal formation(1). This method is good enough that several recent patents(6, 7, 8) make use of this method in the production of CME. Others use the same method, substituting chlorinating agents such as thionyl chloride(9), or chlorosulfonic acid(10). Other preparations include the reaction of chlorine with dimethyl ether(11) and the reaction of methylal with chloromethyl silanes(12).

Since the 1930's the reactions of α -haloethers with olefins have become the subject of considerable research(2, 13, 14). Addition across the double bond follows Markownikoff's rule, thus:



The reaction is catalyzed by Lewis acids. Most commonly used were HgCl₂, ZnCl₂, FeCl₃, BiCl₃, and AlCl₃(2). Hall, Dormish, and Hurley(15) report that on a small scale titanium tetrachloride is the best all-round catalyst, but Kelly and Hall(16) preferred zirconium tetrachloride.

Importance of the γ -chloroethers formed by the above reaction was demonstrated by Hall and co-workers(15, 16, 17, 18) in experiments in which the γ -chloroethers were pyrolyzed over solid aluminosilicate catalysts or decomposed in dipolar aprotic solvents to form conjugated dienes. Straus and Thiel (19) had proposed a similar reaction, but they suggested conversion to the alcohol followed by dehydration. The specific reaction in which Hall's group was interested was the formation of isoprene(17):

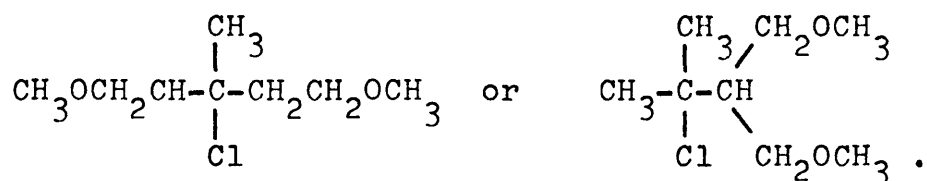


Conjugated dienes are building blocks for many polymers and are used extensively in the plastic, dye and synthetic rubber industry. The use, especially in the synthetic rubber industry, is very high and is increasing steadily(17, 20, 21, 22). Predictions are that the requirements for polyisoprene rubber will double each five years until industrial growth starts to slow near the end of this century(20, 23).

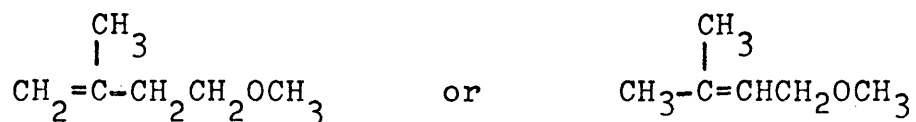
The importance of the above process for the formation of conjugated dienes becomes obvious. Recycling of methanol and hydrogen chloride from reaction -4- back to the formation of CME in reaction -2- makes this process less expensive and less wasteful than other processes using the same raw materials.

A major consideration in determining the financial feasibility of a process is whether the starting materials must be in pure form or whether they can be used in a less

expensive mixture from a refinery unit. Here is the problem with this process. Hall and co-workers(15) reported that in the presence of inert hydrocarbons, which would be present in feed from a refinery cracking unit, the yield was decreased because a by-product was formed. The by-product was suggested to be one of:



These might arise if the unsaturated ethers:



are formed from the γ -chloroether and attacked by CME.

Reactions of CME with straight chain and shorter branched chain unsaturated ethers have been studied(24, 25) and it was shown(25) that in the presence of inert solvents the rate of reaction increased as the dielectric constant of the solvent increased.

Although it is easy to understand where the by-product might be formed, there is more than meets the eye. Hall and co-workers(15) showed that the unsaturated ethers are much less reactive than the olefin under comparable conditions. They proposed that "... a transient reaction intermediate, possibly still complexed with the catalyst ..." seemed to be a likely source of these by-products.

Kinetics is a useful tool in determining mechanisms of reactions. Frost and Pearson(26) offer the following definition of kinetics: "Kinetics deals with the rate of chemical reactions, with all factors which influence the rate of reaction, and with the explanation of the rate in terms of the reaction mechanism." Thus, to understand fully the kinetics and mechanism of a reaction, an exhaustive study must be done to determine the rate of the reaction under a great number of different conditions(27, 28, 29). The present study is a first necessary step in the elucidation of the kinetics and mechanism of the reaction of CME with olefins.

Shikhmamedbekova and co-workers studied the kinetics of reactions between CME and: 2-chloro-1,3-butadiene(30); 1,3-pentadiene(31); and allylic ethers(25), which indicated that this kind of reaction is second order overall. Most of these reactions were run using diethyl ether as the solvent. The study concerned with allylic ethers was the only exception, in that study the effects of four solvents on the reaction rates was observed. Reactants and products were followed by the use of a gas chromatograph. With this evidence, it was logical to start out by demonstrating whether the reaction of CME with branched olefins is also first order in each reactant.

For a second order reaction, first order in each reactant, with the stoichiometry: $A + B = \dots$, the rate is expressed

as(32):

$$\frac{1}{A_0 - B_0} \ln \frac{B_0 A}{A_0 B} = k t.$$

If reactants are initially in stoichiometric proportions, then $A = B$ throughout the reaction and the rate is expressed by(32):

$$1 / A - 1 / A_0 = k t.$$

This equation also holds for a reaction which is second order in a single component.

If initial concentrations of the compounds are greatly different, say a ratio of twenty to one or greater, then in the course of a reaction, one compound will change its concentration by only 5% or less. In this case the reaction may be considered pseudo-first order and the rate expression is(32, 33):

$$\ln A - \ln A_0 = e^{-k' t} \quad \text{where } k' = k B_0.$$

To prove whether a reaction is truly second order, first order in each of two reactants, it is necessary first to prove stoichiometry, then to follow the concentrations of reactants through the kinetic region varying the concentrations of each reactant under pseudo order conditions, and/or under stoichiometric conditions. The portion of the reaction during which data is taken is preferred to be the time required for the reaction to go from 0 to 90% completion (33, 34).

EXPERIMENTAL WORK

Instrumentation

Balance

An Ainsworth Right-A-Weigh analytical balance was used to weigh out standards and to weigh aliquots from the reactions.

Infrared Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer 521 Grating Infrared Spectrophotometer. The chemicals were all liquid, and analyses were made using matched sodium chloride fixed thickness cells of 0.022 mm pathlength, using an empty cell as the reference.

Gas Liquid Chromatography

Chromatographic analyses were done on an F & M model 720 dual column Gas Liquid Chromatograph (GLC). The columns were 0.25-in. stainless steel (12 ft.) with a packing of 15% silicone fluid SF-96 (Hewlett-Packard no. 8501 - 3420) on Chromosorb-W (Hewlett-Packard no. 8501 - 6119).

Analyses were performed by injecting the sample through an on-column-injection-port adapter.

The instrument was equipped with a programmed column temperature control: this was used extensively to compensate for the greatly differing retention times of reactants and products. Column temperatures during a single analysis were programmed to run from room temperature to 200°C in a 20 minute period.

The recorder was equipped with a Disc Integrator (Disc Instruments Inc. no. 201 - 4890), which was used to determine peak areas for all analyses.

Burets

For titrations requiring at least 10 ml of liquid, a 50 ml capacity buret which reads directly to 0.1 ml was used. For titrations requiring less than 10 ml of liquid, a 10 ml capacity buret which reads directly to 0.02 ml was used.

Constant Temperature Bath

A Blue M Electric Company Magni-Whirl refrigerated constant temperature bath was used to control the temperature for all reactions. This instrument has provision for simultaneous heating and cooling of the bath, working the two against one another to maintain a constant temperature from -5°C up to 50°C. Above 50°C the heater is worked against ambient temperature. The bath is equipped with a stirring

mechanism which does not stir vigorously. This was supplemented with an overhead electric stirrer to ensure uniform temperature throughout the bath. Under these conditions the temperature was maintained within 0.01 degree throughout the bath for periods of up to a week. This was checked by the use of a thermometer which could be interpolated to 0.01 degree. It was left in the bath at all times and moved occasionally to a new location in the bath.

Refrigerator

A special explosion proof refrigerator was used for the storage of volatile hazardous chemicals.

Reagents and Solvents

Nitrogen

High purity dry grade Nitrogen from the Linde Division of Union Carbide was used. This was passed through a drying tube, 4-in. by 1/2-in. diameter, full of calcium chloride.

Titanium Tetrachloride

Titanium tetrachloride was 99% pure grade obtained from Matheson Coleman and Bell. It was distilled under dry nitrogen and the fraction distilling at 127 - 128°C at 620 torr was used. The purified material was stored in a glass stoppered erlenmeyer flask wrapped with aluminum foil to exclude light. This flask was stored in a desiccator over anhydrous calcium chloride.

Hydrocarbons

All hydrocarbons used were Phillips Petroleum pure grade. They were stored in their original containers in the refrigerator over molecular sieves (Hewlett-Packard no. 8501 - 5208).

Chloromethyl Methyl Ether

Chloromethyl methyl ether (CME) was Eastman Kodak's yellow lable grade. This was distilled under dry nitrogen according to the method of Hall, Dormish, and Hurley(15); 5g of $TiCl_4$ was added to each 100g of CME to remove the methylal contaminant before distillation. The 53 - 55°C fraction (620 torr) was stored in a glass stoppered erlenmeyer flask wrapped with aluminum foil to exclude light. The flask was stored in a desiccator over anhydrous calcium chloride.

Water

Deionized water from the school's deionizer was distilled three times, once from basic potassium permanganate to destroy trace organics, then with no special conditions to ensure removal of trace metals, and the third time under a nitrogen atmosphere to remove carbon dioxide. The water was stored in glass stoppered Pyrex gallon bottles under nitrogen.

Sodium Hydroxide

Sodium hydroxide used in titrations was analytical Reagent grade from Mallinckrodt. Sodium hydroxide solutions were made with the distilled water described above and stored

in polyethylene bottles under a nitrogen atmosphere. They were standardized against potassium hydrogen phthalate (Matheson Colman & Bell analytical reagent grade), and also against samples similar to those which would be used in actual experiments. These methods agreed to within 0.5%. Concentrations used were 0.0512 N and 0.0457 N.

2-Pyrrolidone

2-Pyrrolidone was produced by K & K Laboratories, and used directly. This amide is a base and was used for dehydrochlorination procedures.

3-Chloro-3-methylbutyl Methyl Ether

3-Chloro-3-methylbutyl methyl ether (CMBME) was prepared by the addition of CME to isobutylene under dry nitrogen, then vacuum distilled. The heart cut distilled at 69 - 71°C at 70 torr; it had a refractive index of 1.4208 at 21°C, literature value 1.4216 at 20°C(15). The infrared spectrum showed the characteristic absorptions reported(15) at 1370 and 1385 cm^{-1} for the C-H symmetric deformation of the methyl groups, 1113 cm^{-1} due to the asymmetric stretching of the ether, and 582 cm^{-1} due to the chlorine atom C-Cl stretching(35, 36). This spectrum is illustrated in figure 1.

3-Chloro-3-methylpentyl Methyl Ether

3-Chloro-3-methylpentyl methyl ether (CMPME) was prepared by the addition of CME to 2-methyl-1-butene under an atmosphere

of dry nitrogen, and purified by vacuum distillation. The heart cut distilled at 46 - 50°C at 10 torr; it had a refractive index of 1.4338 at 24°C. The infrared spectrum showed a 3-methyl adsorption at 1380cm^{-1} , an ether absorption at 1110cm^{-1} , and a low intensity absorption at 570cm^{-1} due to the tertiary chlorine atom(35, 36). This spectrum is illustrated in figure 2.

3-Chloro-3-methylhexyl Methyl Ether

3-Chloro-3-methylhexyl methyl ether (CMHME) was prepared by the addition of CME to 2-methyl-1-pentene under dry nitrogen. This product was purified by vacuum distillation at 51 - 53°C at 5 torr. The infrared spectrum showed the absorption due to the 3-methyl group at 1378cm^{-1} , an ether absorption at 1110cm^{-1} , and a low intensity absorption at 570cm^{-1} believed to be due to the tertiary chlorine atom(35, 36). This spectrum is illustrated in figure 3.

Mixture of 3-Methyl-(2&3)-pentenyl Methyl Ethers

A mixture of 3-methyl-2-pentenyl and 3-methyl-3-pentenyl methyl ethers was prepared according to the method of Hall, Dormish, and Hurley(15), in which CMPME was added dropwise to N-methyl-2-pyrrolidone maintained at a temperature of 110 to 165°C. Due to the availability of 2-pyrrolidone, that chemical was used instead of the N-methyl-2-pyrrolidone. Temperature was maintained at 240°C. The lower boiling

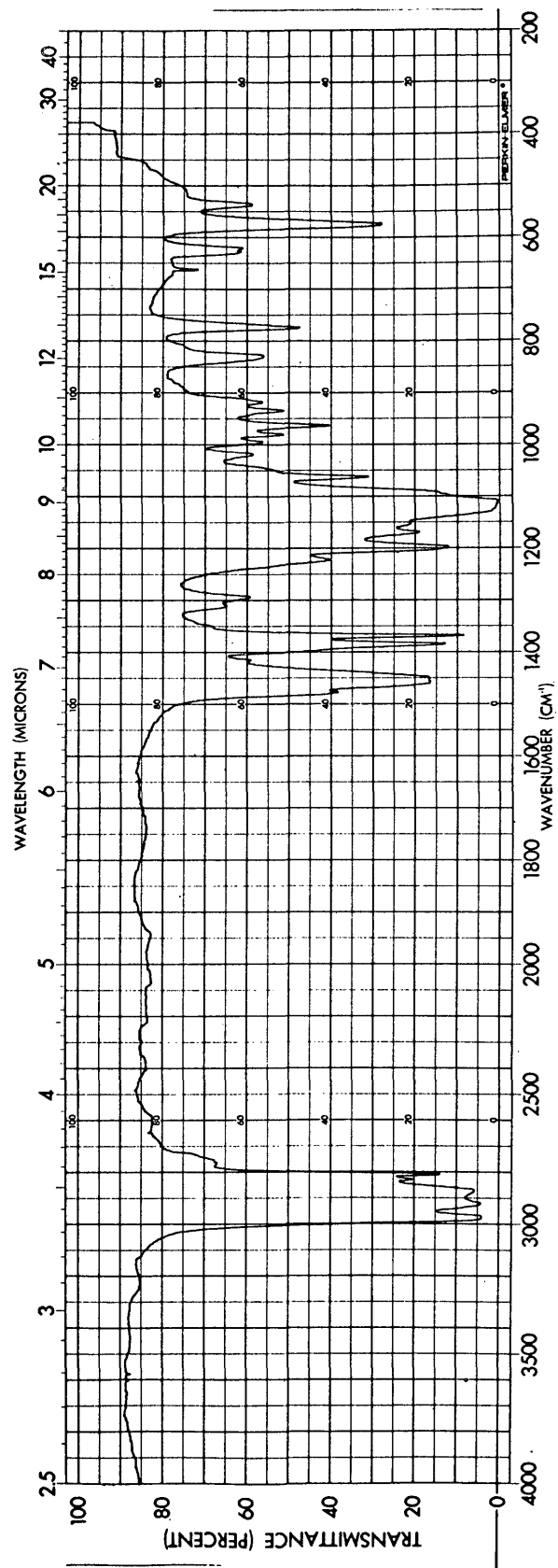


Figure 1. The infrared spectrum of 3-chloro-3-methylbutyl methyl ether.

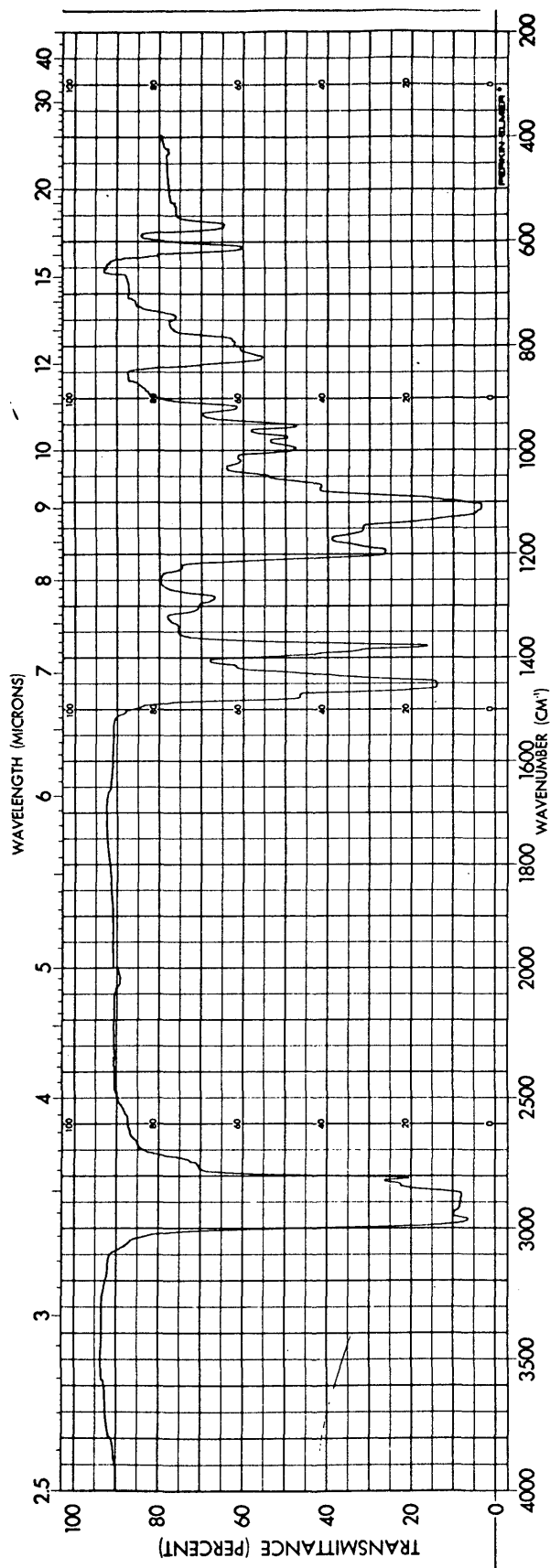


Figure 2. The infrared spectrum of 3-chloro-3-methylpentyl methyl ether.

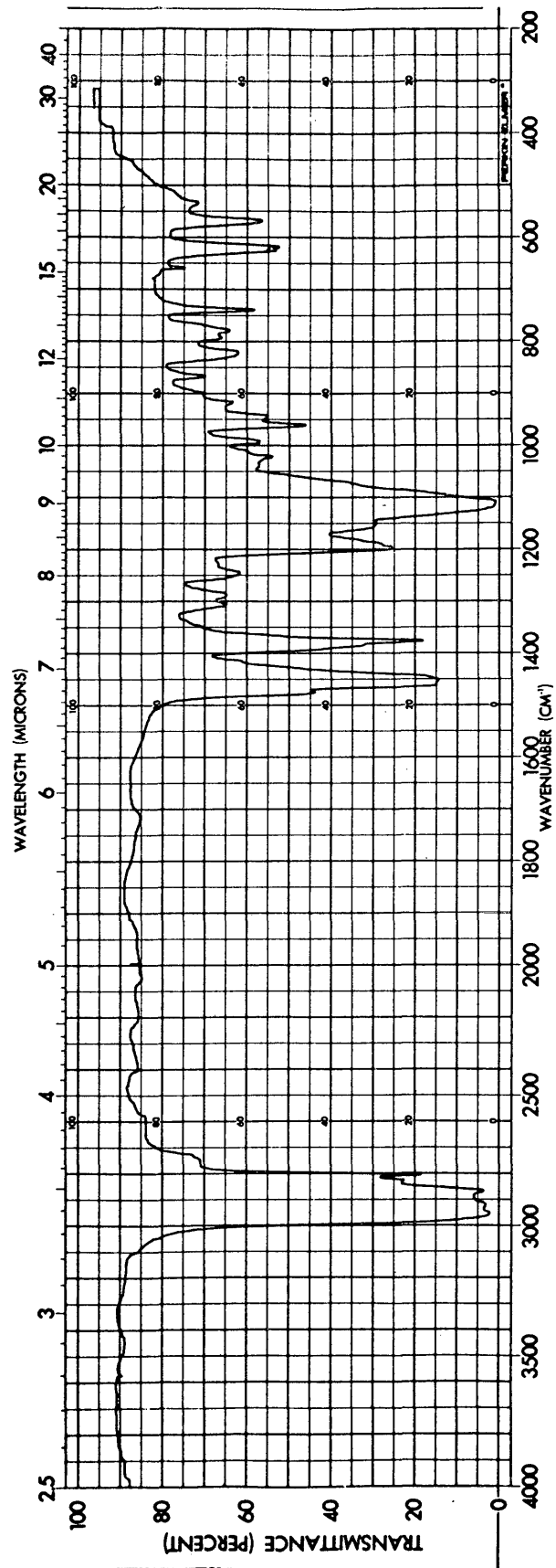


Figure 3. The infrared spectrum of 3-chloro-3-methylhexyl methyl ether.

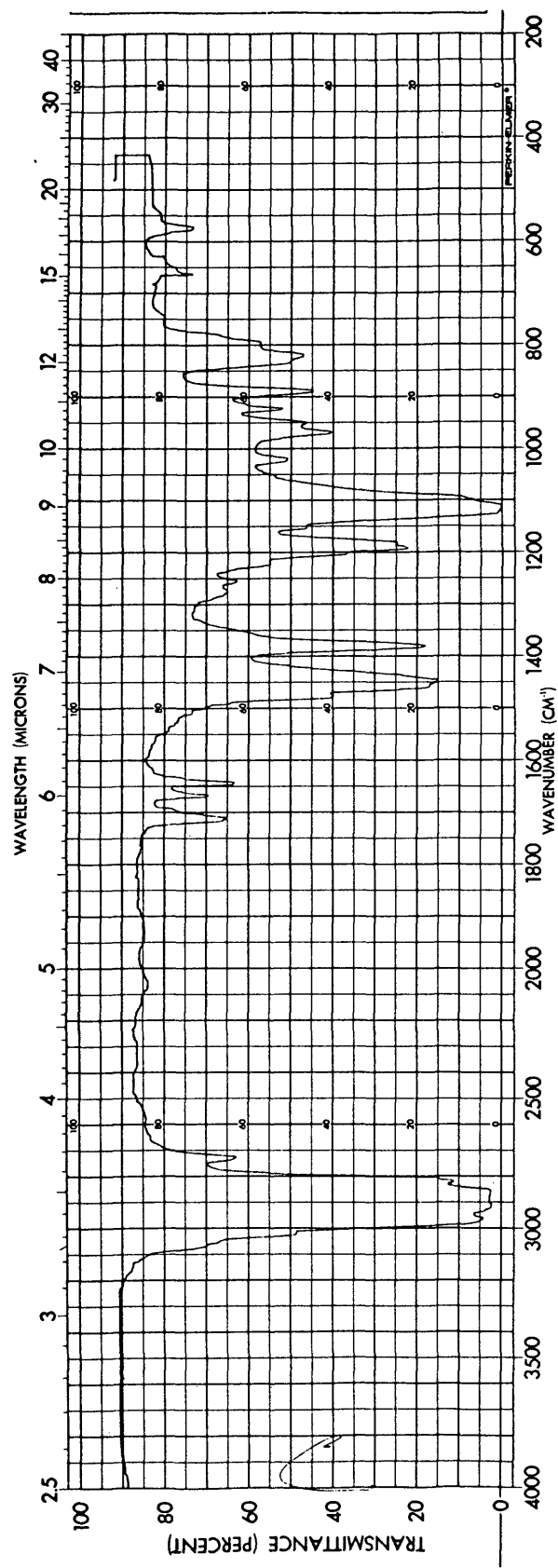


Figure 4. The infrared spectrum of the mixture of 3-methyl-2-pentenyl and 3-methyl-3-pentenyl methyl ethers.

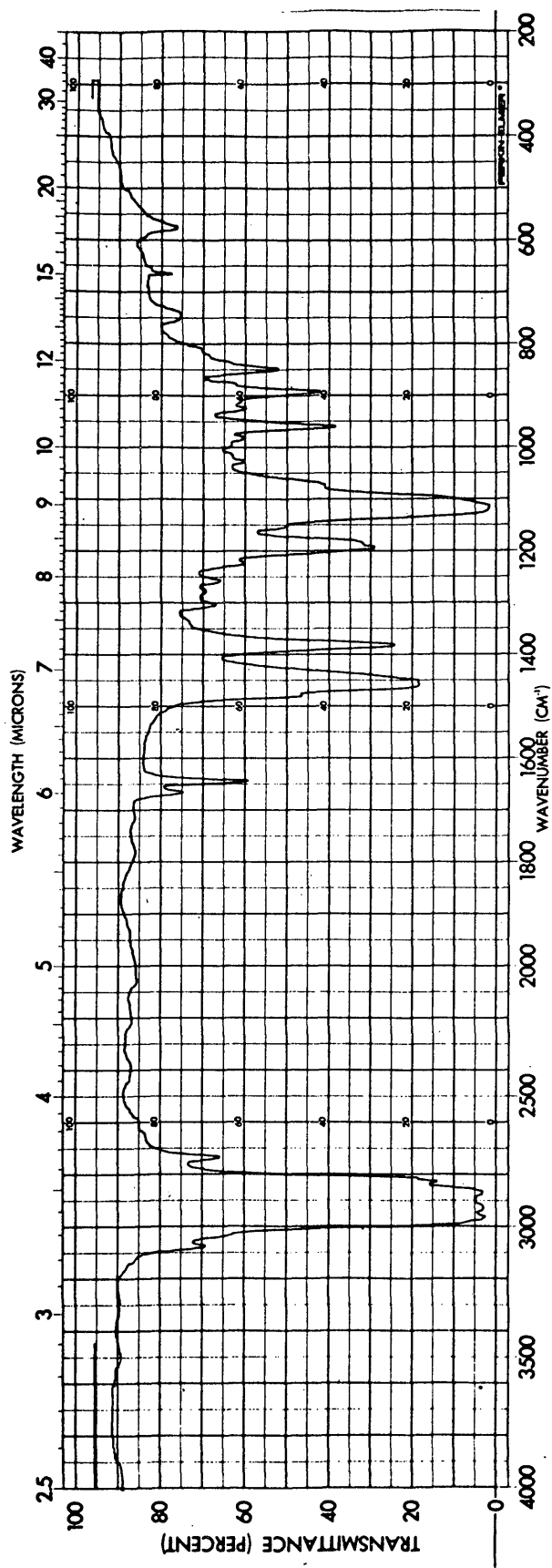


Figure 5. The infrared spectrum of the mixture of 3-methyl-2-hexenyl and 3-methyl-3-hexenyl methyl ethers.

unsaturated ethers distilled at this temperature, and were not in contact with the solution long enough to decompose to the conjugated diene. The unsaturated ether was then redistilled at 67 - 69.5°C at 100 torr; it had a refractive index of 1.4184 at 25°C. Isomers were not separated. The infrared spectrum showed the absorption due to the 3-methyl group at 1380cm^{-1} , an ether absorption at 1113cm^{-1} , and a doublet olefin absorption at 1645 and 1658cm^{-1} caused by the presence of both isomers(35, 36). This spectrum is illustrated in figure 4.

Mixture of 3-Methyl-(2&3)-hexenyl Methyl Ethers

A mixture of 3-methyl-2-hexenyl and 3-methyl-3-hexenyl methyl ethers was prepared by dropwise addition of CMHME to 2-pyrrolidone at 240°C. It was purified by vacuum distillation at 31 - 34.5°C at 7 torr. The refractive index was 1.4249 at 25°C. Isomers were not separated. The infrared spectrum showed the absorption due to the 3-methyl group at 1381cm^{-1} , an ether absorption at 1113cm^{-1} , and a doublet olefin absorption at 1643 and 1665cm^{-1} caused by the presence of both isomers(35, 36). This spectrum is illustrated in figure 5.

Diethyl Ether

Diethyl ether used was Baker's Analyzed anhydrous reagent grade. This was stored in the refrigerator over molecular sieves.

Apparatus

Titration was performed in the apparatus depicted in figure 6. The apparatus was designed to exclude CO_2 from the sample during titration, thus ensuring that each end point was as accurate as possible and that there was no end point fade caused by reaction of CO_2 with the titrated sample. The apparatus is made from the top section of a large reaction kettle placed on a white porcelain topped Corning magnetic stirrer. One opening is fitted with an inlet tube attached to a nitrogen tank. Titration is accomplished through another opening and excess nitrogen escapes through the titration opening. All other openings were stoppered. Inside is a glass beaker in which the solution to be titrated was stirred with a teflon coated magnetic stir bar. A slow steady flow of nitrogen prevented contamination by CO_2 .

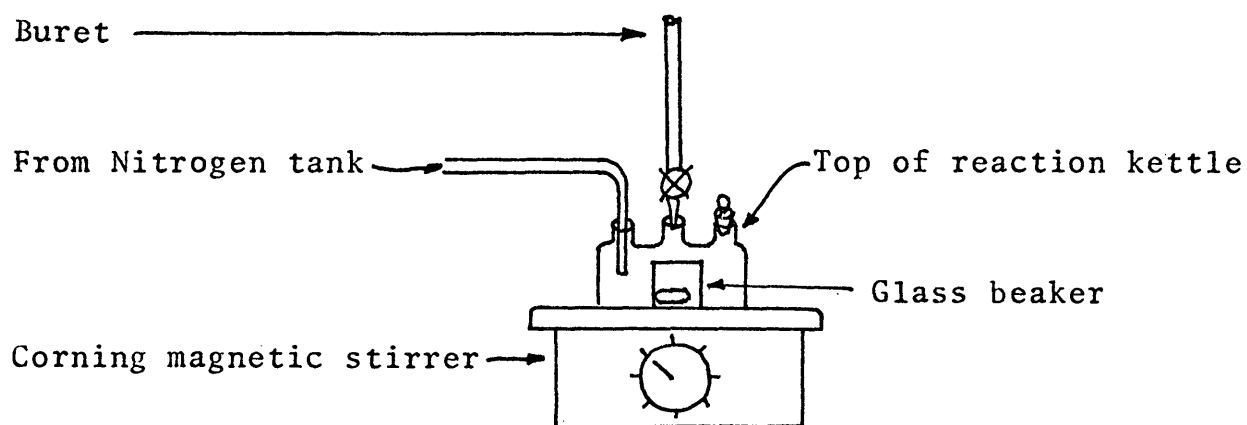


Figure 6. Titration Apparatus.

Reactions were run in an apparatus of the type illustrated in figure 7. The reaction chamber is a three neck round bottomed flask fitted with a rubber cap sample port, a coldfinger condenser, nitrogen inlet, and stirrer. To the top of the coldfinger condenser was attached a drying tube, 4-in. by 1/2-in. diameter, packed with anhydrous calcium chloride. The reaction solution was stirred by an overhead air driven motor driving a teflon stir blade. A water cooled ground glass stirrer bushing was employed. The purpose of the air driven motor was to avoid breaking the glass shaft of the stirrer. Since the air driven motor has very little torque, compared with a conventional electric motor, any minor mishap should stop the motor before breaking the glass shaft.

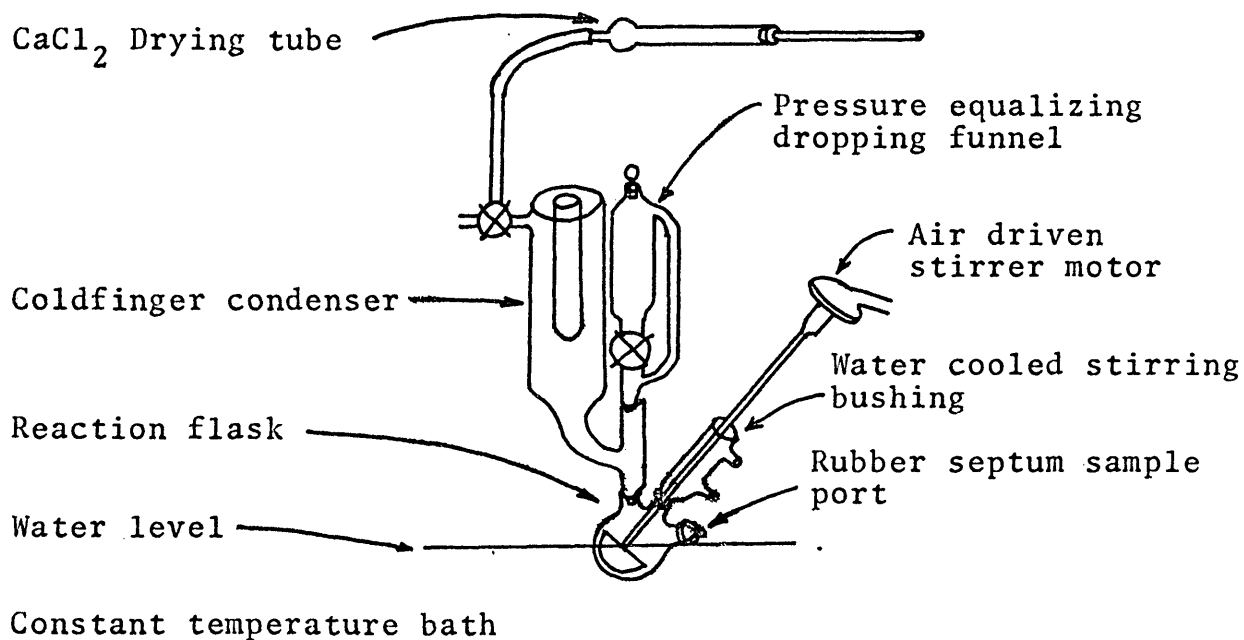


Figure 7. Reaction Apparatus.

Reagents were added via a pressure equalizing dropping funnel. Temperature was controlled by a constant temperature bath. Temperature was observed by means of a 0 - 100°C thermometer which could be read directly in tenths of a degree, and could be interpolated to hundredths.

Technique

After reaction products were identified by the use of infrared spectra, standards were made and run on the GLC to find the retention time of each compound present in a reaction mixture. Normal heptane was chosen as an internal standard because its retention time did not correspond to that of any product or reactant. A typical chromatogram is shown in figure 8.

A typical reaction procedure follows: During the week before the reaction was to be started, a calculated amount of the catalyst, TiCl_4 , was added to the CME. This measurement was made according to sample weight.

The evening before the reaction was to be started, the reaction apparatus was assembled and purged with dry nitrogen for at least a half hour. Two kinds of sample vials were weighed. Some were empty for titration samples, others contained a weighed amount of heptane for GLC samples. Vials containing heptane were left on blocks of dry ice in an ice chest from the time of weighing until the time of use. This was done to prevent heptane evaporation through the cap and

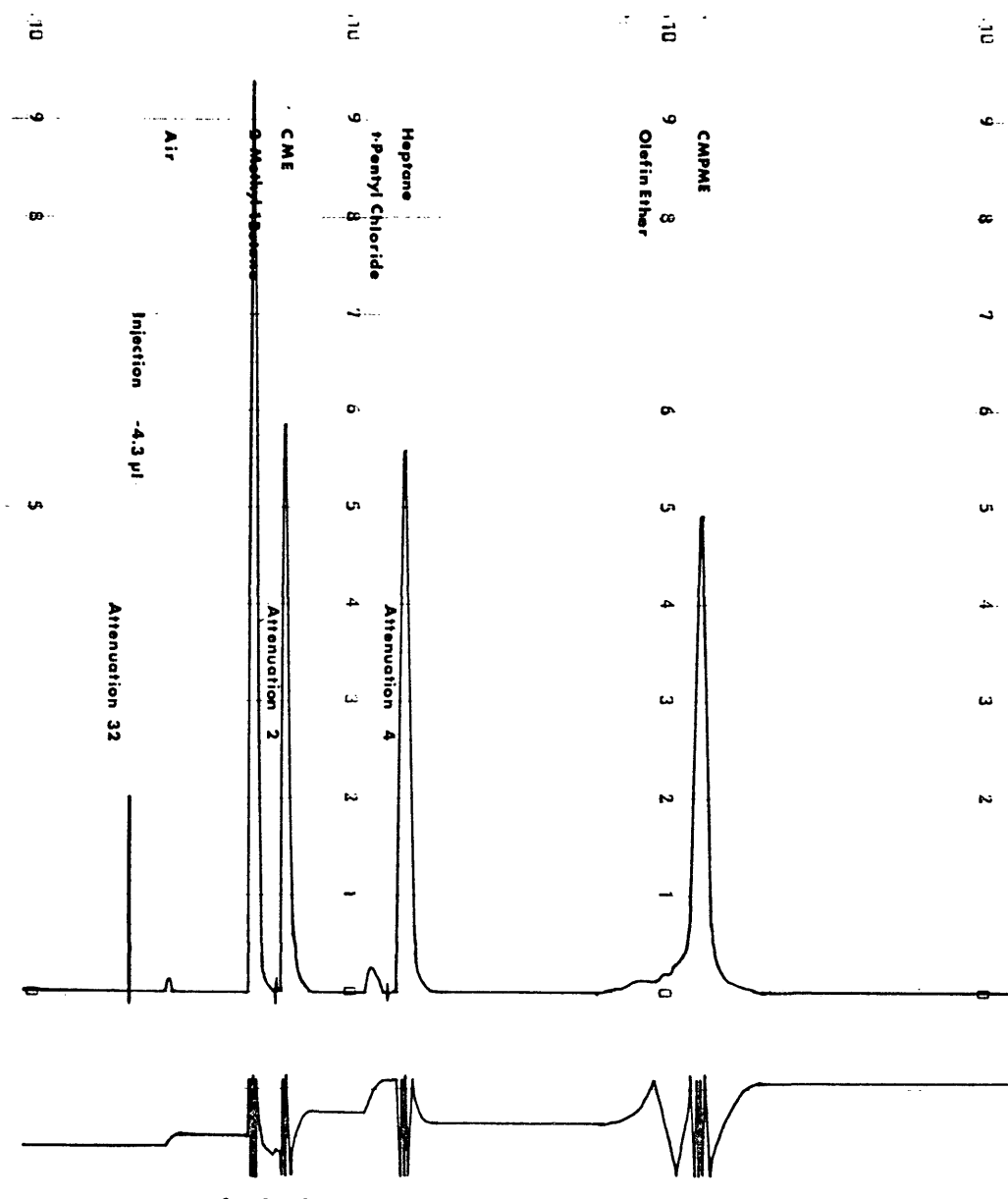


Figure 8. Typical chromatogram of a sample analyzed by GLC. This was a sample taken after 30 min. of reaction from a run in which there was initially a twenty-fold excess of 2-methyl-1-butene over CME.

to cause thermal quenching of the sample at the time the sample was taken.

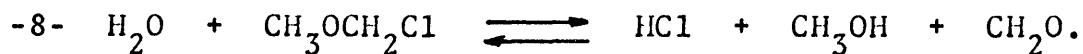
The morning before the reaction was to be started, a dry bag (Instruments for Research and Industry no. X-17-17) was purged with dry nitrogen. Inside the dry bag, the calculated amount of CME and any other ether used in that reaction were added to the pressure equalizing dropping funnel. An aliquot of this solution was removed and kept as a control. 2-Methyl-1-butene was added under a counter-current flow of dry nitrogen to the reaction flask. These last additions were measured by volume.

The pressure equalizing dropping funnel containing the ethers and catalyst was then set in place. A dry ice-acetone mixture was put in the coldfinger trap to prevent evaporation of the volatile olefin. The valve at the top of the coldfinger was left open to vent through a drying tube, primarily as a pressure safety release in case of accident.

After the constant temperature bath had stabilized at the desired temperature, and the air driven stirrer was working properly, the reaction was started by opening the stopcock to the pressure equalizing dropping funnel. Thus the CME-catalyst solution was added to the olefin in as short a time span as possible. Since reactions were run at 25°C, which was usually a few degrees above room temperature, there should have been a very slight decrease in temperature at the time of addition. The reaction is exothermic, but

under these conditions the heat of reaction was small enough to be handled by the constant temperature bath. There was no temperature change observed at the time of addition. The vigorous stirring quickly re-established thermal equilibrium.

Samples were then taken at predetermined intervals by inserting a pre-cooled syringe through the rubber sample port and extracting an aliquot of the reaction mixture. The sampling syringe was cleaned by drawing acetone through it, dried by drawing air through it, and left in a plastic bag on a block of dry ice between samplings. If the sample was to be analyzed by GLC it was quenched by injection into a heptane-containing sample vial which had been pre-cooled to -70°C . The vial was then weighed and a 4 - 5 ul aliquot was immediately injected into the GLC. These sample vials were then left on dry ice to prevent further reaction in case they had to be re-analyzed. The samples remained homogeneous at dry ice temperatures. If the sample was to be titrated it was injected into an empty sample vial, weighed, quenched with 10 ml of water and titrated immediately against a standardized sodium hydroxide solution. The water quenching depends on the reaction:



The time from sampling to quenching usually was about a half minute. Since the reactions were run very near to room temperature, quenching time was recorded rather than sampling time. This minimized error and made all errors nearly equal.

The reaction was allowed to run for the time necessary to reach 90% completion, and in most cases one last sample was taken at 99% completion as an infinity reading. At the time of the infinity reading the control sample was analyzed by GLC to check for decomposition or side reactions.

GLC analyses were used to determine the CME balance, i.e. that the chemicals reacted according to predicted stoichiometry, and that for each mole of CME that disappeared one mole of CMPME was formed. The reaction rate was followed by titrations. Extensive preliminary experiments, described below, showed that the GLC used in these experiments is adequate for obtaining CME balance, but not for following the rate.

The GLC was calibrated by the use of solutions of the chemicals which would be present in the test solution. Carefully measured quantities of the chemicals were weighed so that the compositions of these solutions were accurately known. These solutions were then analyzed on the GLC. All peak areas were compared to the peak area of the internal standard, heptane.

The titanium tetrachloride catalyst was initially 0.0048 M for each run. The catalyst was mixed with the ether prior to each set of replicates so that each experiment in a replicate would start with the same catalyst concentration.

In most experiments a sixteen to one or greater excess of olefin over CME was used to produce pseudo order conditions for the rate of disappearance of CME.

The preliminary experiments to which repeated reference has been made are described here. GLC was used for all analyses. CME was allowed to react with 2-methyl-1-propene, 2-methyl-1-butene, and 2-methyl-1-pentene to determine which would be best to use. 2-Methyl-1-propene is a gas, b.p. -6.6°C at 1 atm., and is therefore very difficult to work with quantitatively at room temperature. 2-Methyl-1-pentene is a liquid and very easy to work with. Its product ether, CMHME, is so high boiling and unstable that it makes GLC an impractical tool for its analysis. 2-Methyl-1-butene is a good compromise, boiling at 38.6°C at 1 atm., and forming a product ether which is eluted from the GLC column with relative ease.

Several experiments were run using a one to one molar ratio of CME to 2-methyl-1-butene with no solvent. CME and olefin balances were obtained from these, but the volume could not be measured, so no concentration data were obtained. Since Hall and co-workers(15) had reported anomalous side reactions in the presence of "inert" solvents, it was decided to avoid solvents until some idea of the kinetics without a solvent was available.

The pseudo order reaction is one in which the concentration of one reactant remains nearly constant during a run. This

would be the case if one of the reactants is the solvent. For this reason the pseudo order reaction was chosen next, with 2-methyl-1-butene as the solvent-reactant. This afforded both CME balance and concentration data.

It was suspected that the product ether was complicating the reaction and that the addition of an inert ether might simplify the apparent kinetics. Therefore an inert ether was added to the reaction mixture. The pseudo order reaction was repeated several times under these conditions. Although the addition of another ether made the data appear to conform to first order equations, scatter in the data gave specific rate constants which varied from run to run. One time the rate constant might appear to be three times what it was in another run. Due to these poor results the analytical procedure was changed to the titration technique described above.

Difficulties Encountered

The purpose of this section is to outline briefly some of the problems encountered, and the methods of solution.

In the original proposal, all rates were to be followed by GLC until a more suitable technique was found. To ensure that all components of a solution are vaporized immediately upon injection, the injection port of the GLC should be maintained at least 50°C above the boiling point of the highest boiling compound in the solution(37). The detector

should also be maintained at this temperature to avoid condensation of vapors in it. Since the product ether begins thermal decomposition below its atmospheric boiling temperature, this posed an immediate problem. The solution was to install an on-column injection port, which bypasses the normal injection port, and allows the solution to be injected directly onto the packing in the column. The on-column injection port is shown in figure 9.

As described in the previous section, many experiments were run under the same conditions. The data from these had scatter beyond reasonable tolerance limits. After repeated checks as suggested by the instrument manual it was decided that there were problems in electronics and in column packing of the GLC.

It was decided to develop a different procedure for following the course of the reaction. Adequate data had

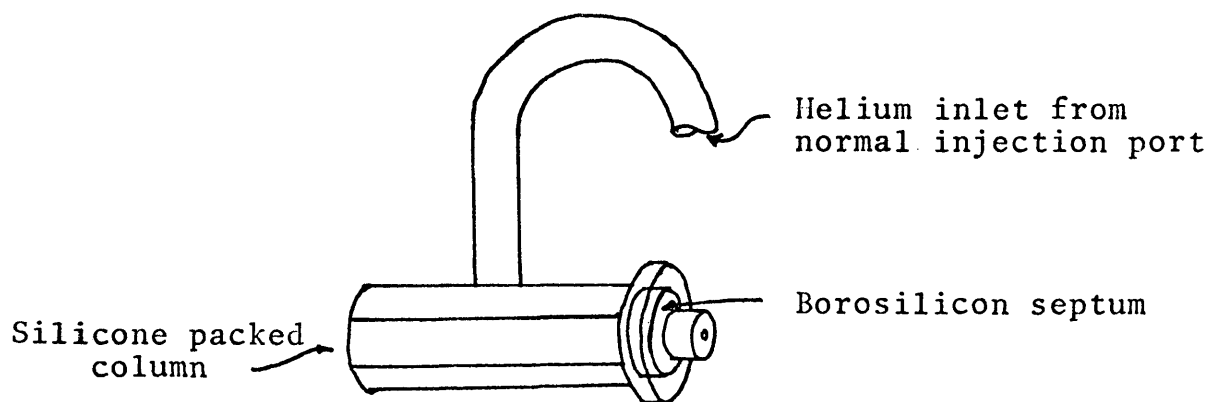


Figure 9. On-column injection port. This adapter was a donation from Marathon Oil Company.

been obtained from the GLC to demonstrate a good CME balance and that CME and olefin disappear at the same rate. Therefore it would be necessary to follow the concentration of only one component and thereby determine the rate.

Titration was chosen as the new technique. Since the CME reacts vigorously(1, 38, 39) with water to form HCl as was shown in equation 1, a titration with a base(39) to determine HCl concentration pinpoints the CME concentration at any given time. A difficulty with this technique is the fact that there are tertiary chlorides in the reaction mixture which slowly(40) react in aqueous media to form HCl. Dr. George Lucas suggested titrating a sample to multiple end points and interpolating back to the quenching time. This suggestion was accepted and used in all titrations. A correction was also made for the presence of the $TiCl_4$ catalyst, which reacts vigorously with water to form HCl.

RESULTS AND DISCUSSION

Preliminary experiments indicated that a small amount (about 5%) of the product γ -chloroether was decomposing during the course of each experiment. The only literature reference to the 3-chloro-3-methylpentyl methyl ether (CMPME) or to the unsaturated ethers derived from it (18) gave very sparse information. Therefore, the corresponding 3-chloro-3-methylbutyl methyl ether (CMBME) was made and comparative infrared spectra used in compound identification. CMBME and its derived unsaturated ethers had been characterized by Hall, Dormish, and Hurley (15). The corresponding 3-chloro-3-methylhexyl methyl ether (CMHME) and its unsaturated ether were also prepared so that characteristics of the family of compounds could be compared. Figures 1, 2, and 3 show the infrared spectra of CMBME, CMPME, and CMHME respectively, and figures 4 and 5 show the infrared spectra of the corresponding unsaturated ethers.

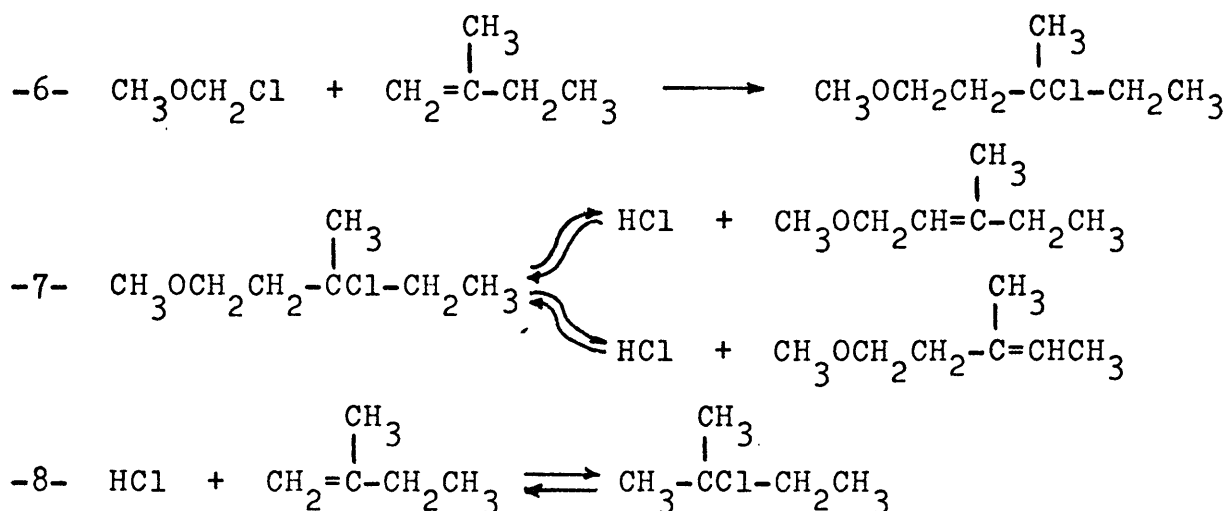
Compound retention times on the GLC are shown in table I. The presence of the components may be explained by a series of

Table I. Retention times of compounds on the gas chromatograph, and column conditions. The instrument used was the F & M model 720 gas liquid chromatograph. Columns were 0.25-in. stainless steel packed with 15% SF-96 on Chromosorb-W.

<u>Compound</u>	<u>Time (min)</u>
2-Methyl-1-butene	2.3
Chloromethyl methyl ether	2.9
Methylal (contaminant in CME)	3.5
Bis(chloromethyl)ether (contaminant in CME)	3.8
2-Chloro-2-methylbutane	4.6
Heptane	5.2
3-Methyl-(2&3)-pentenyl methyl ethers	9.6
3-Chloro-3-methylpentyl methyl ether	10.8
 <u>Column Conditions</u>	
Carrier gas	Helium
Carrier gas flow rate	100 cc/min
Initial column temperature	25°C
Programmed temperature initial setting*	36°C
Programmed temperature rise	2°/min

* After injection the thermostat was set up to 36°C from 25°C. This was found to be preferable to using a higher rate on the programmed temperature rise.

Reactions shown below. In reaction -6-, the γ -chloroether is formed. About 5% of the γ -chloroether spontaneously dehydrohalogenates according to reaction -7-. The HCl in solution then attacks the starting olefin by reaction -8-.



Preliminary experiments showed a change in apparent reaction order with respect to CME as the reaction proceeded, and it appeared that the product was inhibiting the reaction. This hypothesis, that the product inhibited the reaction, was tested by adding the product to the starting mixture at the same concentration as the CME. With this change the data showed that the reaction was first order, thus demonstrating some validity to the hypothesis. The CME balance remained very acceptable, accounting for 95 - 99% of the starting CME.

After the procedure was changed to include analyses by titration these experiments were repeated. Runs 1 and 2, without any other ether added, showed a decrease in first

order rate constant as the experiment proceeded. A computer program was used to fit the data to several standard kinetic equations. A flow chart for the program is shown in Appendix II. The program cycles through fractional orders from 0.25th order to third order. The data did not conform satisfactorily to any of the equations tried. Figure 10 shows a plot of run 1.

Runs 3, 4, and 5, which were similar to runs 1 and 2 except that they all contained the product ether added to the original CME-catalyst solution prior to the run, conformed well to the first order rate equation. Figure 11 shows a plot of run 4. In the next set, 6 - 8, diethyl ether was substituted for the product ether. Under these conditions similar results were obtained as with the runs containing CMPME. Figure 12 shows a plot of run 6. From then on, diethyl ether was used in all experiments.

The results in table II show that if an aliphatic ether is initially present in the reaction mixture, the reaction rate constants are reasonably constant throughout the course of a run. The rates were determined by fitting the data using a least squares method, and error reported at the 95% significance level(41, 42). Since most experiments were run under pseudo-first order conditions, the equation used was the pseudo-first order equation. Data from the one to one run were fit to a second order equation. All data points were included and fits were made through 90% of each reaction. In these reactions, CME balances were between 95 and 99%.

SEMILOG PLOT OF CME CONCENTRATION VS TIME FOR RUN OF DEC 15

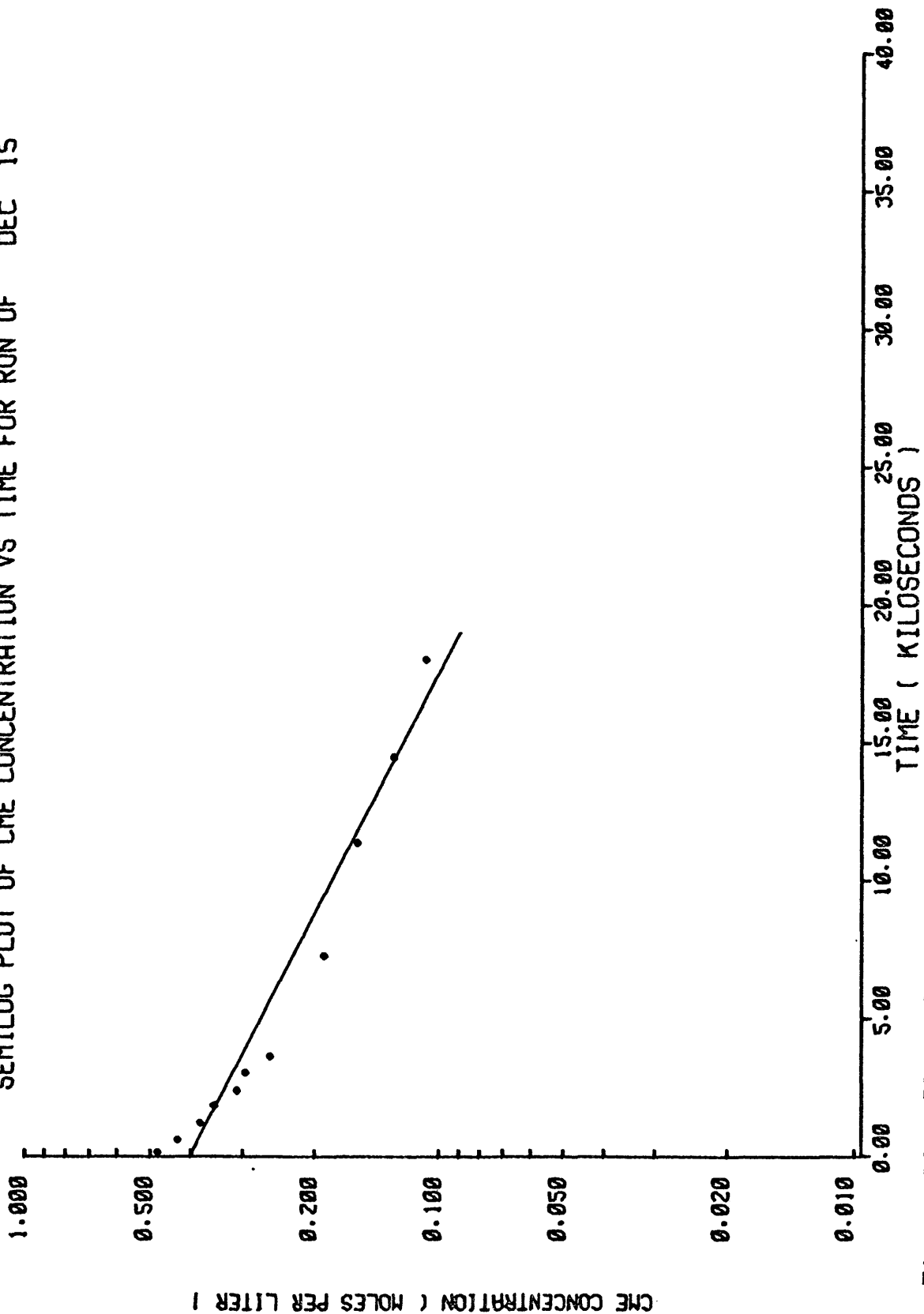


Figure 10. Plot of run 1.

SEMILOG PLOT OF CME CONCENTRATION VS TIME FOR RUN OF NOV 16

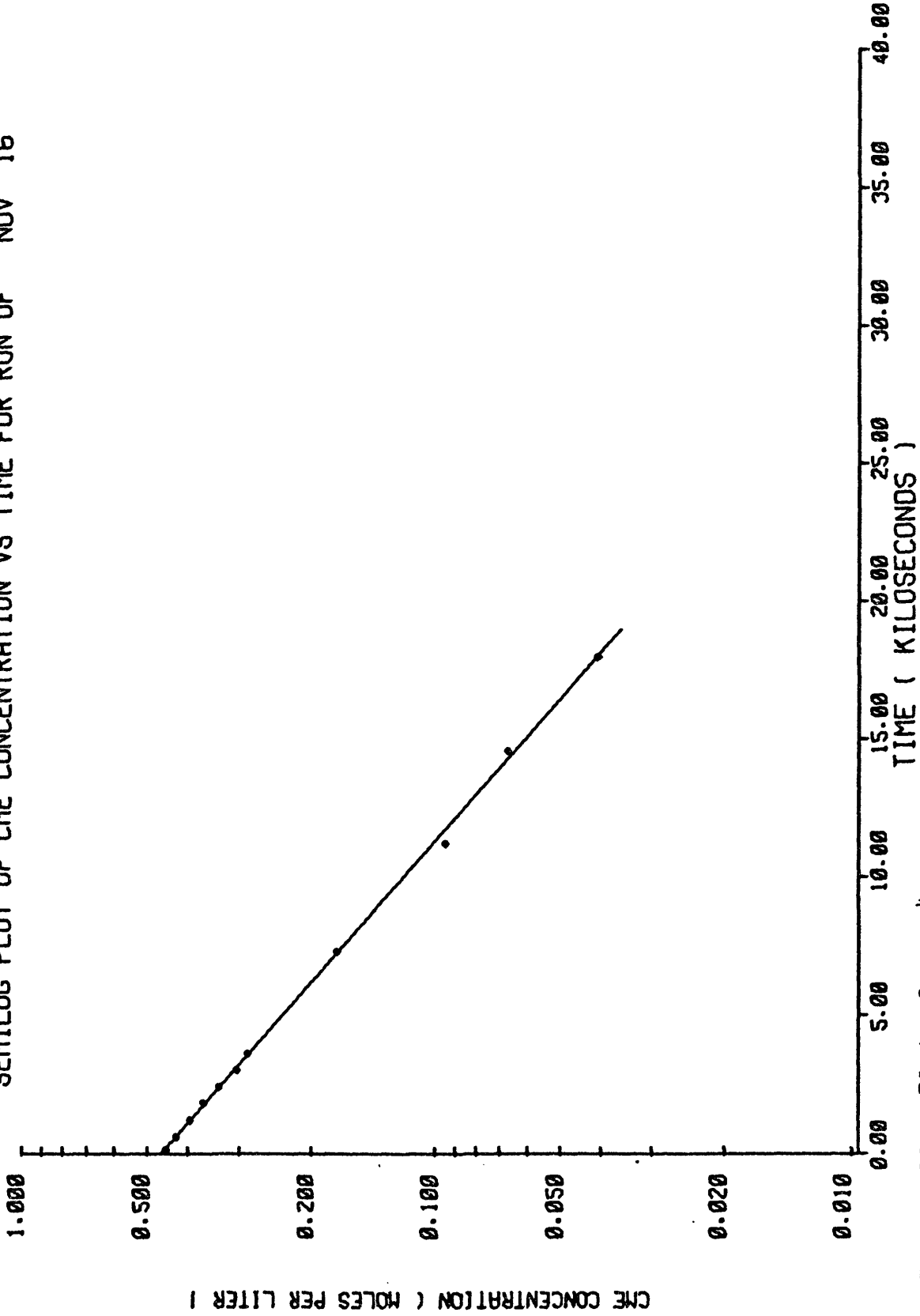


Figure 11. Plot of run 4.

SEMILOG PLOT OF CME CONCENTRATION VS TIME FOR RUN OF NOV 25

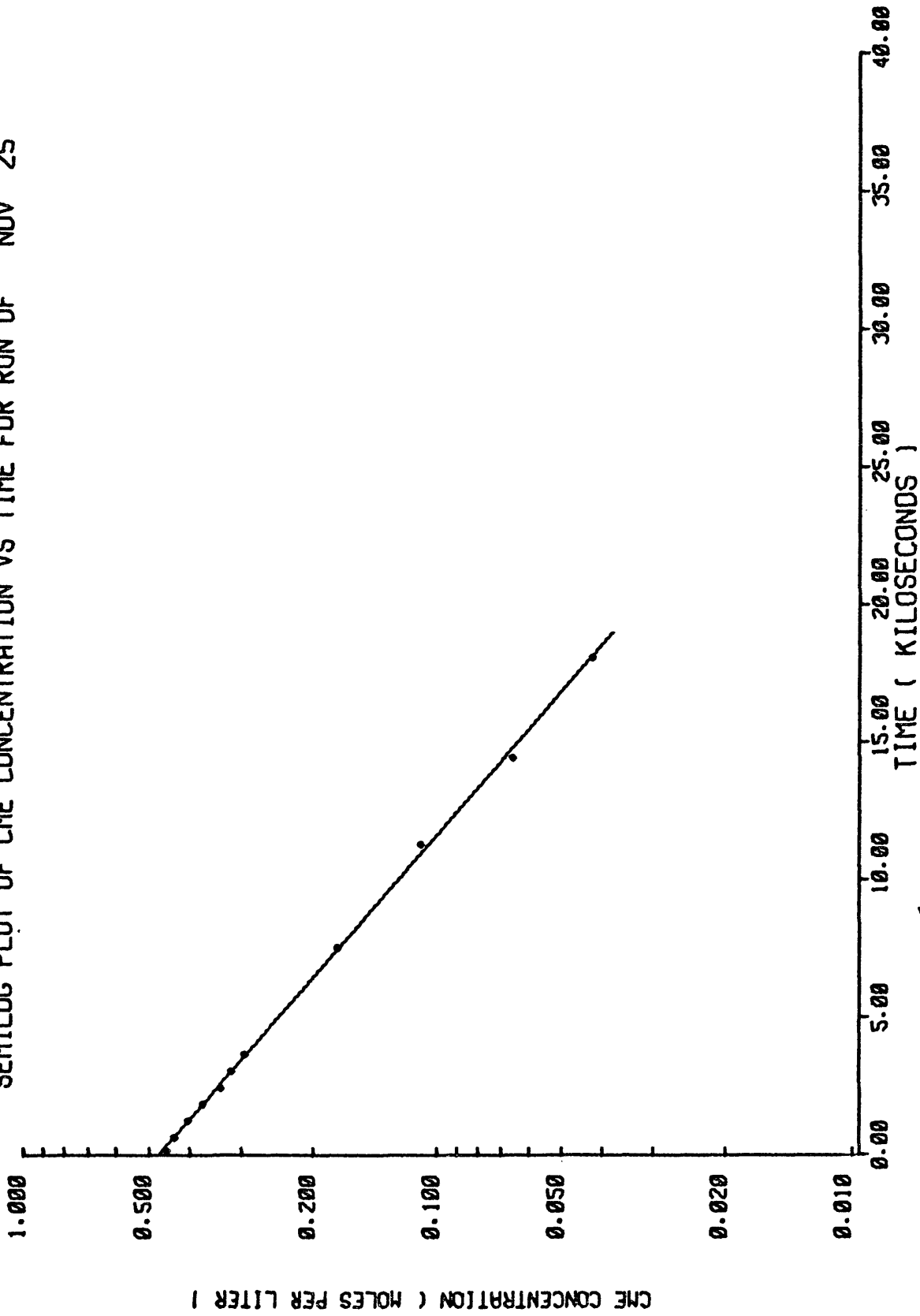


Figure 12. Plot of run 6.

Table II. Conditions and rate constants for the reactions(a).

<u>Run Number</u>	<u>Reagent Concentrations</u> (moles / liter)		<u>Ratio of Olefin TO CME</u>	<u>Observed(b) Rate Constant</u> $\text{Sec}^{-1} \times 10^{-5}$	<u>Specific(b) Rate Constant</u> $\frac{\text{Liters}}{\text{Sec}^{-1} \times 10^{-5}}$	<u>Correlation(b) Coefficient</u>
	<u>Olefin CME</u>	<u>Ether</u>				
1,2	7.65	0.48	16	16.90 ⁺ 1.5(c)	2.21 ⁺ .20(c)	.9960(c)
3,4,5	7.65	0.48	16	13.57 ⁺ 1.9	1.77 ⁺ .25	.9988
6,7,8	7.65	0.48	16	13.67 ⁺ 1.5	1.79 ⁺ .20	.9988
9,10,11	7.65	0.30	25	15.63 ⁺ 2.5	2.04 ⁺ .33	.9867
12,13,14	7.65	0.20	38	14.83 ⁺ 1.9	1.93 ⁺ .25	.9947
15,16,17	3.00	0.188	16	5.23 ⁺ .62	1.74 ⁺ .21	.9956
18,19,20	3.00	0.118	25	5.40 ⁺ 1.3	1.80 ⁺ .43	.9894
21,22,23	3.00	0.078	38	5.27 ⁺ 1.7	1.76 ⁺ .57	.9768
24,25,26	1.00	1.00	1	1.73 ⁺ .24	1.73 ⁺ .24	.9996

- (a) Data for individual runs are shown in Appendix I. See table III to convert from run conditions to appendix pages. All reactions were run at 25°C with a catalyst concentration of 0.0048 M.
- (b) Values are averages of repeated runs. For the first set of conditions this is an average of two runs. For all others it is an average of three runs. Errors are shown at the 95% confidence level.
- (c) The rate constant shown is calculated on the basis of the first 50% of reaction because of curvature in the rest of the line.

Although the kinetics are more complicated in the absence of an aliphatic ether, in the presence of such an ether the reaction conforms well to known rate equations. The rate constant for the one to one run was determined by a fit of the data to the equation(32):

$$1 / \text{CME} - 1 / \text{CME}_0 = k t.$$

All other reactions were performed under pseudo-first order conditions, and the equation used was(32, 33):

$$\ln \text{CME} - \ln \text{CME}_0 = - k' t$$

in which $k' = [\text{olefin}] k$. That the reaction is first order with respect to each reactant is demonstrated by the constancy of the specific rate constant as shown in table II. Since the specific rate constant is found by dividing the observed rate constant by the olefin concentration, a different constant would have been found for runs 6 - 14 than for runs 15 - 23 if the order with respect to olefin were not one.

A demonstration that the reaction is first order with respect to olefin occurs in the one to one run. The rate equation for an nth order reaction is(29, 32):

$$- dA / dt = k A^a B^b \text{ where } a + b = n.$$

The pseudo order reaction had shown that the reaction is first order with respect to CME. The equation which was used for the one to one run, as described above, is for a reaction which is second order in only one reactant. Therefore the

equation fit for this reaction not only assumes that $CME_0 = olefin_0$, but also that $a = b = 1$. If there had been a discrepancy here, a very low correlation between the data and the equation would have existed. The correlation of .9996 is a good indication that the reaction is first order with respect to olefin.

A further demonstration was made by recomputing the specific rate constants for all pseudo order reactions according to the equation(32):

$$\frac{1}{olefin_0 - CME_0} \ln \frac{olefin CME_0}{CME olefin_0} = k t .$$

This equation describes a second order reaction which is first order with respect to each reactant. In all cases this check produced the same numbers for the rate constant and correlation as were obtained by the previous calculations. If the reaction had not had this order the rate constant would not have been the same as before and the correlation would have been poor. This equation is no more sensitive than the ones used above, but it also proves that the reaction occurs stoichiometrically throughout, otherwise a poor correlation would have existed between the equation and data.

Since the specific rate constant, k , remained nearly the same under the combinations of concentrations studied, the order of the reaction must be second order overall, first order with respect to each reactant. If any other kinetics held, the k would have varied under the conditions chosen.

The school's PDP 10 computer was used for all computations. Flow charts for the programs designed to process the data are shown in Appendix II. Several sets of calculations were done on a Hewlett Packard 9100B calculator in order to double check the computer programs.

Computer printouts of the data and fits to equations are shown in Appendix I. For convenience the computer program was written so that printouts show dates of runs rather than run numbers. Table III in Appendix I shows the conversion from run numbers and conditions to the appropriate date and page in the appendix.

Shikhamedbekova and co-workers(25, 30, 31) reported no difficulty in kinetics work with similar compounds. They studied the reaction of CME with allylic ethers and esters(25), 1,3-pentadiene(30), and 2-chloro-1,3-butadiene(31). All of these studies were made in a solution containing diethyl ether except the allylic ethers study, which had varying solvents including: benzene, chloroform, diethyl ether, tetrahydrofuran, and nitromethane. Each of their experiments started with a one to one ratio of concentrations of CME to olefin. Concentrations were followed by GLC and one was verified by argentometric titration(31). In all cases the reaction kinetics were described by a second order equation. In the case of 1,3-pentadiene, Shikhamedbekova(30) found that after the

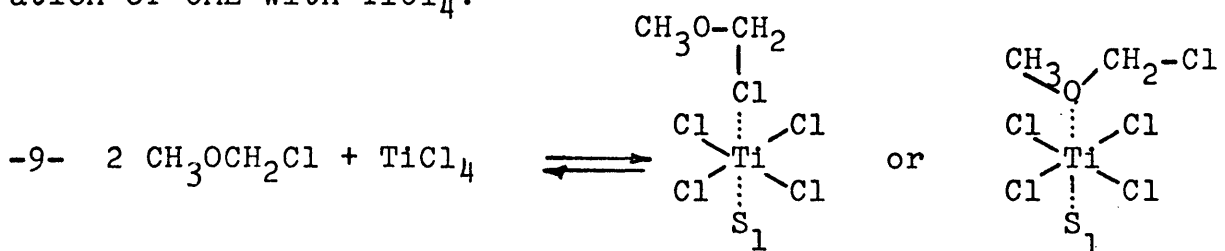
reaction had gone to 30% completion the kinetics were complicated by formation of "condensation products". A correlation was reported between solvent polarity and reaction rates for allylic ethers and esters(25).

It is necessary at this point to digress into the subject of Lewis acids and bases. This is to demonstrate that it is realistic to discuss a competition between ethers for catalyst coordination sites. The descriptions of acids and bases used below are adopted from R. G. Pearson's theories of hard and soft Lewis acids(43). According to this theory a hard base is one which is highly electronegative, demonstrates low polarizability, and is hard to oxidize. Hard acids bond preferentially to hard bases while soft acids bond preferentially to soft bases.

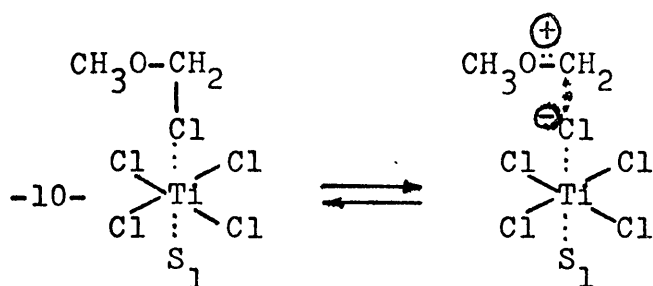
Several references(43-46) were found in which it is stated that alkyl ethers and monochloroethers are hard Lewis bases and tend to form strong bonds with a hard Lewis acid such as titanium tetrachloride. McCusker and Scholastica-Kennard(44), and Fratiello and Schuster(45) also report that alkyl ethers through di-n-butyl have the same solvation effect on Lewis acids. Thus, it seems reasonable to assume that any ether present in solution will compete with CME for catalyst coordination. The two electron withdrawing groups on the same carbon of a CME molecule will act to reduce the basicity

of CME as compared with other ethers. So in a competition between CME and an ether which does not have a halogen atom in the α position, equilibrium will slightly favor the later ether. If the only other ether present is the product, the reaction rate constant will change due to the increase of product ether as the reaction proceeds. The fact that the rate constant does not change within a given run when another ether is present in a 0.5 M concentration, indicates a leveling of this effect.

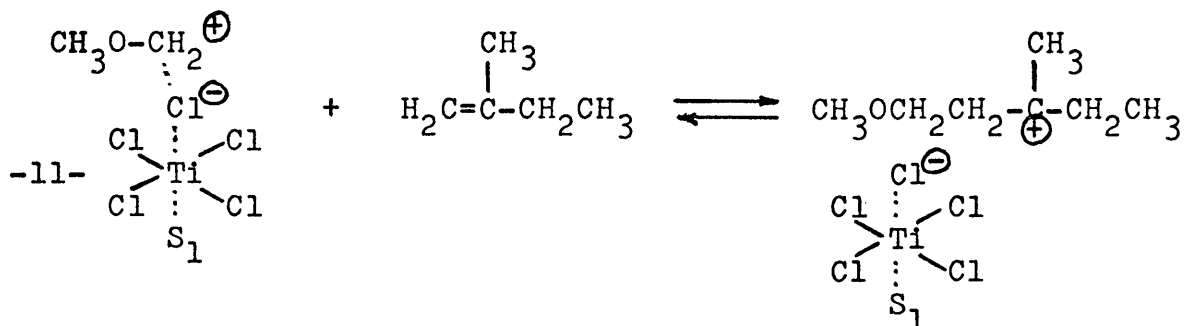
The importance of this solvation effect is seen in the following discussion of the steps in the reaction of this study. First consider the path taken when the only ether present is CME, i.e. no product or other ether is present. For most of the following discussion only one of the coordination sites will be of interest. For this reason only one coordinated ether will be shown, and the other will be denoted as a solvating molecule, S_1 . The first step is the coordination of CME with $TiCl_4$:



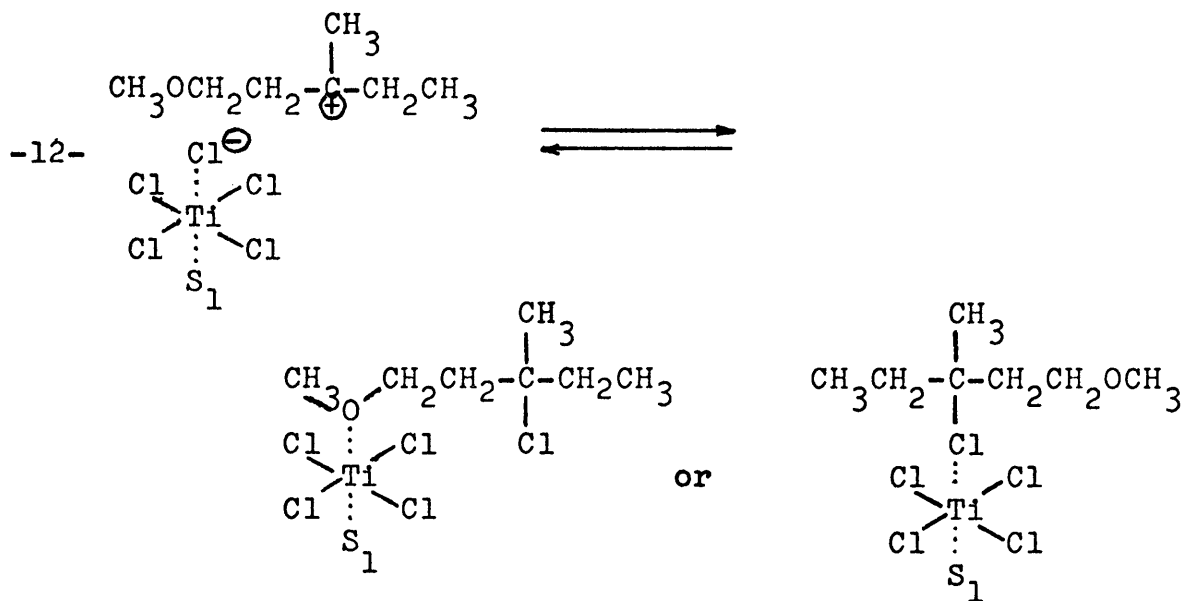
The next step is the formation of a tight ion pair, as shown on the next page.



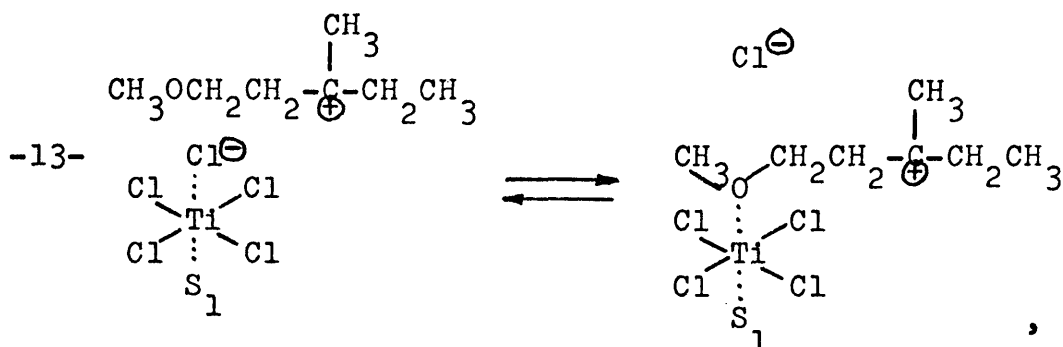
Since the solvent is mainly hydrocarbon there is very little tendency for this ion pair to separate. This complex is now ready for direct reaction with the olefin in solution:



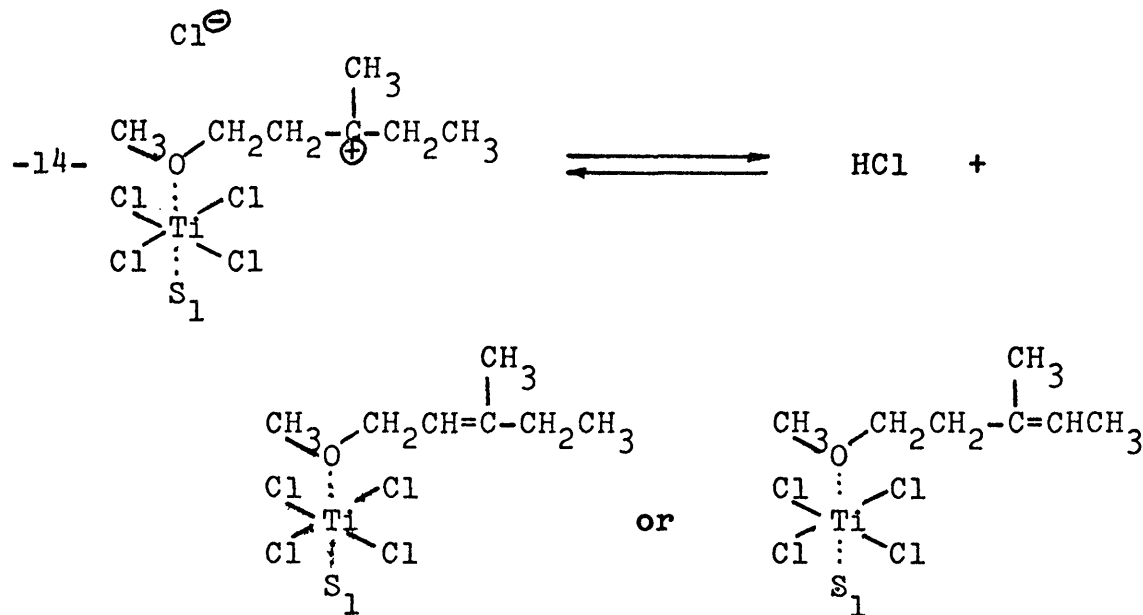
In the majority of reactions a chlorine bonds to the tertiary carbon and the newly formed molecule coordinates with the TiCl_4 :



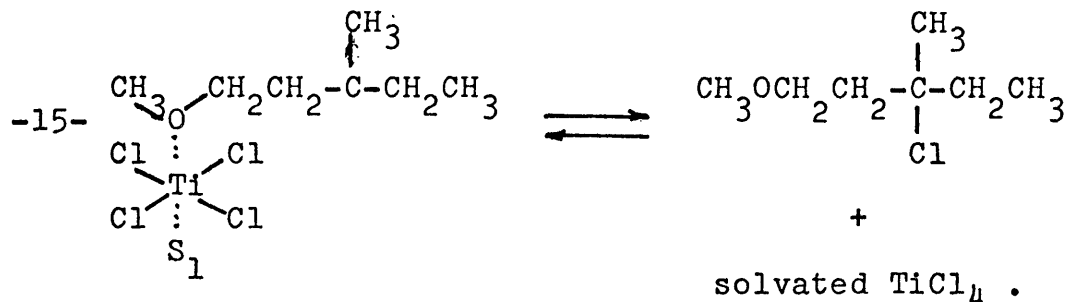
It is possible that the ion pair rearranges slightly so that the oxygen is coordinated with $TiCl_4$ in place of a chloride:



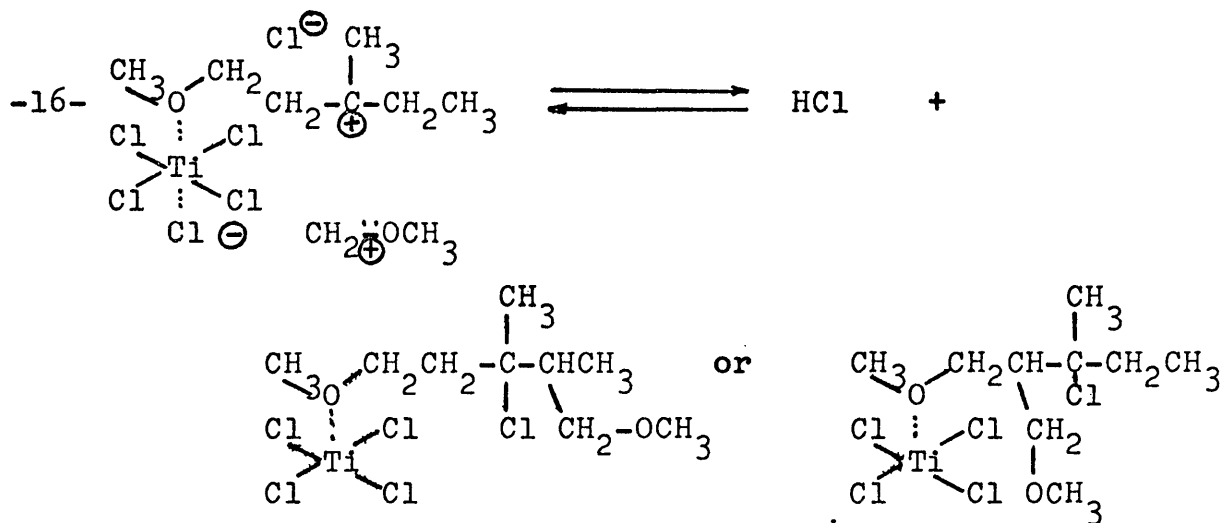
In which case the chlorine normally still bonds to the tertiary carbon as in -12- above. In this step there is another possible reaction which seems to occur only to a small extent, as evidenced by the observed presence of unsaturated ethers accounting for about 5% of reacted CME:



The desirable next step is for the product ether to separate from the TiCl_4 which would then be solvated by another CME:

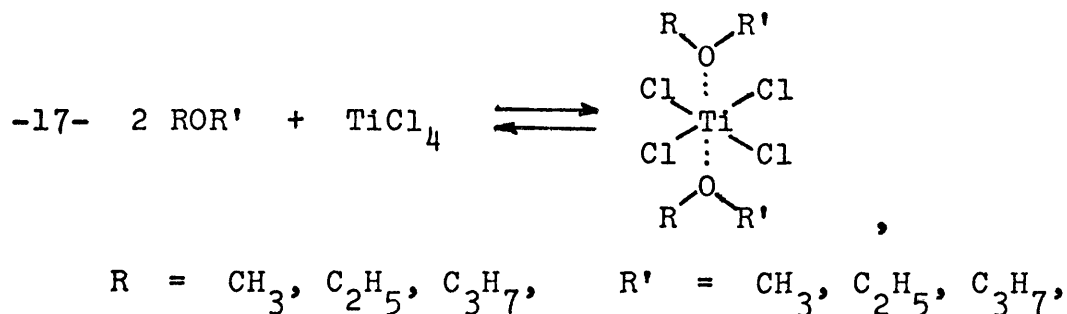


In hydrocarbon solvents the equilibrium probably favors the left side of this reaction and the product ether remains coordinated with the catalyst where it possibly can undergo further reaction to produce the previously mentioned by-product. The most likely time for the formation of the by-product would be an alteration of reaction -14- in which S_1 is in the ion-pair configuration:



The reason for the curve in the plot of data from runs 1 and 2 in which CME was the only ether initially present is now apparent. The product ether ties up an increasing number of catalyst coordination sites, thus slowing the reaction as the reaction proceeds.

If an aliphatic ether is present there is competition for catalyst coordination sites from the start of the reaction with very little change as the reaction proceeds. Reaction -9- above would be in competition with the simultaneous reaction:



causing the presence of three species in solution:



The equilibrium position in reaction -10- would be shifted slightly by the polarity of the solvent and the nature of the species solvating the other end of the catalyst. This effect would be small in comparison to the competitive reaction mentioned above. The more polar solvents would allow the ion-pair to separate and not to remain in the tight configuration shown in reaction -10-. The by-product

formation is also reduced by the presence of the aliphatic ether because product ether and $TiCl_4$ are both solvated and the equilibrium in reaction -15- is shifted to the right.

A levelling of the effect which is caused by the product ether, is indicated by stabilization of the rate constant when another ether is present in a 0.5 M concentration. In the pseudo-first order runs the CME concentration is a hundred times as great as the catalyst. When another ether is present in this concentration, the effect is a rate constant that does not vary as the reaction proceeds. An interesting follow-up study would be to determine the minimum concentration of inert ether necessary to cause this levelling effect.

Summary

Time lost to the previously mentioned difficulties encountered during the course of this study, and the lack of a convenient analytical method for the olefin shortened this study. However, an important first step was made toward the final elucidation of the kinetics of the reaction between CME and olefins.

In the absence of an aliphatic ether, the reaction kinetics are not described by a simple mathematical expression because of competition for coordination with the catalyst between CME and the product ether during the course of the reaction. When an aliphatic ether is added to the reaction

solution there is competition between the CME and the aliphatic ether for coordination with the catalyst. This competition slows the rate of formation of the intermediate species, thus making that the rate determining step. In the presence of an aliphatic ether the reaction proceeds by second order kinetics, first order with respect to each reactant.

Since ethers coordinate with the catalyst, it can be seen why the by-product mentioned by Hall and co-workers(15) might be produced. This by-product was thought to be one molecule of olefin combined with two molecules of CME as was shown in equation -16-. It might also explain the anomalous solvent effect which they reported, in which an inert aliphatic non-polar solvent caused the formation of the by-product. In the presence of an inert aliphatic non-polar solvent any product formed will preferentially stay with the catalyst and react further.

APPENDIX I

COMPUTER PRINTOUTS OF DATA
AND FITS TO EQUATIONS

Table III. Conversion from run numbers to dates as shown on computer printouts in Appendix I.

<u>Reaction Number</u>	<u>Initial Concentrations</u> (moles / liter)			<u>Date</u>	<u>Page</u>
	<u>Olefin</u>	<u>CME</u>	<u>Ether</u>		
1	7.65	0.48	0.00	Dec. 15	52
2	7.65	0.48	0.00	Dec. 20	53
3	7.65	0.48	0.48 CMPME	Nov. 13	54
4	7.65	0.48	0.48 CMPME	Nov. 16	55
5	7.65	0.48	0.48 CMPME	Nov. 21	56
6	7.65	0.48	0.48 Diethyl	Nov. 25	57
7	7.65	0.48	0.48 Diethyl	Nov. 28	58
8	7.65	0.48	0.48 Diethyl	Nov. 30	59
9	7.65	0.30	0.48 Diethyl	Jan. 20	60
10	7.65	0.30	0.48 Diethyl	Jan. 22	61
11	7.65	0.30	0.48 Diethyl	Jan. 24	62
12	7.65	0.20	0.48 Diethyl	Jan. 26	63
13	7.65	0.20	0.48 Diethyl	Jan. 28	64
14	7.65	0.20	0.48 Diethyl	Jan. 30	65
15	3.00	0.188	6.08 Diethyl	Feb. 2	66
16	3.00	0.188	6.08 Diethyl	Feb. 4	67
17	3.00	0.188	6.08 Diethyl	Feb. 6	68
18	3.00	0.118	6.08 Diethyl	Feb. 9	69
19	3.00	0.118	6.08 Diethyl	Feb. 12	70
20	3.00	0.118	6.08 Diethyl	Feb. 14	71

Table III. Conversion from run numbers to dates as shown on computer printouts in Appendix I. (continued)

<u>Reaction Number</u>	<u>Initial Concentrations</u> (moles / liter)			<u>Date</u>	<u>Page</u>
	<u>Olefin</u>	<u>CME</u>	<u>Ether</u>		
	21	3.00	0.078		
22	3.00	0.078	6.08	Diethyl Feb. 18	73
23	3.00	0.078	6.08	Diethyl Feb. 20	74
24	1.00	1.00	7.69	Diethyl Feb. 24	75
25	1.00	1.00	7.69	Diethyl Feb. 28	76
26	1.00	1.00	7.69	Diethyl Mar. 4	77

THE DATE FOR THIS RUN WAS DEC. 15

TIME	CME
158.4	0.484
618.0	0.434
1237.0	0.383
1848.0	0.355
2400.0	0.314
3254.0	0.299
3640.0	0.261
7270.0	0.194
11376.0	0.162
14484.0	0.132
18024.0	0.111
21990.0	0.087
25266.0	0.082
28878.0	0.070
32988.0	0.067
36084.0	0.051
4000.0	0.000

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\ln (CME) = \ln (CME-INITIAL) - KT ,$$

$$\begin{aligned} L (CME-INITIAL) &= -0.901974 \pm .110385 \\ K &= 0.000078 \pm .000013 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4058 .
THE CONCENTRATION AT 10000.0 SECONDS IS 0.0916 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9740 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS DEC, 20

TIME	CME
176.0	0.476
632.0	0.444
1242.0	0.390
1800.0	0.354
2454.0	0.319
3024.0	0.295
3660.0	0.264
7692.0	0.187
10848.0	0.152
14568.0	0.138
18450.0	0.103
1918.0	0.103
2520.0	0.078
29022.0	0.071
32472.0	0.050
36204.0	0.053
84000.0	0.008

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -0.895716 \text{ +/- } .114648 \\ \text{K} &= 0.000080 \text{ +/- } .000014 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4083 .
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0885 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9738 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS NOV. 13

TIME	CME
138.0	0.466
604.2	0.431
1216.2	0.395
1838.4	0.359
3003.6	0.313
3611.4	0.291
7632.0	0.176
11250.0	0.102
14784.0	0.058
18480.0	0.032
21648.0	0.025
25320.0	0.014
28986.0	0.012
32940.0	0.015
36018.0	0.003
84000.0	0.000

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -0.730997 \pm 0.050044 \\ \text{K} &= 0.000143 \pm 0.000006 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4814 .
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0316 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9987 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS NOV, 16

TIME	CME
150.6	0.453
606.0	0.430
1206.0	0.399
1824.0	0.370
2412.0	0.340
3024.0	0.308
3612.0	0.290
7308.0	0.178
11214.0	0.098
14592.0	0.069
18006.0	0.042
21774.0	0.022
25464.0	0.011
29214.0	0.002
32862.0	0.013
36048.0	0.003
84000.0	0.003

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM;

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} .$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -0.762939 \pm .026175 \\ \text{K} &= 0.000134 \pm .000003 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4663 .
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0368 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9995 .

SEE THE CORRESPONDING PLOT,

THE DATE FOR THIS RUN WAS NOV, 21

TIME	CME
165.0	0.455
636.0	0.424
1224.0	0.392
1830.0	0.371
2412.0	0.341
3012.0	0.310
3630.0	0.293
7590.0	0.163
11322.0	0.094
14862.0	0.072
18222.0	0.044
22098.0	0.016
25776.0	0.024
28878.0	0.011
32736.0	0.011
36408.0	0.003
84000.0	0.005

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN}(\text{CME}) = \text{LN}(\text{CME-INITIAL}) - \text{KT}$$

$$\begin{aligned} \text{LN}(\text{CME-INITIAL}) &= -0.777595 \pm 0.046860 \\ K &= 0.000130 \pm 0.000006 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4595 ,
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0391 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9983 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS NOV, 25

TIME	CME
141.0	0.457
618.0	0.438
1230.0	0.406
1830.0	0.375
2418.0	0.340
3036.0	0.321
3648.0	0.298
7512.0	0.179
11268.0	0.113
14454.0	0.068
18078.0	0.044
21756.0	0.023
25710.0	0.007
28860.0	0.009
32436.0	0.005
36444.0	0.011
84000.0	0.005

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -0.742000 \pm 0.022403 \\ \text{K} &= 0.000132 \pm 0.000003 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4762 ,
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0387 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9996 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS NOV, 28

TIME	CME
135.6	0.472
624.0	0.439
1206.0	0.404
1824.0	0.367
2406.0	0.342
3006.0	0.318
3612.0	0.294
7284.0	0.180
10830.0	0.111
14760.0	0.060
18048.0	0.042
21702.0	0.028
25524.0	0.021
29088.0	0.005
32508.0	0.008
36402.0	0.003
84000.0	0.007

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\ln (CME) = \ln (CME-INITIAL) - KT ,$$

$$\begin{aligned} \ln (CME-INITIAL) &= -0.738067 \pm .022250 \\ K &= 0.000137 \pm .000003 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4780 ,
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0356 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9996 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS NOV, 30

TIME	CME
176.4	0.461
636.0	0.440
1248.0	0.408
1830.0	0.366
2412.0	0.340
3036.0	0.321
3600.0	0.292
7518.0	0.179
11076.0	0.103
14634.0	0.071
18534.0	0.031
21696.0	0.028
25464.0	0.011
29358.0	0.019
32448.0	0.005
36228.0	0.008
84000.0	0.008

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM;

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -0.721299 \pm 0.064935 \\ \text{K} &= 0.000141 \pm 0.000008 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.4861 ,
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0334 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9972 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS JAN. 20

TIME	CME
130.2	0.282
648.0	0.265
1224.0	0.243
1806.0	0.220
2448.0	0.203
3006.0	0.189
3618.0	0.182
7626.0	0.109
10854.0	0.058
14676.0	0.043
18588.0	0.009
21642.0	0.005
25500.0	-0.004
29226.0	-0.007
32892.0	0.002
36432.0	0.002
84000.0	-0.005

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM;

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\text{LN} (\text{CME-INITIAL}) = -1.153882 \pm .223953$$

$$K = 0.000166 \pm .000027$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.3154 ,
 THE CONCENTRATION AT 19000.0 SECONDS IS 0.0134 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9767 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS JAN, 22

TIME	CNE
123.6	0.292
642.0	0.270
1230.0	0.248
1812.0	0.226
2436.0	0.200
3012.0	0.191
3648.0	0.166
7224.0	0.105
10890.0	0.063
14544.0	0.033
18216.0	0.022
21738.0	0.007
25404.0	0.006
28896.0	0.001
32442.0	-0.004
36354.0	0.001
84000.0	-0.004

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CNE}) = \text{LN} (\text{CNE-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CNE-INITIAL}) &= -1.229525 \pm .040146 \\ \text{K} &= 0.000144 \pm .000005 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.2924 .
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0189 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9989 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS JAN. 24

TIME	CME
152.4	0.281
636.0	0.263
1200.0	0.241
1830.0	0.224
2436.0	0.209
3036.0	0.195
3618.0	0.174
7656.0	0.102
11334.0	0.067
14748.0	0.038
18522.0	0.011
21660.0	0.013
25296.0	-0.001
29250.0	-0.006
32946.0	-0.032
36054.0	0.001
84000.0	0.000

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} .$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -1.170783 \pm .174463 \\ \text{K} &= 0.000159 \pm .000021 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.3101 .
THE CONCENTRATION AT 19000.0 SECONDS IS 0.0151 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0.9846 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS JAN, 26

TIME	CME
156.0	0.184
642.0	0.161
1260.0	0.164
1854.0	0.151
2406.0	0.130
3048.0	0.127
3648.0	0.101
7272.0	0.064
10920.0	0.033
14946.0	0.024
18378.0	-0.001
21942.0	0.005
25578.0	-0.011
29316.0	-0.007
32772.0	-0.008
36162.0	-0.010
84000.0	-0.007

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} .$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -1.684343 \text{ +/- } .008294 \\ \text{K} &= 0.000144 \text{ +/- } .000013 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.1856 .
THE CONCENTRATION AT 16000.0 SECONDS IS 0.0184 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9930 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS JAN, 28

TIME	CME
169,8	0,182
654,0	0,159
1230,0	0,160
1818,0	0,146
2460,0	0,139
3060,0	0,128
3618,0	0,107
7680,0	0,051
10974,0	0,031
14718,0	0,022
18126,0	0,004
21786,0	0,003
25464,0	0,001
28944,0	=0,009
32916,0	=0,005
36222,0	=0,006
84000,0	=0,009

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -1,665094 \text{ +/- } ,081854 \\ \text{K} &= 0,000155 \text{ +/- } ,000012 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0,1892 ,
THE CONCENTRATION AT 16000,0 SECONDS IS 0,0158 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0,9948 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS JAN, 30

TIME	CME
144,0	0,175
648,0	0,160
1230,0	0,160
1824,0	0,146
2448,0	0,138
3054,0	0,128
3630,0	0,115
7386,0	0,065
10848,0	0,034
14826,0	0,023
18462,0	0,013
21696,0	0,001
25434,0	=0,001
29358,0	0,002
32520,0	=0,007
36348,0	=0,004
84000,0	=0,004

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -1,671871 \text{ +/- } ,065087 \\ \text{K} &= 0,000146 \text{ +/- } ,000010 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0,1879 ,
THE CONCENTRATION AT 16000,0 SECONDS IS 0,0182 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0,9962 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 02

TIME	CME
120.6	0.185
1200.0	0.172
2448.0	0.157
3612.0	0.150
7746.0	0.126
10974.0	0.101
14946.0	0.088
18024.0	0.071
21708.0	0.059
25338.0	0.047
28854.0	0.040
32424.0	0.033
36546.0	0.031
39672.0	0.023
43272.0	0.019
47034.0	0.017
90000.0	0.003

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -1.699927 \text{ +/- } .038776 \\ \text{K} &= 0.000052 \text{ +/- } .000002 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.1827 .
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0179 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0.9986 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 04

TIME	CME
134.4	0.186
1206.0	0.172
2454.0	0.166
3630.0	0.149
7752.0	0.127
10848.0	0.103
14490.0	0.086
18384.0	0.067
21702.0	0.059
25494.0	0.046
29328.0	0.035
32478.0	0.034
36480.0	0.031
39804.0	0.024
43494.0	0.016
46944.0	0.014
90000.0	0.002

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\ln (CME) = \ln (CME-INITIAL) - KT ,$$

$$\begin{aligned} \ln (CME-INITIAL) &= -1.686627 \pm .064377 \\ K &= 0.000053 \pm .000003 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.1851 .
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0168 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0.9964 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 06

TIME	CME
123.0	0.187
1242.0	0.175
2442.0	0.165
3612.0	0.151
7302.0	0.126
11334.0	0.097
14766.0	0.081
18414.0	0.066
21636.0	0.058
25764.0	0.052
29310.0	0.035
32964.0	0.037
36240.0	0.029
40110.0	0.018
43752.0	0.023
47172.0	0.012
90000.0	0.001

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\ln (CME) = \ln (CME-INITIAL) - KT ,$$

$$\begin{aligned} \ln (CME-INITIAL) &= -1.704382 \pm .094556 \\ K &= 0.000052 \pm .000004 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.1819 ,
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0177 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9919 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 09

TIME	CME
130.8	0.110
1224.0	0.109
2412.0	0.100
3636.0	0.098
7320.0	0.077
10938.0	0.063
14550.0	0.052
18384.0	0.040
21720.0	0.037
25482.0	0.028
29166.0	0.022
32964.0	0.025
36222.0	0.019
39780.0	0.012
43524.0	0.014
46824.0	0.009
90000.0	0.000

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -2.196380 \pm .090769 \\ \text{K} &= 0.000051 \pm .000004 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.1112 .
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0112 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9922 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 12

TIME	CME
169,8	0,114
1254,0	0,103
2430,0	0,103
3618,0	0,096
7788,0	0,081
11388,0	0,068
14574,0	0,052
18480,0	0,039
21774,0	0,035
25518,0	0,032
28926,0	0,024
32586,0	0,022
36324,0	0,019
39744,0	0,013
43716,0	0,007
47022,0	0,011
90000,0	-0,000

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -2,116707 \text{ +/- } ,125483 \\ \text{K} &= 0,000056 \text{ +/- } ,000005 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0,1264 ,
THE CONCENTRATION AT 45000,0 SECONDS IS 0,0095 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0,9879 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 14

TIME	CME
172.8	0.114
1248.0	0.103
2406.0	0.101
3636.0	0.097
7518.0	0.080
11226.0	0.067
14472.0	0.054
18312.0	0.046
21888.0	0.034
25428.0	0.032
29172.0	0.022
32982.0	0.025
36006.0	0.017
40134.0	0.009
43278.0	0.012
46908.0	0.010
90000.0	-0.000

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -2.135956 \pm .120310 \\ \text{K} &= 0.000055 \pm .000005 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.1181 .
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0100 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0.9882 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 16

TIME	CME
142.8	0.072
1236.0	0.073
2454.0	0.071
3606.0	0.062
7476.0	0.049
11232.0	0.045
14970.0	0.039
18396.0	0.025
22044.0	0.027
25470.0	0.017
29136.0	0.019
32544.0	0.012
36264.0	0.009
40026.0	0.012
43296.0	0.008
47328.0	0.002
90000.0	0.001

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -2.577814 \pm .130327 \\ \text{K} &= 0.000052 \pm .000005 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.0759 .
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0073 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0.9847 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB. 18

TIME	CME
163,8	0,073
1248,0	0,075
2454,0	0,071
3606,0	0,063
7434,0	0,053
11304,0	0,038
14868,0	0,038
18252,0	0,027
21804,0	0,025
25350,0	0,019
28986,0	0,018
32466,0	0,014
36174,0	0,010
40110,0	0,005
43428,0	0,009
47376,0	0,011
90000,0	0,003

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM;

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} ,$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -2,535690 \pm 0,173645 \\ \text{K} &= 0,000057 \pm 0,000007 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL,

THE INITIAL CONCENTRATION FROM THIS FIT IS 0,0792 ,
THE CONCENTRATION AT 45000,0 SECONDS IS 0,0062 ,

THE CORRELATION COEFFICIENT FOR THIS FIT IS -0,9773 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB, 20

TIME	CME
157.2	0.077
1248.0	0.074
2424.0	0.068
3630.0	0.065
7446.0	0.049
11388.0	0.046
14934.0	0.030
18546.0	0.033
22116.0	0.019
25308.0	0.021
29214.0	0.011
32490.0	0.014
36204.0	0.013
39828.0	0.011
43788.0	0.012
46860.0	0.006
90000.0	0.001

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM;

$$\text{LN} (\text{CME}) = \text{LN} (\text{CME-INITIAL}) - \text{KT} .$$

$$\begin{aligned} \text{LN} (\text{CME-INITIAL}) &= -2.622197 \pm .179326 \\ \text{K} &= 0.000049 \pm .000007 \end{aligned}$$

AT THE 95% CONFIDENCE LEVEL.

THE INITIAL CONCENTRATION FROM THIS FIT IS 0.0726 .
THE CONCENTRATION AT 45000.0 SECONDS IS 0.0079 .

THE CORRELATION COEFFICIENT FOR THIS FIT IS =0.9685 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB.24

TIME	CME
441.6	1.006
3660.0	0.948
10992.0	0.850
21336.0	0.741
32556.0	0.649
43344.0	0.580
86298.0	0.405
97476.0	0.377
107928.0	0.349
118848.0	0.331
129786.0	0.307
172920.0	0.257
183720.0	0.241
194220.0	0.226
275020.0	0.222
216120.0	0.213
259200.0	0.182
345600.0	0.141
432000.0	0.119
518400.0	0.101

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$1.0 / CME - 1.0 / CMEINITIAL = KT.$$

THE Y INTERCEPT IS $-.0237781 \pm .0351002$

K = $.0000174 \pm .0000002$

AT THE 95% CONFIDENCE LEVEL.

THE CORRELATION COEFFICIENT FOR THIS FIT IS 0.9998 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS FEB.28

TIME	CME
327.6	1.012
3762.0	0.955
10716.0	0.855
21324.0	0.738
32262.0	0.647
43404.0	0.572
56454.0	0.407
97320.0	0.372
108114.0	0.347
119020.0	0.325
129894.0	0.315
172920.0	0.249
183420.0	0.242
194160.0	0.232
245320.0	0.218
216180.0	0.208
239200.0	0.184
345600.0	0.140
432000.0	0.121
518400.0	0.106

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$1.0 / CME - 1.0 / CMEINITIAL = KT,$$

THE Y INTERCEPT IS .0015753 +/- .0586354
 K = .0000172 +/- .0000003

AT THE 95% CONFIDENCE LEVEL,

THE CORRELATION COEFFICIENT FOR THIS FIT IS 0.9993 .

SEE THE CORRESPONDING PLOT.

THE DATE FOR THIS RUN WAS MAR.04

TIME	CME
483.6	.1.007
3798.0	0.946
11004.0	0.846
21696.0	0.732
32274.0	0.646
43128.0	0.580
56166.0	0.485
97488.0	0.380
128270.0	0.355
118824.0	0.332
129580.0	0.308
172980.0	0.256
183540.0	0.243
194400.0	0.233
205440.0	0.217
215880.0	0.214
259200.0	0.180
345600.0	0.145
432000.0	0.117
518400.0	0.106

FIT FOR FIRST 90% OF REACTION

THE EQUATION FIT HAS THE FORM:

$$1.0 / CME - 1.0 / CMEINITIAL = KT.$$

THE Y INTERCEPT IS $-.0292253 \pm .0347399$

K = $.0000173 \pm .0000002$

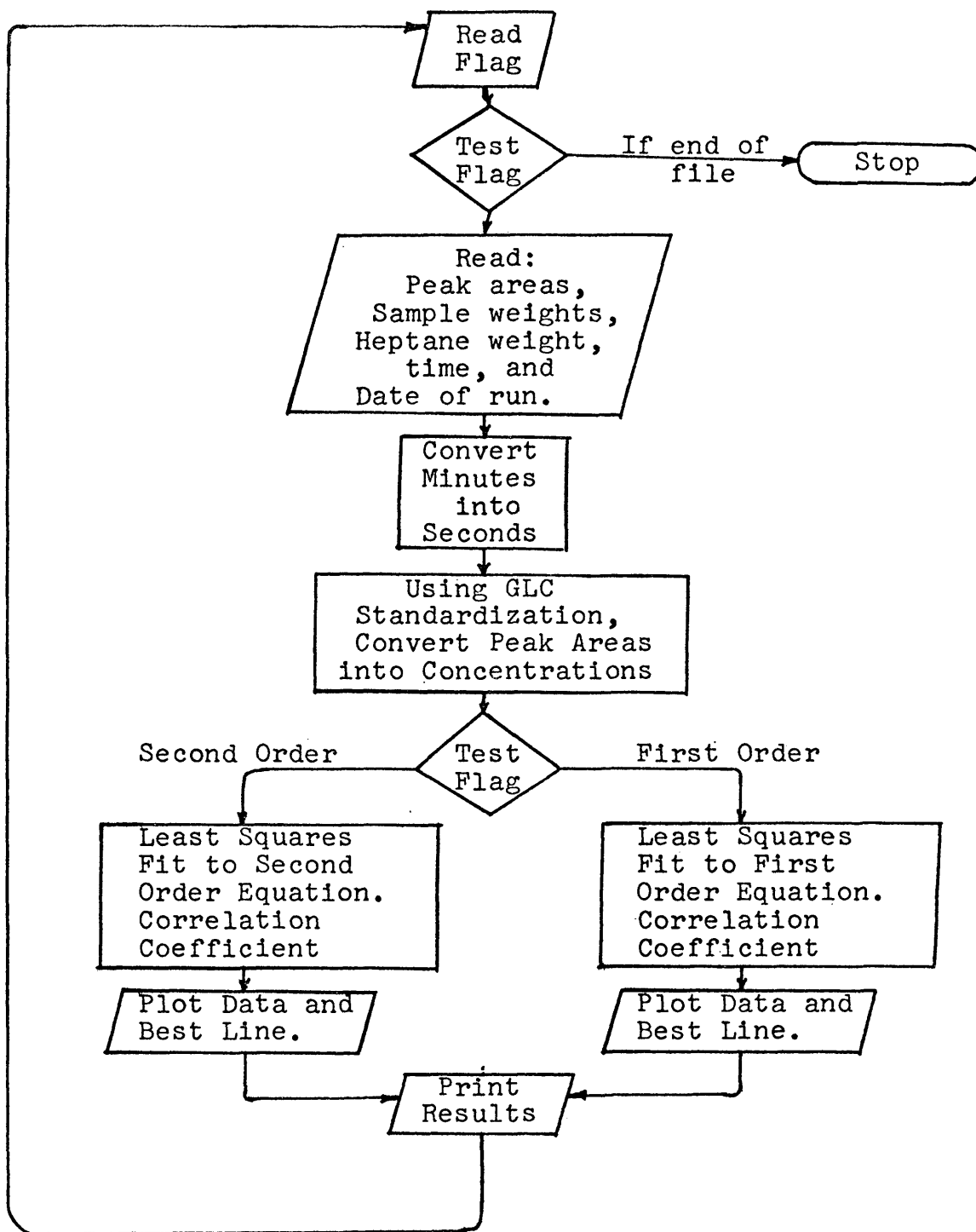
AT THE 95% CONFIDENCE LEVEL.

THE CORRELATION COEFFICIENT FOR THIS FIT IS 0.9996 .

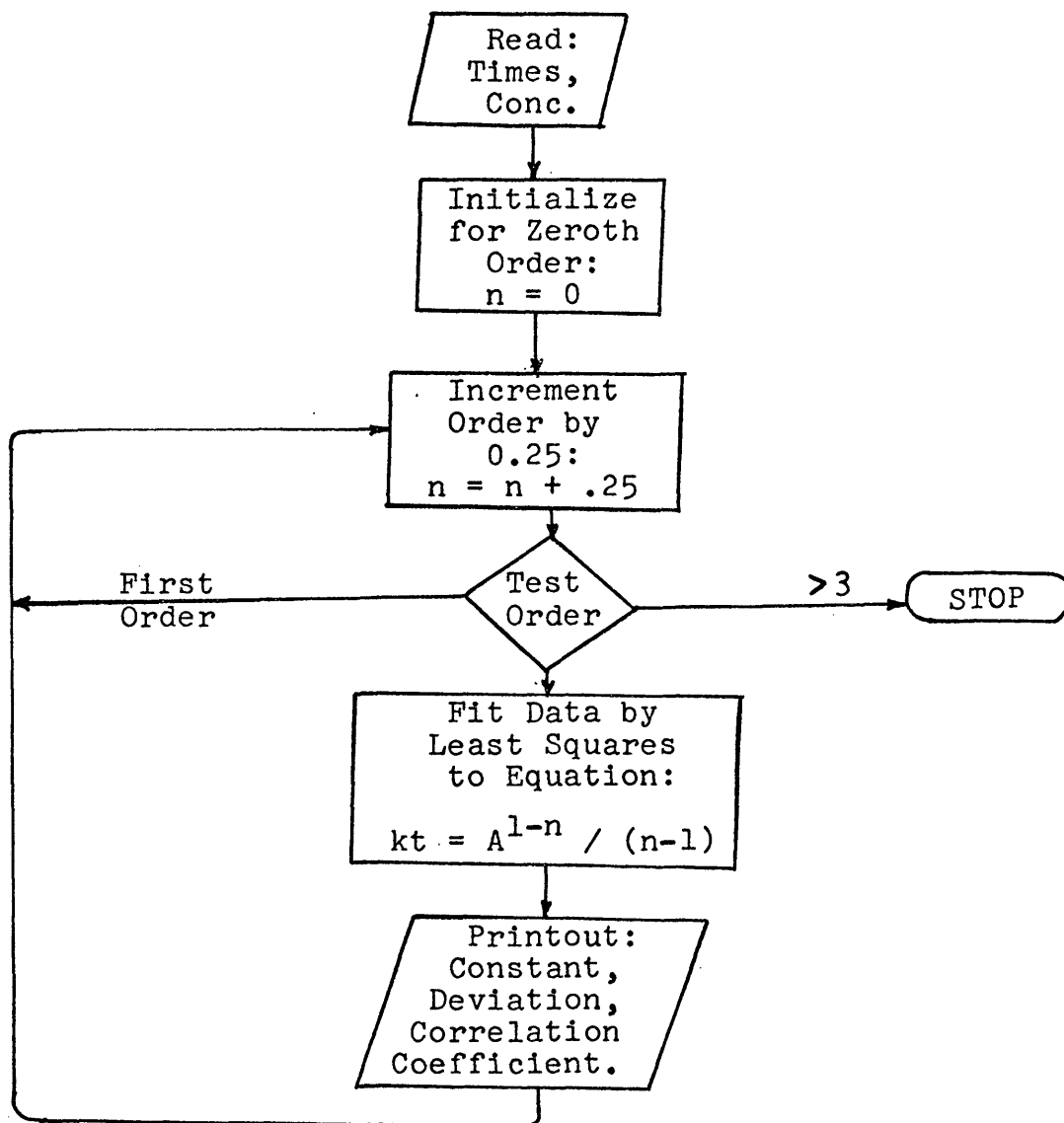
SEE THE CORRESPONDING PLOT.

APPENDIX II

FLOW CHARTS OF COMPUTER PROGRAMS



Flow diagram for the computer program to reduce data from the GLC.



Flow diagram for the computer program to fit data to alternate kinetic equations.

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