

A KINETIC STUDY OF THE GAS PHASE THERMAL DECOMPOSITION
OF 2-CHLOROETHYLSILICON COMPOUNDS

A THESIS

submitted by

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for the degree of

DOCTOR OF PHILOSOPHY

in the

UNIVERSITY OF LEICESTER

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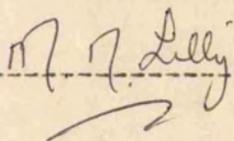
Signed

----- M. J. Lilly -----
2

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between September 1960 and September 1963.

The work has not been presented, and is not being concurrently presented, in candidature for any other degree.

Signed

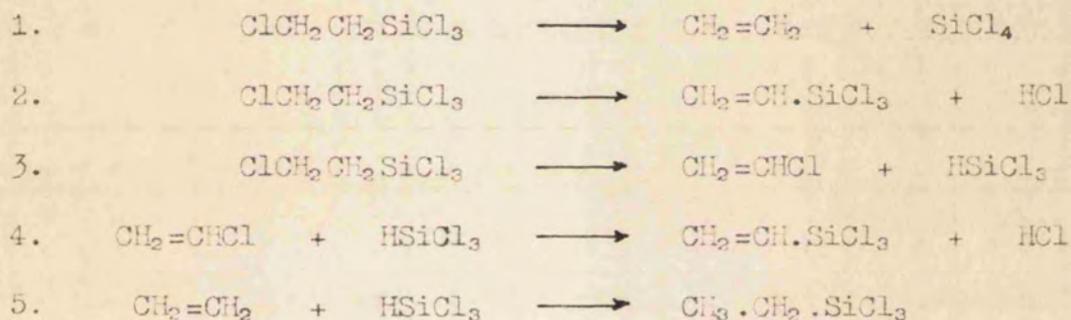
A handwritten signature in dark ink, appearing to read "M. J. Lilly", is written over a horizontal dashed line. The signature is cursive and includes a long horizontal stroke at the bottom.

June, 1964.

S U M M A R Y

The chemical reactivity of the halogenoalkylsilicon compounds has been reviewed and the published quantitative work on the decomposition of 2-halogenoalkylsilicon compounds outlined.

The gas phase thermal decomposition of 2--chloroethyltrichlorosilane has been investigated in a static system between 356° and 417°C at initial pressures of 12 - 138 mm. Hg. Use has been made of pressure measurement, gas chromatography and mass spectrometry to obtain kinetic data and to establish the mechanism of the reaction. The over-all reaction scheme is,



where ethylene and silicon tetrachloride account for 72% of the reaction products.

A brief study of the subsidiary reactions, 4 and 5, has been made and approximate kinetic data obtained. These reactions are suppressed by nitric oxide and cyclohexene.

Reactions 1, 2 and 3 are shown to be simultaneous unimolecular eliminations and the Arrhenius equation for the major reaction, ethylene elimination, is:

$$k_1 \text{ (sec.}^{-1} \text{)} = 10^{11.26 \pm 0.16} e^{-45,500 \pm 500 / RT}$$

The low pre-exponential term corresponds to $\Delta S_1^\ddagger = -8.0 \pm 0.7$ e.u., which suggests a cyclic transition state. In particular, a " quasi-heterolytic " transition state may be involved, as in the thermal decomposition of alkyl halides and carboxylic esters, and this possibility is discussed, although accurate correlation cannot be made until more results are available on other 2-halogenoalkylsilicon compounds.

An analogous study has been carried out on 2-chloroethyl-dimethylphenylsilane between 236° and 390°C. It has been shown that the reaction,



accounts for more than 99% of the reaction products.

However, the reaction is very sensitive to surface condition and it was not found possible to isolate the homogeneous decomposition. Suggestions for resolving this difficulty are made.

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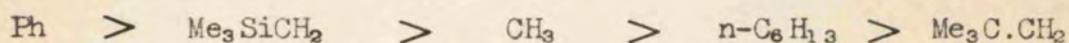
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CHAPTER ONE

(A) GENERAL REACTIVITY OF α -, β - AND γ -HALOGENOALKYLSILICON COMPOUNDS

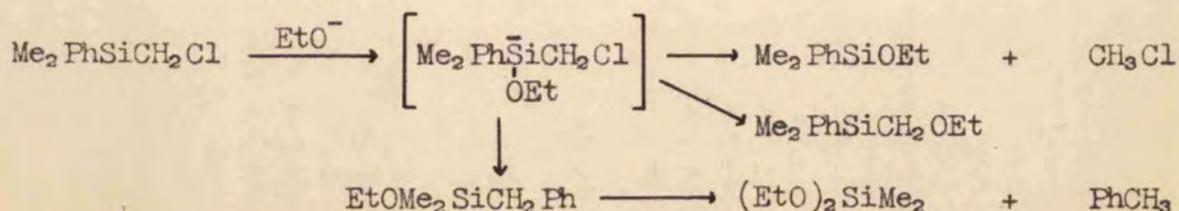
(i) α -HALOGENOALKYLSILANES

Chloromethyltrimethylsilane, $\text{ClCH}_2\text{SiMe}_3$, the silicon equivalent to neopentyl chloride, exhibits the normal properties common to organic halides in nucleophilic substitution although the chlorine atom is more readily displaced from the silicon compound. Neopentyl halides are relatively inert to $\text{S}_{\text{N}}2$ reactions with sodium ethoxide, potassium acetate and sodium iodide. A decreasing electronegativity series has been determined by the Kharasch method.



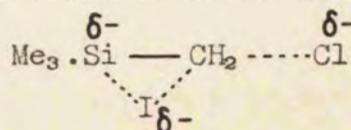
The lower reactivity of the neopentyl system is attributed to the shielding effect of the tertiary butyl group preventing rearward attack on the methylenic carbon opposite the halogen. This rearward attack is easier when $\text{Me}_3\text{Si-}$ replaces $\text{Me}_3\text{C-}$ because of the greater covalent radius of silicon ($\text{Si} = 1.17$, $\text{C} = 0.77$) and hence less interaction between methyl groups.¹

With sodium ethoxide, chloromethyltrimethylsilane is however 2.5 times less reactive than n-hexyl chloride, 4 times less reactive than n-butyl chloride and 16 times less reactive than ethyl chloride.² Sodium ethoxide reacts with chloromethyldimethylphenylsilane giving rise to three schemes: cleavage, substitution and rearrangement, the latter being followed by cleavage.²



The rearrangement is facilitated by electron withdrawing chlorine on the phenyl group and all the processes would involve the common penta-covalent silicon intermediate or the mechanism may be concerted. Other nucleophiles (e.g. potassium acetate in glacial acetic acid, potassium acetate in ethanol, and aqueous or ethanolic potassium hydroxide) are also less reactive towards the silicon compound but the difference in reactivity is less. The trimethylsilyl group releases electrons inductively and so would be expected to prevent nucleophilic attack. Similarly the trimethylsilyl group could provide some steric hindrance to reaction.³ Nucleophilic attack by base will cleave the CH_2Cl group from silicon giving CH_3Cl as a product.⁴

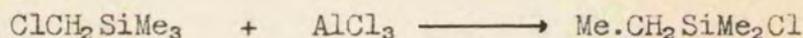
Primary and secondary halogenoalkylsilanes exhibit a reactivity ratio similar to primary and secondary alkyl halides towards iodide ion in acetone,⁵ the primary being about 200 times more reactive than the secondary. α -chloroalkylsilanes are far more active than neopentyl halides towards this reagent which attacks alkyl halides by a bimolecular $\text{S}_{\text{N}}2$ reaction, Walden inversion. Chloromethyltrimethylsilane is 16 times more reactive than n-butyl chloride and 8 times more reactive than ethyl chloride. Possibly the iodide ion gives a stabilized transition state utilizing the d-orbitals of silicon.^{6,7}



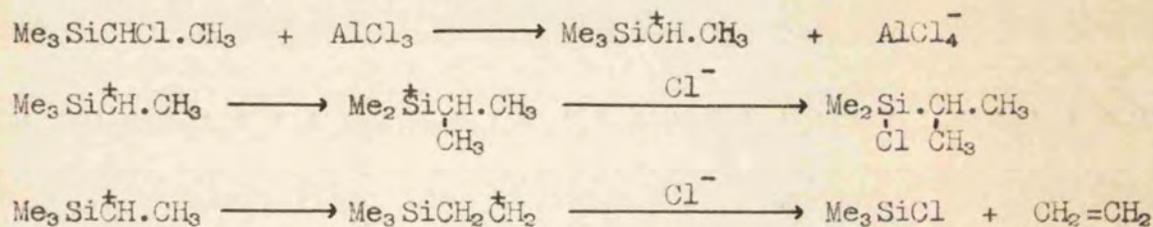
Although alkyl halides, including neopentyl halides, react readily with silver nitrate in ethanol by electrophilic attack of Ag^+ on the halogen, the compounds $\text{Me}_3\text{SiCH}_2\text{X}$ do not give a precipitate although one would expect the Me_3Si - group to stabilize a carbonium ion intermediate by supplying electrons inductively. Similarly the

α -chloroethylsilanes do not react with this reagent although sec-butyl chloride does.^{3,8}

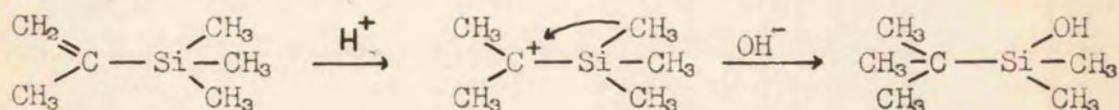
Rearrangement of chloromethyltrimethylsilane in the presence of aluminium chloride is known to occur⁹ in a manner strictly analogous to the Wagner-Meerwein rearrangement of carbon chemistry.



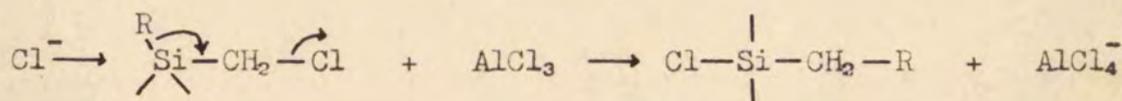
The α -chloroethylsilanes also rearrange in the presence of aluminium chloride and some elimination, E.1, also occurs.



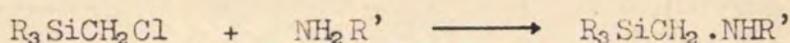
If one of the alkyl groups in $\text{R}_3\text{Si}-$ is replaced by chlorine then only olefin elimination, or sometimes dehydrochlorination, occurs.¹⁰ Similarly methyl rearrangement of isopropenyltrimethylsilane to t-butyl dimethylsilanol passes through an intermediate α -carbonium ion in the presence of concentrated sulphuric acid.



With the compounds $\text{Me}_3\text{Si}\cdot\text{SiMe}_2\text{CH}_2\text{Cl}$ and $\text{Me}_2\text{ClSi}\cdot\text{SiMe}_2\text{CH}_2\text{Cl}$ in the presence of aluminium chloride the $\text{Me}_3\text{Si}-$ and $\text{Me}_2\text{ClSi}-$ groups respectively migrate from silicon to carbon¹¹ because of their greater electron release than methyl. These rearrangements probably pass through siliconium or carbonium ion intermediates although discrete steps may not occur and the process could be concerted.

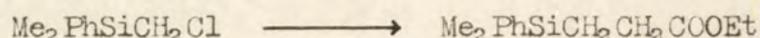


α -halogenoalkylsilanes react readily with amines to form substitution products with cleavage of the silicon - carbon bond occurring to a varying extent.^{12,13,14,15}

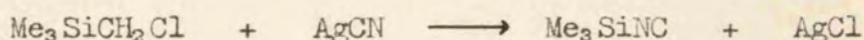


The amines form stable hydrochlorides. Sodamide in liquid ammonia rapidly cleaves chloromethyltrimethylsilane.¹³

With acetoacetic ester the α -halogenoalkylsilanes generally give ketones^{16,17} but react normally with malonic ester.¹⁷



Potassium cyanide in methanol¹⁸ and silver cyanide¹⁹ rapidly cleave the silicon - carbon bond in halogenomethyltrimethylsilanes. The mechanisms are not known but the following reaction is known to occur.



α -chloroethyltriethylsilane is very resistant to cleavage by nucleophiles. It is unaffected by hot alcoholic sodium hydroxide and only dehydrochlorinates with alcoholic potash²⁰ at 145°C. The stability is brought about by the additional α -Me group which supplies electrons and hinders the separation of the CH₂Cl group with the electrons of the silicon - carbon bond.

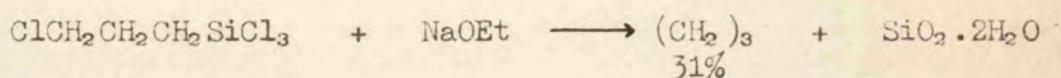
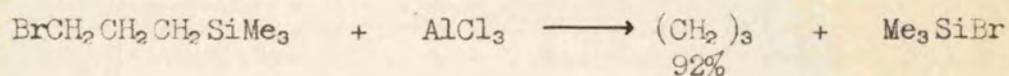
Other nucleophilic displacements of X in R₃SiCH₂X are:

REAGENT	PRODUCT	REFERENCE
NaSCH ₂ COONa	-SCH ₂ COOH	21
Na ₂ S	-S.CH ₂ SiR ₃	22
NaS.Me	-S.Me	22
KOOC.C(Me)=CH ₂	-OOC.C(Me)=CH ₂	23
NaOP(O)(OBu ⁿ) ₂	-OP(O)(OBu ⁿ) ₂	24

α -halogenoalkylsilanes form Grignard reagents normally.

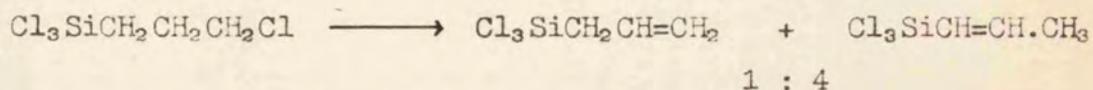
(ii) γ-HALOGENOALKYLSILANES

These compounds in general undergo the normal reactions by analogy with their equivalent carbon compounds. However, reaction of γ-bromopropyltrimethylsilane with aluminium chloride or γ-chloropropyltrichlorosilane with sodium ethoxide gives cyclopropane as a cleavage product.²⁵



Reversing of the reagents did not produce the above reactions. The mechanisms are not known but they appear similar to 1:3 eliminations in organic chemistry when an activated hydrogen atom is γ to halogen,²⁶ for example, $\text{BrCH}_2\text{CH}_2\text{CH}(\text{COOEt})_2$. γ-chloropropylmethyldiethylsilane decomposes on distillation to yield methyldiethylchlorosilane and cyclopropane.²⁷

With aluminium chloride, γ-chloropropyltrichlorosilane gives a mixture of products. A rearrangement occurs in which a γ-carbonium ion is converted into the more stable β-carbonium ion.²⁸



γ-halogenoalkylsilanes form Grignard reagents normally.

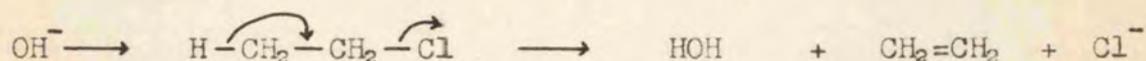
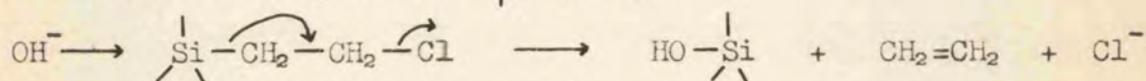
(iii) β-HALOGENOALKYLSILANES

β-halogenoalkyl groups are much more readily cleaved from silicon than the α- and γ- isomers and result in olefin elimination. Compounds like β-chloroethyltrimethylsilane decompose on distillation although β-chloroethyltrichlorosilane can be distilled at atmospheric

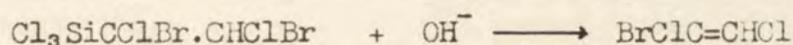
pressure with no appreciable decomposition.^{28,29,30}

(a) Attack by nucleophiles

β -halogenoalkylsilanes are very much more reactive towards alkali, aqueous or alcoholic, than the α - and γ - isomers and exhibit a much greater reactivity than the analogous carbon compounds. Even sodium acetate in glacial acetic acid or water alone will decompose these compounds when one or more electronegative halogen atoms are attached to silicon. The reaction mechanism has been suggested^{29,30} to be closely analogous to the E.2 elimination reactions of alkyl halides with silicon behaving like a β -hydrogen.

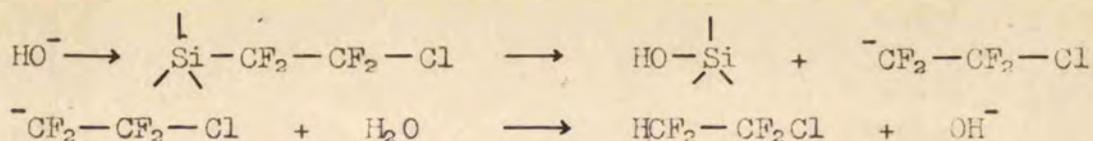


The β -silicon is attacked very much more readily than a β -hydrogen. Therefore, although two β -hydrogens are present in the silane, the attack is exclusively on silicon. Many other β -halogenoalkylsilanes have been prepared and shown to undergo this reaction.^{28,31,32} The β -bromo compound is more reactive than the β -chloro and this has been neatly shown by bromine being removed in preference to chlorine when both were present on the β - position.^{32,33}



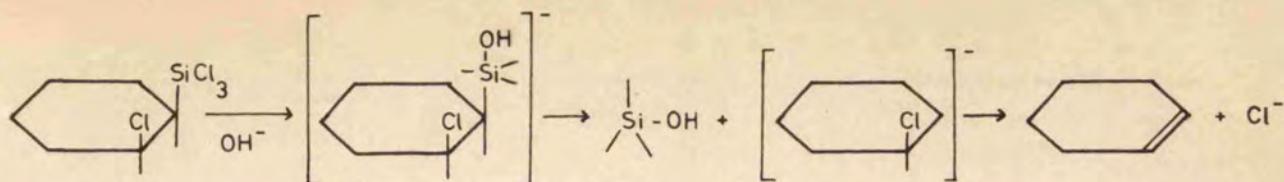
β -chlorotetrafluoroethyltrichlorosilane reacts with aqueous 10% sodium hydroxide to give silica, tetrafluorochloroethane and no olefin.³⁴ Because of the electronegativity of fluorine the Si - C ^{α} bond would be strongly polarized Si ^{δ^+} - C ^{δ^-} relative to hydrogen thus increasing the incidence to nucleophilic attack on silicon. The fluorine substituents also render the β -carbon atom more positive and electron

release to chlorine becomes more difficult.



Whereas the α - and γ -chloroalkyltrichlorosilanes react with the three equivalents of base required to solvolyse the Si - Cl bonds,³⁵ the β -chloroalkyltrichlorosilanes react rapidly with four equivalents,³⁶ the C-Cl bond reacting as completely as the Si-Cl bonds. The presence of two α -methyl groups does not hinder this reaction and β -chloro- α, α -dimethylethyltrichlorosilane produces isobutylene quantitatively.³⁷ Electron supplying groups attached to silicon retard the reaction and $\text{Et}_3\text{SiCH}_2\text{CH}_2\text{Cl}$ reacts only slowly with dilute alkali. If excess alkali is added then the reaction is completed in 20 minutes. The reaction is therefore base catalysed. This is substantiated by the fact that a silicone resin has been produced by a neutral reaction with the $-\text{CH}_2\text{CH}_2\text{Cl}$ group intact;³⁰ addition of base evolved ethylene. Likewise making 50% aqueous methanol 1.25N in sodium hydroxide increased the yield of ethylene from $\text{ClCH}_2\text{CH}_2\text{SiR}_3$, where $\text{R}_3 = \text{Et}_3, \text{Et}_2\text{Cl}$ and Et_2F , from < 5 to ≥ 50 per cent.^{8,29}

Reaction of trichlorosilane with 1-chlorocyclohexene using a peroxide catalyst produces a mixture of cis- and trans-1-chloro-2-trichlorosilylcyclohexane in low yield. Titration with base showed four active chlorine atoms.^{38,39} It was suggested, in view of the predominantly cis product and the rapidity of the reaction, that this was a non-stereospecific β -elimination involving a pentacovalent intermediate as has been postulated for nucleophilic substitutions involving silicon.⁴⁰

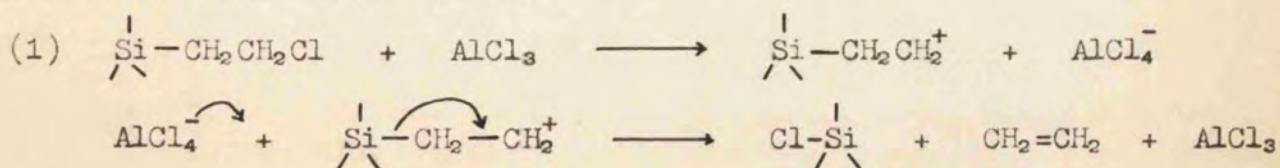


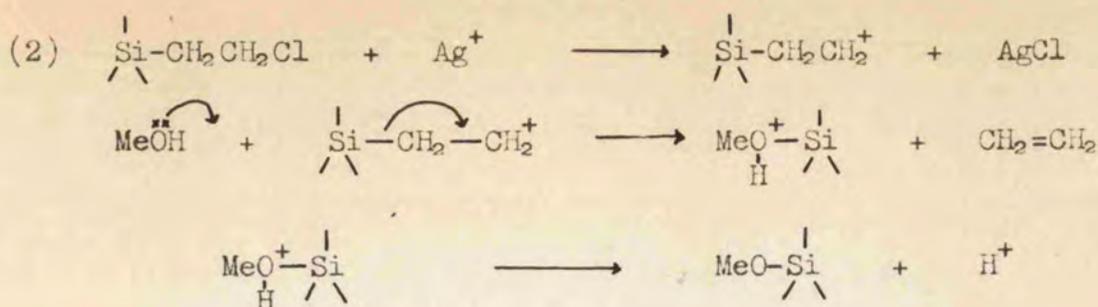
It was found possible to only partially resolve the cis and trans components on gas chromatographic analysis during which appreciable decomposition occurred.

β -chlorovinyltrichlorosilane reacts with only three equivalents of base leaving the chlorovinyl group intact.⁴¹ Conjugation between silicon and carbon occurs using the available d -orbitals of silicon. This $d\pi$ - $p\pi$ overlap causes the non-Markovnikov addition of HX to vinylsilanes. It also accounts for the bathochromic shift in infra-red absorption due to the vinyl double bond which is attributed to a lowering of the stretching force constant by conjugation.⁴² This conjugation causes the inertness of the chlorovinyl group as compared with the chloroalkyl group and makes silicon reluctant to function in its normal electron releasing, inductive, capacity.^{43,44,45}

(b) Attack by electrophiles

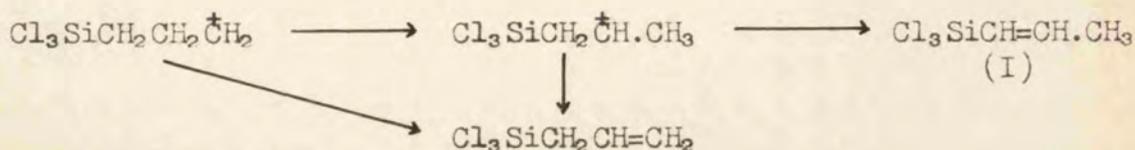
Electrophilic reagents like aluminium chloride and silver nitrate in methanol also produce olefins on reaction with β -halogenoalkylsilanes²⁹ and the reactions are similar to E.1 eliminations of alkyl halides although the silicon compounds react at a much faster rate. The mechanisms would appear to be:-





The rate determining step may not be simple ionization of the C^β-Cl bond as olefins are produced much less readily from alkyl halides. No structural work has been done to find the effect of substituents but electron releasing groups on silicon should facilitate these electrophilic reactions. With aluminium chloride the compound ClCH₂CH₂SiCl₃ dehydrochlorinates rather than desilylates.⁴⁶ In this case it appears that the electron withdrawing chlorine atoms prevent release of electrons to the β-carbon atom and removal of a proton becomes more energetically feasible than removal of the -SiCl₃ group.

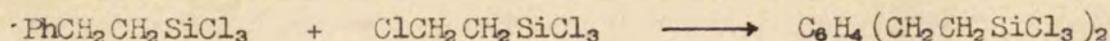
In a study of the aluminium chloride catalysed dehydrochlorination of β- and γ-chloropropyltrichlorosilane²⁸ some silicon - carbon bond cleavage took place at higher aluminium chloride concentrations or higher temperature and propene was formed. At small aluminium chloride concentrations dehydrochlorination occurred giving two isomeric products.



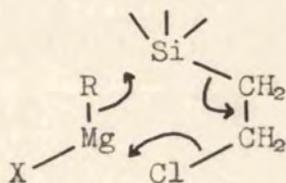
A γ ← β hydrogen shift is necessary to explain the formation of (I). Also it appears that with β-chloropropyltrichlorosilane the β-methyl group makes the secondary carbonium ion formed stable enough for some desilylation to compete with dehydrochlorination.

β-chloroethyltrichlorosilane has been found to undergo Friedel-

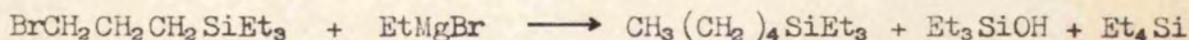
Crafts coupling in the presence of aluminium chloride.⁴⁷



Grignard reagents of the β -halogenoalkylsilanes are very difficult to prepare and the addition of RMgX usually leads to olefin elimination. Slow addition of methyl-Grignard to $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ resulted in most of the ethylene being evolved on addition of the fourth equivalent of reagent.³⁰ After reaction of the Si-Cl bonds normally it was suggested that a cyclic transition state was formed by co-ordination of the β -chlorine atom to magnesium.



However the β -carbon substituted product has been formed in small yields from β -bromo-n-propylsilanes by hydrolysing soon after the reactants were mixed.⁴⁸



It is therefore suggested as probable that intramolecular elimination occurs with initial formation of R_3SiX which is then hydrolysed to R_3SiOH .⁴⁹ Alternatively nucleophilic attack by OH^- could occur during the hydrolysis step before intramolecular formation of R_3SiX has commenced.

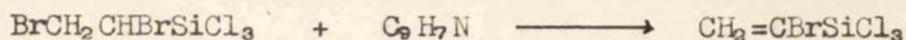
Simultaneous addition of β -bromoethyltriethylsilane and ethyl bromide to magnesium gave only a small amount of n-butyltriethylsilane and the main product was tetraethylsilane. However a similar experiment using allyl bromide gave 4-pentenyltriethylsilane as the predominant product.⁵⁰ Under favourable conditions β -halogenoalkylsilanes will

couple with Grignard reagents and these conditions are set out in Table I, going down the table indicating an increasing tendency to coupling and less β -elimination.

TABLE I

C - X in $R_3Si-C-C-X$	R in $R_3Si-C-C-X$	R' in $R'MgX$
Primary	Ph	Et
Secondary	Me	n-Pr
Tertiary	Et	Ph
	n-Pr	Allyl
	n-Bu	

Dehydrochlorination with quinoline^{29,33,51,52} and isoquinoline⁵³ is very effective with β -halogenoalkylsilanes and has been extensively used when the more vigorous treatment with alkali gives rise to cleavage of the silicon - carbon bond. For example, with α, β -dibromoethyltrichlorosilane only the β -bromine is removed.³³



It is generally found that α - and γ -halogenoalkylsilanes are more resistant to dehydrochlorination using quinoline although isoquinoline is sometimes effective with γ -halogenoalkylsilanes.

(B) REACTIONS RELATED TO THE β -ELIMINATION OF 2-HALOGENOALKYLSILANES

(i) SILYL ACETATES AND KETONES

Silicon compounds with oxygen functions β to the silicon atom are readily cleaved by acids and bases and will be discussed briefly to exemplify the general reactivity of β -substituted silicon compounds.

Trimethylsilyl acetic acid can be prepared from $\text{Me}_3\text{SiCH}_2\text{MgCl}$ and CO_2 if the precautions of neutral hydrolysis and crystallization instead of fractionation are observed.⁴⁴ Treatment with acid results in silicon - carbon bond cleavage giving $\text{Me}_3\text{Si-O-SiMe}_3$ and acetic acid.⁵⁴

Similarly sodium hydroxide reacts with ethyltrimethylsilyl acetate cleaving the silicon - carbon bond and giving $\text{Me}_3\text{Si-O-SiMe}_3$ and ethyl acetate.⁵⁵ It is noteworthy that aqueous base cleaved this compound at room temperature but acid did not. This seems to suggest a greater susceptibility of these compounds to nucleophilic attack.

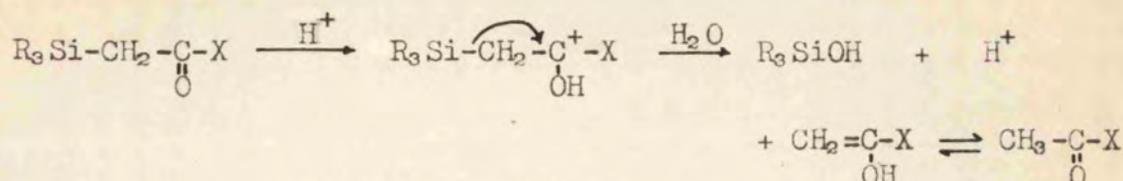
Silyl ketones may be isolated from the products of reaction between $\text{Me}_3\text{SiCH}_2\text{MgX}$ and acetic anhydride at -70°C ; but cleavage of the silicon - carbon bond occurs on attempted preparation at a higher temperature, presumably because of attack by hydroxyl ion in the hydrolysis step, as $(\text{Me}_3\text{Si})_2\text{O}$ and acetone were formed.⁵⁴ Cleavage is also effected in refluxing ethanol giving acetone and the appropriate ethoxysilane.¹⁸ Reaction of $\text{Me}_3\text{SiCH}_2\text{COCH}_3$ with 2,4-dinitrophenylhydrazine results in silicon - carbon bond cleavage and only the derivative of acetone is obtained. However, trimethylsilylbenzyl-methyl ketone does give a hydrazone derivative of the silyl ketone.

In general therefore, cleavage of the silicon - carbon bond occurs in β -carbonyl silicon compounds with acids (including HCl gas),

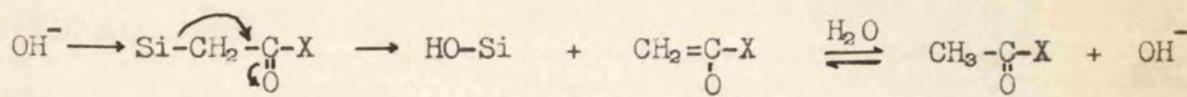
bases, anhydrous bromine and refluxing ethanol. The following mechanisms have been proposed.⁵⁵

X = alkyl, alkoxy or hydroxyl

Acid catalysis



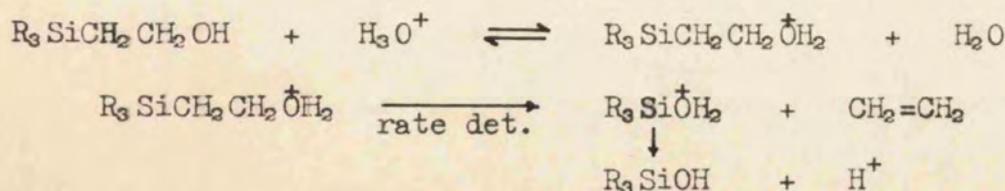
Base catalysis



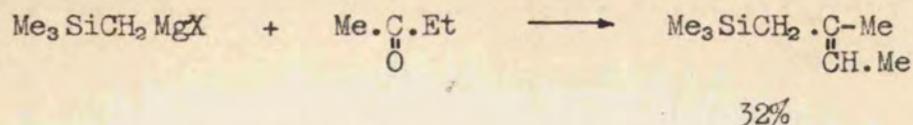
(ii) β-SILYL ALCOHOLS

Acid is required to cleave the Si-C bond in β-silyl alcohols.

β-hydroxypropyltrimethylsilane reacts with dilute aqueous sulphuric acid to give hexamethyldisiloxane and propene. A kinetic investigation of the acid cleavage of 2-silyl ethanols has been carried out.⁵⁶ A linear rate dependence upon acidity was found using the Hammett acidity function, H₀. As would be expected for electrophilic attack, electron withdrawing groups on silicon retarded the rate. The rate of reaction in acidic D₂O was found to be more than 2 times that in H₂O of the same acid concentration. It was suggested that reaction of the protonated alcohol, in which considerable positive charge was developed on silicon in the transition state, was the rate determining step.



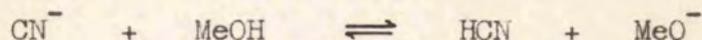
However, when the alcohol is a tertiary one then some dehydration can occur at the expense of desilylhydroxylation.⁵⁷



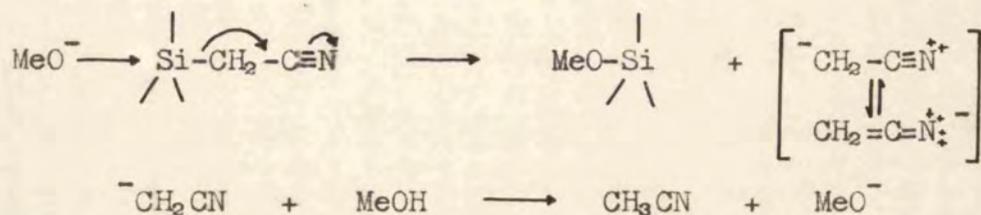
In many cases the tertiary alcohol is not isolated but reacts immediately on working up the products of the appropriate Grignard reaction, although $\text{Me}_3\text{SiCH}_2\text{C}(\text{Me}_2)\text{OH}$ has been prepared in 50% yield by this method.¹⁸

(iii) SILYL ACETONITRILES

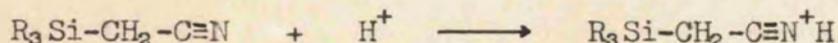
Cleavage of the silyl acetonitriles can be easily effected by aqueous acid or base and by water alone. Reaction of $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{Br}$ with potassium cyanide in methanol yielded only Me_3SiOMe and CH_3CN , presumably.¹⁸ The silylacetonitrile is probably formed but a finite concentration of methoxide ion would arise from the equilibrium:

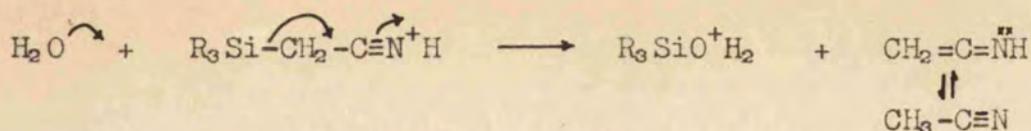


The methoxide ion would then attack the silylacetonitrile nucleophilically.



Preparation of a silylacetonitrile has been achieved by reacting $\text{R}_3\text{SiCH}_2\text{MgX}$ with cyanogen¹⁹ and the mechanism for acid catalysed decomposition is suggested to involve a ketimine.



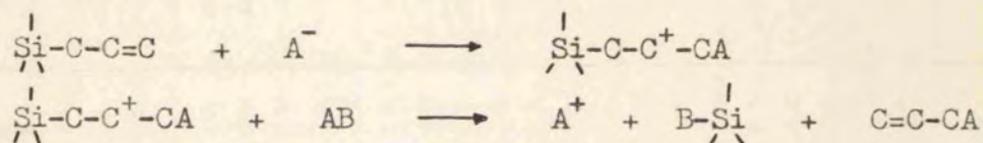


However if the cyano group is further removed from silicon, e.g. trimethylsilylpropionitrile, then reaction with alcoholic base gives trimethylsilylpropionic acid by normal hydrolysis of the cyano group to a carboxy group.

(iv) β - γ UNSATURATED ORGANOSILANES

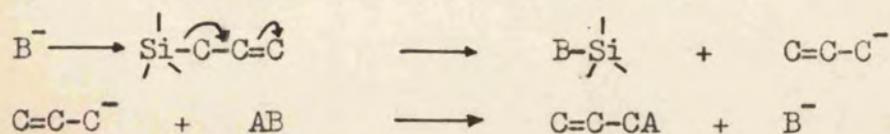
If a double bond is situated β - γ to the silicon atom then both acid and alkali will catalyse the cleavage of the Si-C bond to give an olefin by a mechanism analogous to that for the β -oxygenated silicon compounds.

Acid catalysis



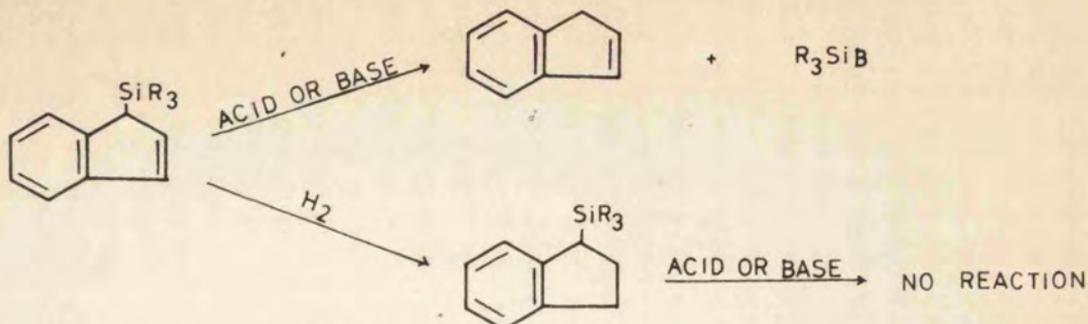
In some cases addition across the double bond can occur. HBr and HI will add to allyltrimethylsilane giving β -halogenopropyltrimethylsilane which then undergoes β -elimination as previously described. Bromine and Iodine give the cleavage products directly and similarly concentrated sulphuric acid or dry hydrogen chloride give propene and trimethylsilyl-sulphate or trimethylchlorosilane respectively.

Base catalysis (methanolic KOH or aqueous NaOH)



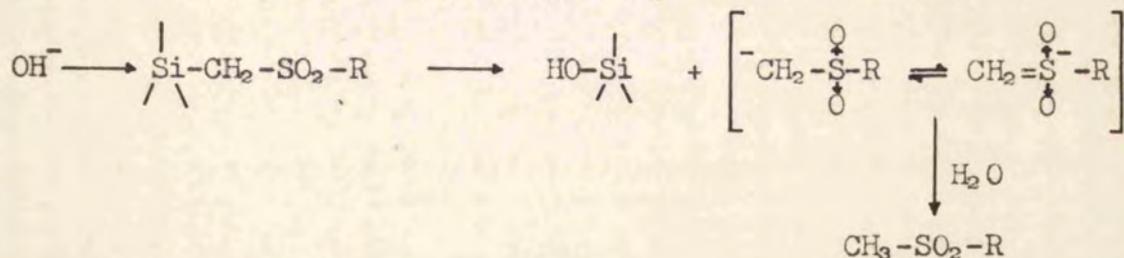
Cleavage of the Si-C bond in trisubstituted 1-silylindenes occurs

with acid or base⁵⁸ and partial reduction of the indene prevented this reaction.



(v) SILYLMETHYLSULPHONES

These compounds are synthesized by oxidation of the sulphides with hydrogen peroxide in either acetic acid/diethyl ether or phthalic acid/ethanol.²² The silicon - carbon bond is cleaved readily by bases but is more resistant to acidic attack than the nitriles or β -oxygenated compounds mentioned above. The stability to acid is attributed to the sulphone group not participating in enol formation. In the cleavage of β -oxygenated silicon compounds this enol formation facilitates the silicon - carbon bond cleavage. A possible mechanism is:



In desilylation of the methylsulphones the silicon behaves more like hydrogen than carbon.

Hence if an atom is β to silicon then, utilizing the electron releasing capacity of silicon, the Si-C bond can be cleaved with the possibility of the silicon obtaining a fractional positive charge and the carbon retaining the electron pair of the Si-C bond.

(C) KINETIC STUDIES OF THE REACTION OF β -HALOGENOALKYLSILICON

COMPOUNDS IN SOLUTION^{59,60}

(i) NEUTRAL CONDITIONS

Kinetic investigations have been carried out using trialkyl-substituted silanes so that hydrolysis of Si-Cl bonds did not complicate the kinetics. The rate of reaction was obtained volumetrically from the rate of production of olefin. Under some conditions the elimination mechanism is more closely similar to the E.1 mechanism than the E.2 mechanism.⁶¹ Since the intermediate formed in the rate determining step is the same in both E.1 and S_N1 reactions then the same factors will influence both reaction mechanisms.

(a) Solvent effects

The unimolecular substitution mechanism has been shown to be operative in the solvolysis of tertiary alkyl halides and the effect of solvent composition on the relative rate has been shown by Winstein and his co-workers⁶² using a parameter, Y, known as the "ionizing power" of the solvent.

$$\log k = mY + \log k_0$$

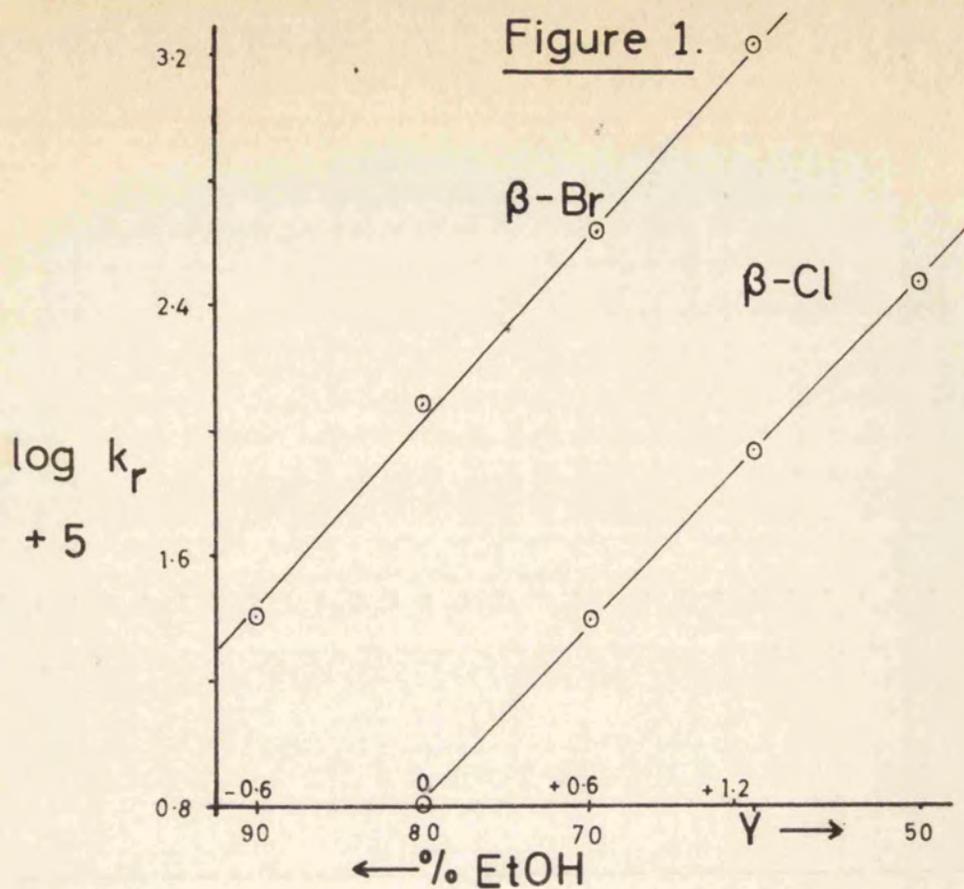
where $\log k$ = rate in experimental medium

$\log k_0$ = rate in standard medium (80% ethanol-water)

m = susceptibility of compound to changes in Y

Y = by definition,⁶³ $\log (k/k_0)_{t\text{-BuCl}}$

where k and k_0 are in experimental and standard medium respectively.



It was found that the decomposition of β -Bromo and β -Chloroethyltrimethylsilane in ethanol-water mixtures had a linear dependence upon Winstein's solvent composition parameter, see Figure 1. Also the solvent effects, $m_{\beta\text{-Cl}} = 1.02$, $m_{\beta\text{-Br}} = 0.99$, indicated that the elimination reaction of β -halogenoalkylsilanes was similar to the S_N1 mechanism for solvolysis of alkyl halides⁶⁴ where considerable separation of charge had occurred in attaining the rate determining transition state.

(b) Structural effects

The organosilicon compounds shown in Table II were studied in 70% ethanol-water at 50°C and the results correlated with the Taft equation for substituent polar effects,⁶⁵ $\log k/k_0 = \sigma^* \rho^*$.

TABLE II

R ₃ Si in R ₃ SiCH ₂ CH ₂ Cl	k/k ₀	log k/k ₀	Σσ*
Me ₃ Si	1.00	0.0	0.0
Et ₂ MeSi	0.955	-0.020	-0.200
iso-PrMe ₂ Si	0.652	-0.186	-0.190
PhMe ₂ Si	0.0955	-1.020	+0.600
<u>m</u> -CF ₃ C ₆ H ₄ Me ₂ Si	0.0123	-1.912	+1.015

$$\Sigma \sigma^* = \sigma_{\text{C}_6\text{H}_5}^* + \sigma_{\text{m-CF}_3}^*$$

The results did not fit the Taft equation very well but the values for the phenyl and m-trifluoromethylphenyl compounds established ρ^* , the susceptibility to changes in polar effects, to be negative and indicated that electron releasing groups on silicon should cause rate acceleration. The rate retardation of the diethylmethyl- and isopropyl dimethyl- compounds was attributed to steric factors. Using the results from the phenyl dimethyl- and m-CF₃-phenyl dimethyl- compounds the values $\rho^* = -1.8$ and $\rho = -2.15$ were obtained. The value ρ being evaluated from the Hammett equation, $\log k/k_0 = \rho \sigma$. These results should be a reasonable indication of the susceptibility to polar effects as the substituents are well removed from the reaction site and indicate a decrease of electron density on silicon in going to the rate determining transition state.

(c) Temperature effect

The effect of temperature on the reaction rate has been investigated for β -chloroethyltrimethylsilane in ethanol-water mixtures of varying composition and the mean values are shown in Table III.

TABLE III

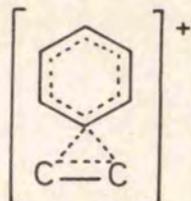
Temperature °C	$10^3 k \text{ sec.}^{-1}$		
	50% EtOH	60% EtOH	70% EtOH
15.0	0.575	-	-
20.0	1.04	0.289	-
25.0	1.71	-	-
30.0	2.90	0.825	0.242
35.0	4.50	-	-
40.0	7.19	-	-
45.0	10.9	-	-
50.0	-	-	1.78

From the results which have been summarized in Table III, using the Arrhenius equation, the parameters shown in Table IV were calculated for β -chloroethyltrimethylsilane.

TABLE IV

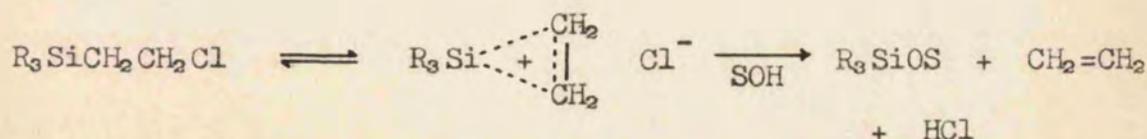
% vol. EtOH	E kcal/mole	ΔG^\ddagger kcal/mole	ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.
50	17.4	21.2	16.7	-14.5
60	18.5	22.0	17.9	-13.5
70	19.4	22.7	18.8	-12.9

The most significant values in Table IV are the large negative entropies of activation. These could be caused by a number of factors and although some aspects of this will be discussed later in relation to the gaseous reactions brief mention here may be useful. The large negative values of ΔS^\ddagger could arise from restriction of internal molecular motions in going to the transition state by the formation of a cyclic intermediate. Alternatively the activated complex may be more solvated than the starting state and increased solvent orientation would occur. The latter case occurs in the solvolysis of t-butyl chloride⁶⁶ although ΔS^\ddagger is only from -4 to -8 e.u. and the solvent orientation is nullified to some extent because of a less crowded activated complex. Winstein,⁶⁷ in a study of the solvolysis of 2-methyl-2-phenylpropyl chloride (neophyl chloride), found $\Delta S^\ddagger = -12$ e.u. in 60% EtOH and has postulated that in the rate determining reaction a cyclic phenonium ion is formed.



Both solvent orientation and restriction of internal motions contribute to the entropy decrease.

The mechanism proposed therefore by Baughman⁶⁰ for the neutral solvolysis of β -halogenoalkyltrialkylsilanes is the rate determining formation of a silacyclopropane system followed by rapid reaction with the solvent.



This mechanism is indicated by the facts that:

- (1) Structural effects indicate that silicon has some positive character in the transition state.
- (2) Analogy to solvolysis of tertiary alkyl halides with respect to reactivity and solvent composition indicate an ionization mechanism with possible formation of a β -carbonium ion in the limiting case.

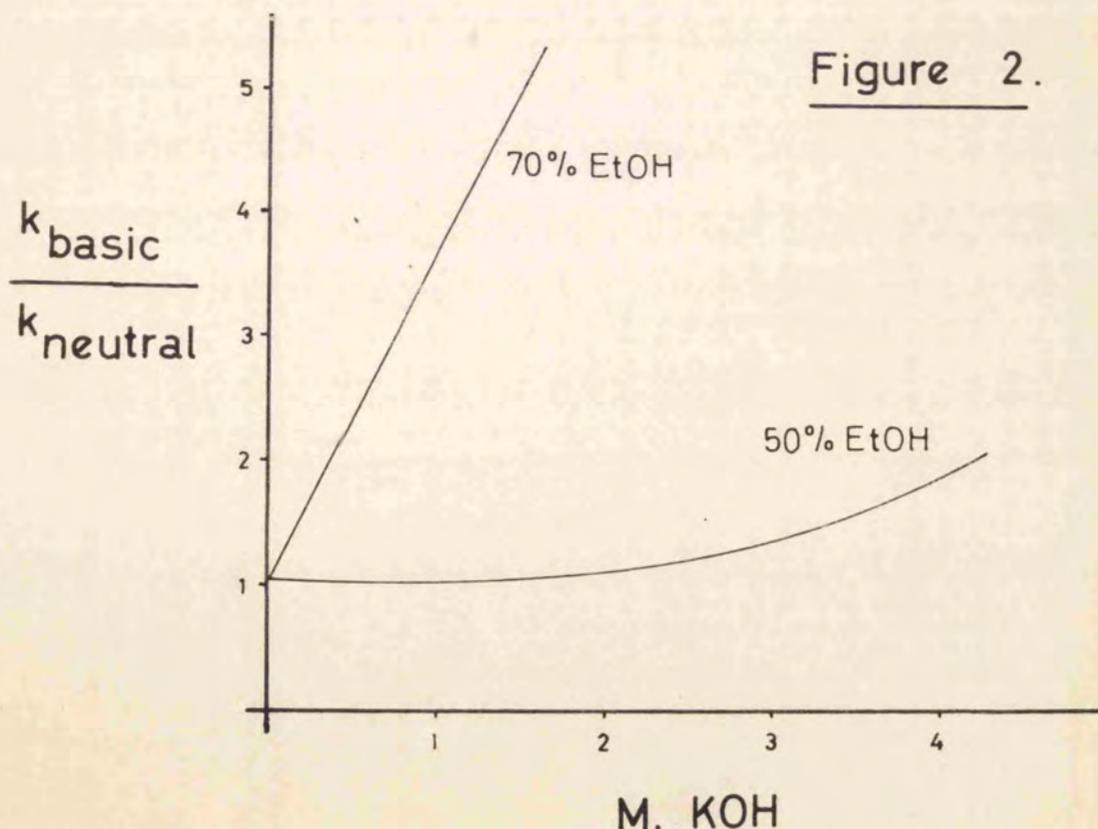
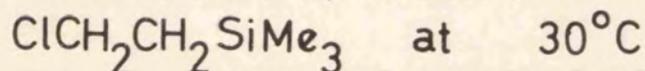


- (3) The large value of $-\Delta S^\ddagger$ indicated that the transition state was more congested and more strongly solvated than the starting state.

(ii) BASE CATALYSED REACTION

Making a 50% ethanol-water solution 0.54M in hydroxyl ions did not affect the rate of reaction of β -chloroethyltrimethylsilane.

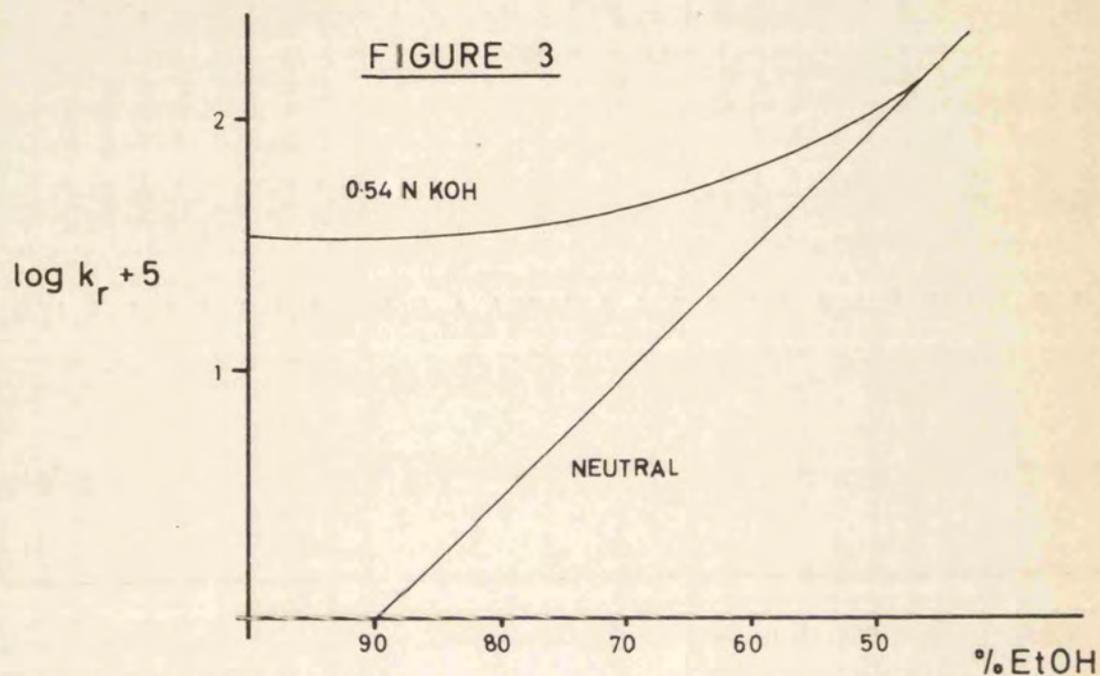
However, if the solvent is 70% ethanol-water then there is an approx-



approximately linear dependence upon hydroxyl ion concentration. The reaction is not a clean second order process as extrapolation to $[\text{OH}^-] = 0$ approximates to k_r for the neutral reaction, see Figure 2.

(a) Effect of solvent composition

Contrary to the neutral reaction the base catalysed reaction is



not strongly dependent upon solvent composition and at 90% ethanol-water becomes almost independent of the ionizing power of the medium, see Figure 3.

(b) Structural effects

Under basic conditions the reaction rate is enhanced by the same electron withdrawing substituents that retard the neutral rate and some numerical values are shown in Table V. The results are not strictly comparable as they were conducted at different temperatures but they do show the general trend of results.

TABLE V

R ₃ Si in R ₃ SiCH ₂ CH ₂ Cl	Base catalysed, 30°C		Neutral, 50°C
	10 ³ k _r	k/k ₀	k/k ₀
Me ₃ Si-	0.575	1.0	1.0
PhMe ₂ Si-	2.20	3.83	0.095
<u>m</u> -CF ₃ .C ₆ H ₄ .Me ₂ Si-	16.70	29.1	0.012

k_r = pseudo first order rate constant

Evaluation of ρ, the susceptibility to polar substituent effects, gave + 2.12 indicating an increase in electron density on silicon in going to the transition state.

Also with the compound Me₃Si-O-Si(Me₂)CH₂CH₂Cl, β-chloroethyl-dimethyl(trimethyl)siloxysilane, the electron withdrawing ability of the siloxy substituent facilitated nucleophilic attack by hydroxide ion and the rate was ca. 100 times faster in the presence of base than under neutral conditions.

(c) Effect of leaving group on rate (Table VI)

TABLE VI

Reaction of Me₃SiCH₂CH₂X at 30°C in 80% ethanol-water

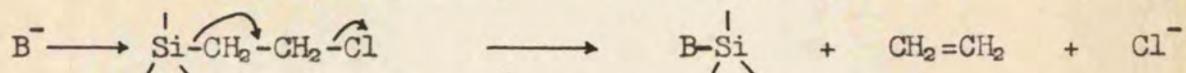
Conditions	Rate constant	
	X = Cl	X = Br
0.54N KOH	0.836	14.7
Neutral	0.0613	1.36

The observed rate under basic conditions was found to obey the law:

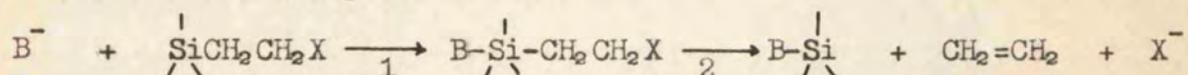
$$k_r = k_1 + k_2 [\text{OH}^-]$$

The assumption was made that in neutral solution $k_r = k_1$ and hence the value of k_2 could be calculated. Utilizing the above results the value $k_2\text{Br}/k_2\text{Cl} = 17$ was obtained which indicated that considerable cleavage of the C-X bond may occur in the rate determining step.

The mechanism of the base catalysed reaction could be concerted,



which could account for the positive value of ρ if there was increased electron density on silicon. Alternatively the mechanism could involve bond formation exceeding bond breaking and this too would account for the appearance of $[\text{OH}^-]$ in the rate law.



The point in favour of this mechanism is the fact that β -Br reacts 17 times faster than β -Cl. The difference in their polar effects is small and steric effects should effectively cancel out in a comparison. Therefore the rate of attack on silicon by base should be about the same for β -Br and β -Cl. This seems to indicate that reaction 2 above is rate determining and the faster rate of reaction of β -Br is caused by stretching of the C-X bond. Sommer and Baughman^{59,60} prefer this second mechanism because of the magnitude of $\rho = +2.12$ whereas in a concerted mechanism such an appreciable electron density on silicon would not be expected.

(iii) FRIEDEL - CRAFTS REACTION⁶⁸

The reactivity of α -, β - and γ -chloroalkylsilanes has been assessed kinetically utilizing the Friedel-Crafts reaction with benzene, chlorobenzene and toluene. The reactions were carried out at 30°C in the presence of 0.01M AlCl_3 and the rate at which hydrogen chloride was

evolved was determined by titration with standard alkali. Some values obtained from reaction between chloroalkylsilanes and benzene are shown in Table VII and the reactivity of β -chloroethyltrichlorosilane with benzene, chlorobenzene and toluene are compared in Table VIII.

TABLE VII

Friedel - Crafts reaction with benzene at 30°C

Silicon compound	$10^4 k$ mole/min.
$\text{Cl}_3\text{SiCH}_2\text{Cl}$	2.36
$\text{MeCl}_2\text{SiCH}_2\text{Cl}$	3.67
$\text{Cl}_3\text{SiCHCl}\cdot\text{CH}_3$	2.39
$\text{EtCl}_2\text{SiCHCl}\cdot\text{CH}_3$	2.96
$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl}$	42.8
$\text{MeCl}_2\text{SiCH}_2\text{CH}_2\text{Cl}$	447.0
$\text{EtCl}_2\text{SiCH}_2\text{CH}_2\text{Cl}$	417.0
$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	54.8
$\text{MeCl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	67.2

TABLE VIII

Friedel - Crafts reaction with β -chloroethyltrichlorosilane

Aromatic compound	$10^4 k$ mole/min.
PhCl	16.7
PhH	42.8
PhMe	59.5

It is to be noted that decrease in the electron withdrawal from silicon

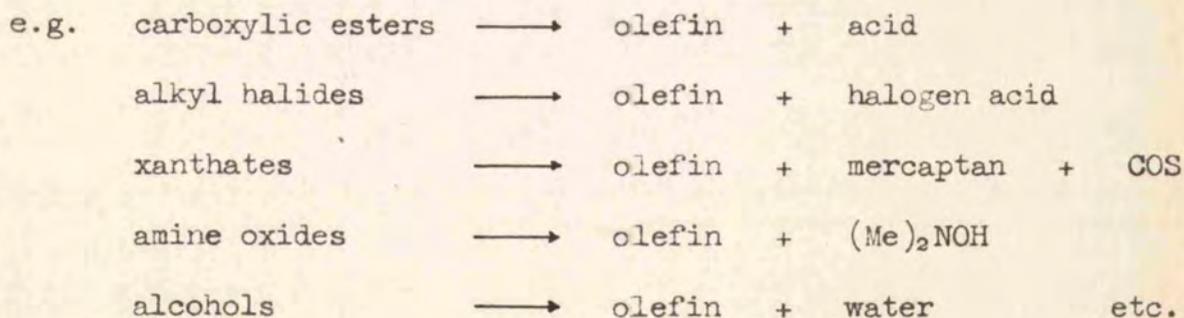
by replacement of a silicon bound chlorine atom by an alkyl group increases the rate noticeably with the α - and γ - compounds. However, with the β - compound the effect is substantial and some form of conjugation (1,4) is suggested to be superimposed in this case.

CHAPTER TWO

GAS PHASE ELIMINATION REACTIONS

The wealth of data on these reactions has increased markedly in the last 15 years and the available information has been collected together for certain classes of chemical compounds. The decomposition of carboxylic esters has been reviewed by dePuy and King⁶⁹ and the decomposition of amine oxides by Cope.⁷⁰ The pyrolysis of alkyl halides has been studied extensively by Maccoll and his co-workers and the information has been formulated into a detailed mechanism showing correlation between solution and gas phase studies.^{71,72} More recently a monograph has been devoted to the elimination reactions in general.⁷³

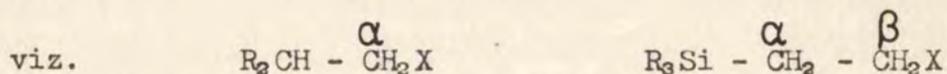
A common product in all these elimination reactions consists of an olefin, or a mixture of olefins. The hydrogen removed is combined with the particular leaving group for the class of compound.



Of these reactions many studies have not been truly in the gas phase. For example, until recently many of the determinations on esters involved conditions of the reaction vessel surface which did not enable accurate determination of the mechanism.

The mechanism proposed with certainty is the intramolecular, E.1, reaction involving a cyclic transition state or intermediate consisting

of either a 4-, 5-, or 6-membered ring structure. The reaction is facilitated by the electronegativity of the group bonded to the α -carbon atom and removal of the hydrogen on the β -position occurs. It is perhaps useful to mention now that in the case of halogenoalkylsilanes the nomenclature is relative to the position of the silicon atom so that the α - and β -positions appear interchanged.



Until recent years the mechanism has usually been taken to involve the synchronous shift of electrons to indicate the mode of attainment of the transition state. Evidence has been presented for the possibility of a process with some heterolytic character, involving bond breaking exceeding bond formation or bond formation exceeding bond breaking, but these topics will be discussed later.

(A) TYPES OF REACTION OCCURRING AND CRITERIA FOR A MOLECULAR REACTION

By far the most predominant process by which organic compounds decompose involves the production of radicals. These radicals can react either by a chain process or, if the radical formed is stable, by a radical non-chain process. In radical reactions it is generally far more difficult to interpret the substituent, or structural, effects on the mechanism and velocity constant of the reaction involved. However, for a radical non-chain process the rate determining step is the homolysis of the C-X bond and hence the observed activation energy is equivalent to the C-X bond energy.

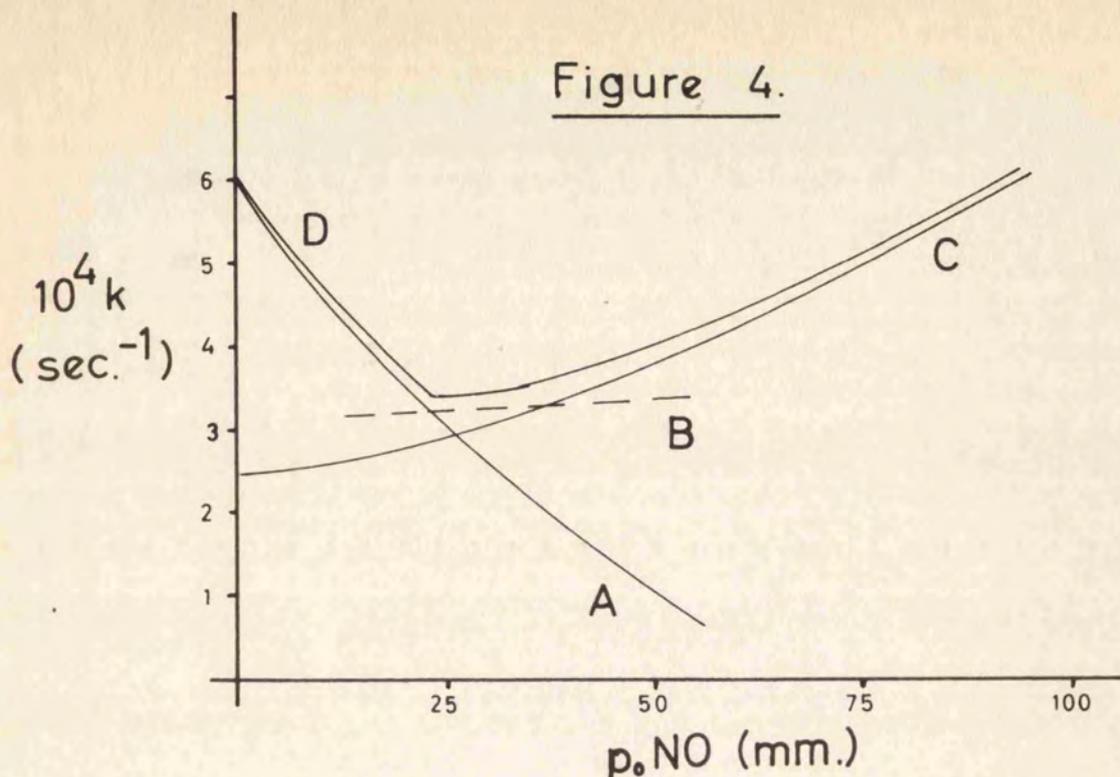
One of the most commonly met difficulties in conducting gas phase reactions is the removal of heterogeneous behaviour. The difficulty is further enhanced by the fact that in many cases the reaction products

are identical with those obtained under homogeneous conditions. It is not possible to indicate structural effects from these heterogeneous processes and it is fortunate that in many cases the heterogeneous component can be removed from the mechanism by studying the reaction at a higher temperature, see discussion on β -chloroethyldimethylphenylsilane. In addition the heterogeneous process can often be removed by coating the reaction vessel walls with a carbonaceous deposit, by conducting a number of pyrolyses before kinetic determinations, and by complete exclusion of oxygen.⁷⁴

To obtain an accurate correlation between the substituent effects in organic pyrolyses following the same mechanism, and also to detect possible changes in the mechanism, the supposedly molecular process is usually isolated for detailed study. A molecular process is often taken to be the one that occurs under maximum inhibition. It has been found in many cases that, for a reaction which proceeds by both molecular and radical mechanisms, any inhibitor reduces the rate to the same limiting value. However the amount of different inhibitors needed to suppress the radical component in a particular pyrolysis may be different. For example, more cyclohexene than nitric oxide is usually needed to effect the same inhibition. "Inhibitors" do not of necessity suppress the rate of all chain reactions but can establish new radical chain mechanisms which may proceed at a faster, slower or at the same rate as the "uninhibited" decomposition. Hence it has been stated⁷⁵ that lack of inhibition is not complete nor certain evidence for a molecular process. For an alkyl halide with and without nitric oxide present the initiation and termination steps could be:



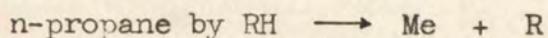
Dependence of the rate of pyrolysis of 100 mm. n-pentane upon nitric oxide concentration at 540°C



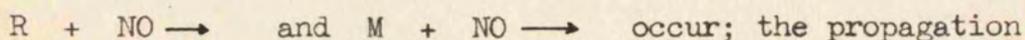
and the rate of reaction could be the same in both cases. Frequently high "inhibitor" pressures cause acceleration of the reaction rate and for various isomeric pentanes and octanes it has been shown⁷⁶ that the inhibitor, nitric oxide, concentration comes into the rate equation. It is possible that the inhibition curve, see Figure 4, can be split into two, or possibly three, separate curves.

Curve D is the experimental curve

Curve A would represent the initial removal of a methyl radical from



Curve B (possibly) would indicate the maximally inhibited process where



reactions are removed by competition and the chain length shortens.

Curve C would represent the stimulated reaction of $RH + NO \rightarrow$

which should in principle go through the origin when extrapolated.

These curves are not additive if different initiation and termination processes are operative for the inhibited, low NO concentration, and stimulated, high NO concentration, reactions.

The maximally inhibited reactions are often found to depend little upon the surface area to volume ratio in seasoned vessels although it has been suggested⁷⁷ that initiation and termination may occur at the surface with reaction to yield the products occurring in the gas phase. It is usually assumed that when the surface requires a carbonaceous deposit before reproducibility is obtained that the heterogeneous radical component is virtually removed. However Wojciechowski and Laidler⁷⁵ suggest that seasoning of the vessel surface increases the number of active sites and hence acts as a partial inhibitor. It should therefore be possible to show in suitably chosen cases whether this argument is correct by the observation that smaller pressures of nitric oxide should now accelerate the reaction.

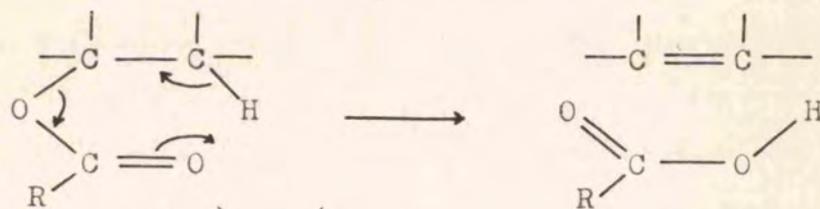
Possibly one of the best criteria for a non-surface-catalysed reaction would be to commence with a scrupulously clean surface and observe no diminution in rate on successive runs. However, in the majority of cases consistency is not obtained until seasoning of the surface has occurred.

If a reaction occurs in which the rate is neither accelerated nor retarded by the presence of small or large amounts of inhibitor then this constitutes extremely strong evidence for the reaction being molecular.

The change from first to second order kinetics, Lindemann fall-off, on reduction of the pressure until the Maxwell-Boltzmann energy distribution is no longer maintained, is in principle a good method for diagnosis of the E.1 reaction. This has been observed for some alkyl halides and interpreted⁷⁸ in terms of the theories of Rice, Ramsperger, Hinshelwood and Slater. In many cases the number of degrees of freedom is large and it becomes impracticable to measure the reaction order at the low pressures at which the fall-off occurs.

(B) THERMAL DECOMPOSITION OF CARBOXYLIC ESTERS

The decomposition has up until recently been taken to involve a concerted mechanism with a cyclic intermediate and rather similar to the E.2 mechanism in solution (e.g. base catalysed reaction of sulphonium salts) although in this case it is more strictly E.1.



More recently evidence has accumulated to suggest that the transition state or intermediate possesses some carbonium ion character by the relationship observed between eliminations carried out in solution and in the gas phase. More credence can be placed on this more recent work in view of the fact that many previous determinations might possibly have involved the surface. Radical decompositions only occur when β -hydrogen atoms are absent⁷⁹ although in many cases mixed mechanisms almost certainly intrude.

Kinetically controlled pyrolyses of a large number of esters have been carried out and for the α -substituted series the relative rates and Arrhenius parameters are given in Table IX. The reference

TABLE IX

Compound	E kcal.	log A	$10^4 k \text{ sec.}^{-1}$ 400°C	$k_{\text{rel.}}$	Reference
EtOAc	47.8	12.49	9.78	1	<u>80,81,82</u>
iso-PrOAc	45.0	13.0	251	25.6	<u>80</u>
t-BuOAc	39.2	12.8	12600	1290	<u>83</u>
CH ₃ CO.OAc	34.5	12.0	63100	6450	<u>85</u>

see also references 69 and 84

underlined in this and subsequent tables is the source of the parameters given.

In general the mechanism of pyrolysis could involve the possible schemes:

- (1) Completely concerted
- (2) OH bond formation exceeding CH or CO bond breaking
- (3) CH or CO bond breaking exceeding OH bond formation

If formation of a cyclic transition state should be indicated by a reduction of entropy over the reactant molecule then the concerted mechanism and the mechanism involving incipient bond formation exceeding bond breaking could be eliminated on the grounds of the normal A-factors observed. This, however, may not be the complete case as the formation of a six-membered ring structure might not involve a particularly large amount of strain.

Deuterium isotope effects on the β - position of between 2 and

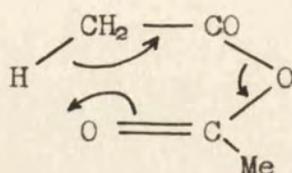
3 indicate that the β C-H stretching vibration has been almost removed.^{86,87,88} and this would be expected in all three modes of reaction above.

Although small amounts of elimination occur obeying the Saytzeff rule, the predominant reaction occurs according to the Hofmann rule giving the olefin carrying the least number of alkyl substituents. This is believed to be due mainly to the fact that more primary than secondary hydrogens are available. Hence in certain cases one can obtain relatively large proportions of Saytzeff products.^{89,90}

e.g.	sec-BuOAc	Hofmann : Saytzeff =	3 : 2
	t-pentylOAc	Hofmann : Saytzeff =	3 : 1

The position is not, however, quite so clear cut as the evidence that increase of temperature from 350 - 500°C in the pyrolysis of t-pentyl acetate has no effect on product composition⁹⁰ has been disputed.^{89,91}

Replacement of the ethyl group in ethyl acetate by an acetyl group (acetic anhydride) increases the rate at 400°C by 6450 times.⁸⁵ The A-factor is reasonably close to the "normal" value and hence the major effect is a decrease in activation energy required to attain the rate determining transition state or intermediate. This example clearly shows that if the mechanism is concerted then flow of electrons can be in either direction round the molecule as both "halves" are identical.



The gas phase pyrolysis of arylethylacetates has been used to assess electrophilic substituent effects^{92,93,94,95} and some results obtained are shown in Table X. Indication that these compounds decompose by a carbonium ion type mechanism, as do the solvolysis reactions, has been given by observance of a $\rho\sigma^+$ correlation.⁹⁶ The results do not agree too well with the Hammett σ constants.

TABLE X

Relative rates of pyrolysis of 1-arylethyl acetates at 600°K⁹²

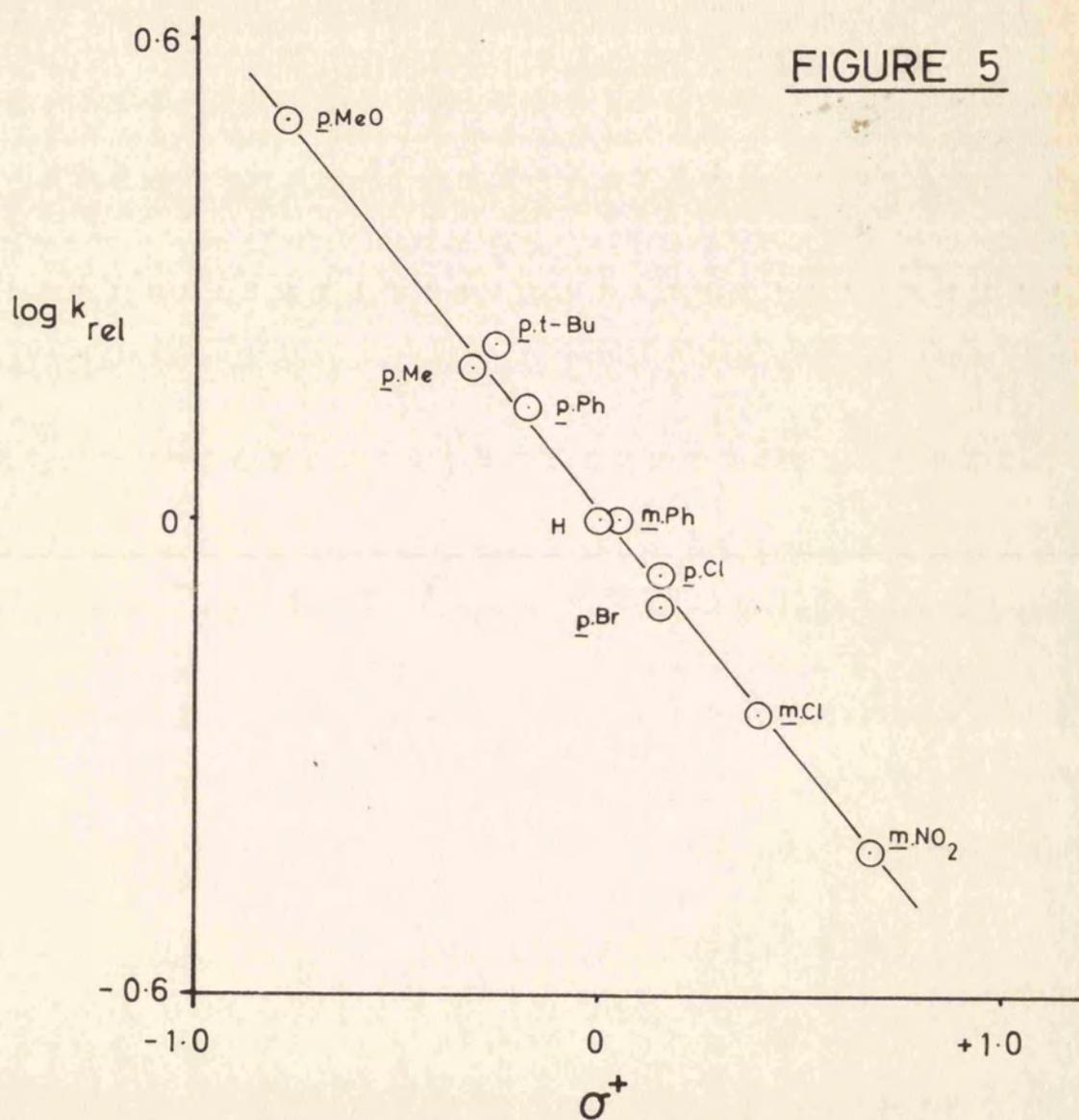
when X = H ; $\log k/k_0 = k_{rel.} = 0$

Substituent	$\log k_{rel.}$	σ^+	see reference 96
<u>p</u> -MeO	0.50	-0.778	
<u>o</u> -MeO	0.26	-	
<u>p</u> -t-Bu	0.22	-0.256	
<u>o</u> -Me	0.215	-	
<u>p</u> -Me	0.190	-0.311	
<u>p</u> -Ph	0.14	-0.179	
H	0.0	0.0	
<u>m</u> -Ph	0.0	0.05	see reference 98
<u>p</u> -Cl	-0.07	0.114	
<u>p</u> -Br	-0.11	0.150	
<u>m</u> -Cl	-0.245	0.399	
<u>m</u> -NO ₂	-0.42	0.674	

The correlation between relative rates of pyrolysis and σ^+ factors, shown in Figure 5, indicates that resonance stabilization of the carbonium ion is approximately the same as in α, α -dimethylbenzyl chlorides. For a more accurate picture in many cases the Yukawa and Tsuno treatment,⁹⁷ or extensions of it have to be used.

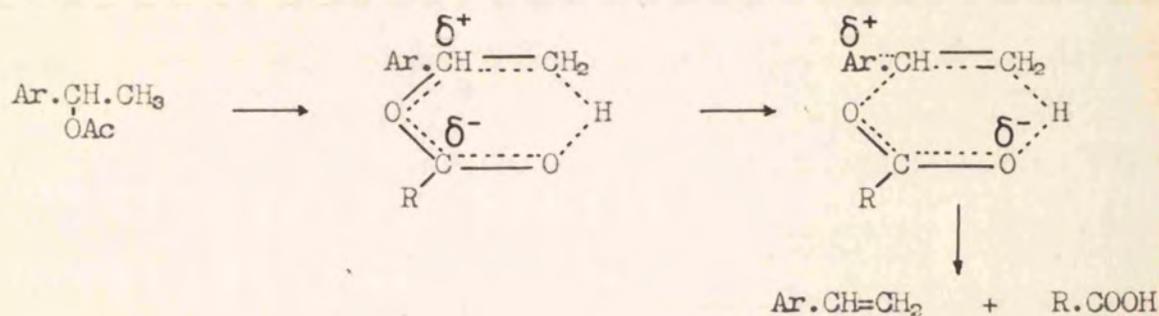
$$\log k/k_0 = \rho [\sigma + r(\sigma^+ - \sigma)]$$
 where r is the resonance interaction between substituent and carbonium ion.

PYROLYSIS OF 1-ARYLETHYL ACETATES AT 600°K



For 1-arylethyl acetates the ρ factor was found to be -0.66 at 600°K and the size of this was considered to indicate that a small amount of charge separation occurs in the transition state. This rate determining transition state being situated early on the reaction co-ordinate. In the case of 2-arylethyl acetates, ca. 12 times less reactive, the ρ factor was only -0.3 and this is taken as evidence that the carbon-oxygen bond strength controls the ester stability and not the carbon-hydrogen bond strength.

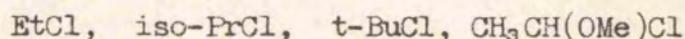
The reaction of 1-arylethyl acetates is therefore indicated to follow a similar mechanism to that in solution studies and proceed via an electron deficient centre. It is suggested that the carbonium ion initially resides on the α -carbon atom, to which the acyl group is attached and stabilization (or the opposite) can then occur by electron supply from the aromatic group.



(C) THERMAL DECOMPOSITION OF ALKYL HALIDES

The alkyl chlorides have been investigated by Barton and more recently Maccoll has studied a large number of alkyl bromides with a view to formulation of a detailed mechanism for their decomposition, and a correlation between reactions in the gas and condensed phases.

In general the molecular, maximally inhibited, reactions are first order and unimolecular and possess A-factors quite close to the "normal" value of $10^{13.5}$. Hence any change in the structure of the alkyl halide has only an effect upon the activation energy. This does not always hold and it can be seen from the results in Table XI that the A-factor is successively reduced by a factor of 10 in the series:



The over-all effect of changes of structure is found to follow the same pattern as in solvolysis reactions of these compounds.

Substitution in the α -position has the greatest effect whereas β -substitution has a very small effect by comparison. Some results obtained for alkyl chlorides and bromides are shown in Tables XI and XII.

TABLE XI

Arrhenius parameters for alkyl chlorides

Compound	log A	E kcal.	Reference
EtCl	14.6	60.8	99,100
n-PrCl	13.45	55.0	101
n-BuCl	14.0	57.0	101
iso-BuCl	14.02	56.8	78b
iso-PrCl	13.5	50.5	102
t-BuCl	12.4	41.2	103
CH ₃ CH(OMe)Cl	11.46	33.3	104

TABLE XII

Arrhenius parameters for alkyl bromides

Compound	log A	E kcal.	Reference
EtBr	13.45	53.9	<u>105</u> , 81, 106
n-PrBr	12.9	50.7	<u>107</u> , 106
n-BuBr	13.18	50.9	107
iso-BuBr	13.05	50.4	108
iso-PrBr	13.62	47.8	<u>109</u> , 106, 110
t-BuBr	14.0	42.0	99
4-Br-pent-1-ene	12.94	44.7	105
sec-BuBr	13.53	46.47	111

From the results outlined in Tables XI and XII the following rate constants and relative rates can be calculated.

TABLE XIII

Rate constants and relative rates for alkyl chlorides and bromides at 400°C

R	X = Cl		X = Br	
	$10^5 k \text{ sec.}^{-1}$	$k_{\text{rel.}}$	$10^5 k \text{ sec.}^{-1}$	$k_{\text{rel.}}$
Et	1.26	1	8.9	1
n-Pr	3.98	3.15	28	3.15
n-Bu	3.16	2.52	48	5.4
iso-Bu	4.17	3.31	50.2	5.65
Et	1.26	1	8.9	1
iso-Pr	126.0	100	1320.0	148
t-Bu	11200.	8900	240000.	27000
CH ₃ (MeO)CH	457000.	371000	-	-
4-X-pent-1-ene	-	-	2760.	310
sec-Bu	-	-	2690	302

The very large increase in relative reactivity on substituting a methoxy group in the α - position of ethyl chloride is noteworthy as it has its counterpart in solution kinetics. When phenyl groups are substituted in the α - position the alkyl bromides decompose at a rate approximating to that of t-butyl bromide whereas phenyl, or vinyl groups in the β - position react at a similar rate to ethyl bromide. This is taken to indicate, as in solution kinetics, that no significant multiple bonding occurs in the transition state.

A similar effect of α - substitution is observed when a hydrogen is replaced by another halogen atom. Some results are shown in Table XIV and these results indicate that the rate increases in the order:

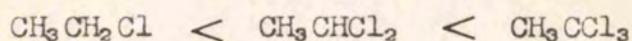


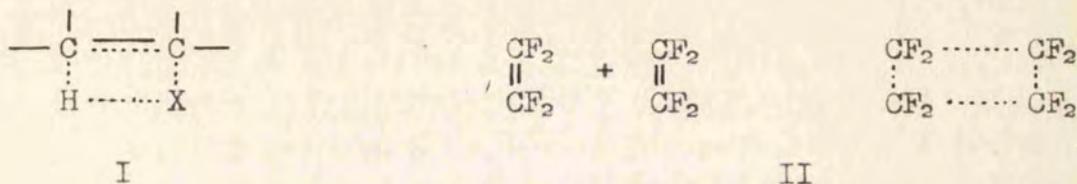
TABLE XIV

Compound	log A	E kcal.	$10^5 k \text{ sec.}^{-1}$ 400°C	$k_{\text{rel.}}$	Reference
$\text{CH}_3\text{CH}_2\text{Cl}$	14.6	60.8	1.26	1	99,100
CH_3CHCl_2	12.08	49.5	9.55	7.6	100
CH_3CCl_3	14.0	54.0	31.6	25.1	112

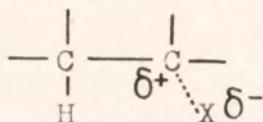
The case of 4-bromopent-1-ene, $\text{CH}_2=\text{CH}.\text{CH}_2\text{CHBr}.\text{CH}_3$, is interesting as decomposition can occur in two ways giving 1:3 or 1:4 pentadiene. The formation of the 1:3 isomer involves elimination of a hydrogen atom in the allylic position and gives a conjugated diene. These factors might be expected to increase the rate of elimination if the process were concerted. However the relative rates at 400°C, $k_{4\text{-Br}}/k_{\text{sec-BuBr}} = 1.03$, indicate that replacement of methyl by vinyl has no effect. Hence it was proposed by Thomas¹⁰⁵ that heterolysis of the C-Br bond was rate deter-

-mining and formation of the double bond occurred later and was non-rate determining.

Until recently it has always been assumed that the transition state was a cyclic four-centre structure, I, like that which almost certainly is involved in the dimerization of tetrafluoroethylene,¹¹³ II.



However in an intermediate of this structure, I, appreciable bending of the bonds will occur and one would expect to obtain lower A-factors than the "normal" ones experimentally observed. In view of the close correlation between solution work on alkyl halides, known to proceed via a carbonium ion type structure, and the work in the gas phase it has been suggested by Maccoll⁷¹ that some separation of charge might occur in the gas phase giving rise to an intermediate of carbonium ion character. This he termed a "quasi-heterolytic" transition state where the $\alpha_{\text{C-X}}$ bond breaks prior to bond formation.



Apart from the kinetic evidence outlined above, further evidence is provided by a consideration of the relation between activation energy and the energy required to dissociate the $\alpha_{\text{C-X}}$ bond either homolytically or heterolytically. Some values of the dissociation energies obtained by mass spectral means⁷² are given along with activation energies in Table XV.⁷²

TABLE XV

Compound	E kcal.	D(R + X)	D(R ⁺ + X ⁻)
EtBr	54	67	180
iso-PrBr	48	68	158
t-BuBr	42	64	138
EtCl	60	81	194
iso-PrCl	51	82	168
t-BuCl	41	78	149

If the α_{C-X} bond is considered to break homolytically then the observed values of change in activation energy on substitution are too high to permit correlation. However, if the bond breaks heterolytically then the difference in activation energy more than accounts for the observed decrease on α -substitution. The activation energies are obviously much less than the true dissociation into ions; this would not be likely to occur and most probably the bond is simply polarized in the direction $C^{\delta+} - X^{\delta-}$ with possibly a slight increase in the C-X bond length. There is also the possibility of the formation of an "intimate" type ion pair in the gas phase.¹¹⁴

If different isomeric halides are taken then a mixture of isomeric olefins is produced, e.g. but-1-ene and but-2-ene from sec-butyl halides,^{115,116} and this substantiates the above results in indicating that complete dissociation (heterolytic) is absent. In E.1, or S_N1 solution mechanisms the ion pair is often solvent separated and therefore the reaction can be independent of the leaving group.

The mechanism of gas phase pyrolysis of alkyl iodides is generally complex involving heterogeneous¹¹⁷ (t-BuI) or chain¹¹⁸ (primary iodides)

reactions. However, iso-PrI, iso-BuI and sec-BuI follow an E.1 mechanism.^{119,71} Some results obtained for isopropyl chloride, bromide and iodide are shown in Table XVI which gives some indication of the relative reactivity of these compounds and the variation of relative rates with temperature.

TABLE XVI

Compound	log A	E kcal.	k _{rel.}		Reference
			350°C	400°C	
iso-PrCl	13.5	50.5	1	1	102
iso-PrBr	13.62	47.8	14	10.5	109
iso-PrI	14.5	48.2	94	56.5	119

An interesting case of Wagner-Meerwein rearrangement in the gas phase has been isolated amongst the reactions of neopentyl chloride.^{120,121} Similar results are obtained with bornyl chloride¹²² which undergoes cis elimination to bornylene and rearrangement to camphene and tricyclene. These reactions, via carbonium ions in solution, would strongly suggest charge separation.

(D) OTHER REACTIONS FOLLOWING THE E.1 MECHANISM IN THE GAS PHASE

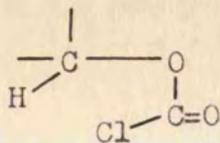
(i) CHLOROFORMATES

With these compounds one obtains two types of product:

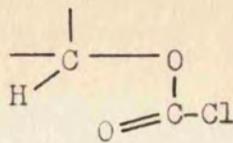
- (1) an alkyl halide by elimination of CO₂ (substitution of Cl)
- (2) an olefin by elimination of HCl and CO₂

As the substitution reaction sometimes occurs without olefin production it appears that the transition state is akin to I below rather than

II, the latter being more similar to that for esters.



I



II

The comparison between relative rates of decarboxylation, substitution of chlorine, of different chloroformates indicates a rate dependence on structure similar to that of the alkyl halides although α -methyl substitution does not increase the relative rate so markedly. This comparison⁷² is shown in Table XVII and the results indicate that

TABLE XVII

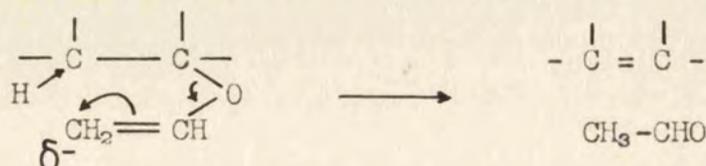
X	Cl	Br	O.COCl	O.COCH ₃
R	361°	320°	240°	400°
CH ₃	-	-	1	-
Et	1	1	2.2	1
iso-Pr	223	280	222	25
sec-Bu	690	980	640	

C - Cl bond cleavage is quite important in the intramolecular substitution reactions of chloroformates so that the transition state is possibly more akin to that of the alkyl halides than the esters. Also the relative rate of alkyl halide formation from both ethyl and neopentyl chloroformates is close to unity.¹²³

(ii) VINYL ETHERS

In the decomposition of certain alkyl vinyl ethers in static¹²⁴ and in flow systems^{125,126} analogous olefin elimination occurs although

the A-factors are noticeably reduced. The decomposition is believed to go via an intermediate of type I, below, which is either concerted or may involve some degree of polarization. It is found that the relative



rates iso-Pr/Et are 17/1 which compares with the corresponding values of iso-Pr/Et of 25/1 for the acetates.

When both the groups attached to oxygen are unsaturated then a Claisen type rearrangement occurs analogous to that of aryl-allyl ethers. A possible mode of rearrangement^{127,128} is illustrated below for isopropenylallyl ether. The A-factor for the rearrangement reaction is the same as for the elimination reactions of these compounds but the



activation energies are much reduced. This is illustrated in the following table, Table XVIII, where the relative rates of reaction are also compared.

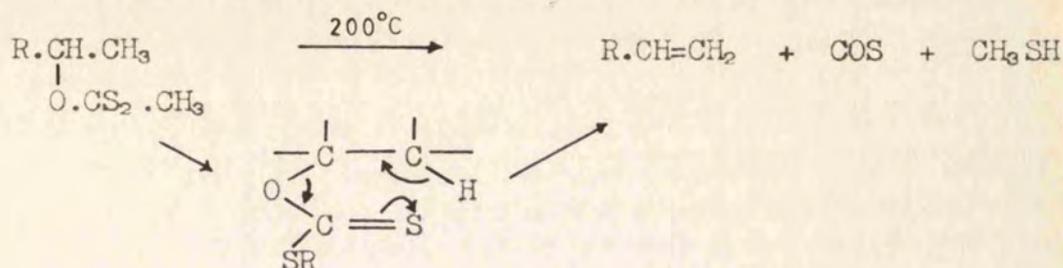
TABLE XVIII

Compound	log A	E kcal.	$10^3 k_{400^\circ}$	$k_{\text{rel.}}$	Reference
ethylvinyl ether (E)	11.43	43.8	1.7	1	125
isopropylvinyl (E)	12.58	43.56	27.5	16.2	126
allylvinyl (R)	11.70	30.6	56300	33100	128
allylisopropenyl (R)	11.73	29.3	170000	100000	127

k in sec.^{-1} ; (E) = elimination ; (R) = rearrangement

The fact that these rearrangements occur adds weight to the idea of a concerted mechanism although carbon - carbon bond formation may exceed carbon - oxygen bond breaking in this case.

(iii) XANTHATES (CHUGAEV REACTION)



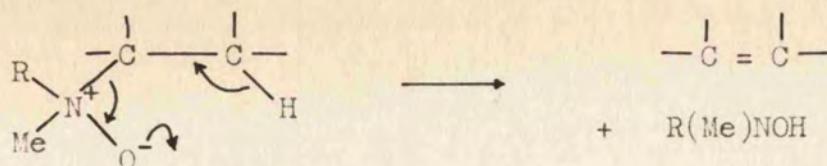
The thermal decomposition has been shown to follow the E.1 mechanism although it is difficult to obtain really reliable rate data because of the difficulty in preparing pure xanthate derivatives.¹²⁹ The elimination is predominantly cis as has been shown using 3-phenyl-2-butyl and 1,2-diphenylpropyl xanthates.¹³⁰

Some kinetic data for the thermal decomposition of xanthates and alkyl carbonates derived from sterols has been provided by Nace.¹³¹ The kinetics were followed by the loss in weight of tared samples due to the formation of volatile products, COS and sometimes volatile mercaptans. The A-factors were found to be near the "normal" values for a unimolecular reaction, $\log A = \text{ca. } 12.5$. Since the pyrolyses of these compounds are about 15 kcal./mole more exothermic than the alkyl halides then the mechanism is most probably concerted involving little charge separation in the transition state.

(iv) AMINE OXIDES

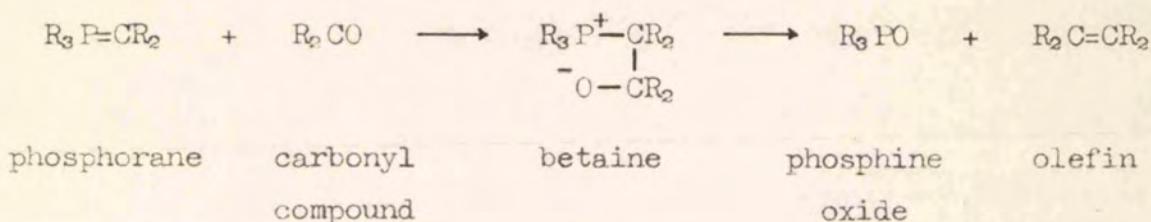
The mechanism of this reaction is, like that of the xanthates

most probably concerted as the reaction is even more exothermic than

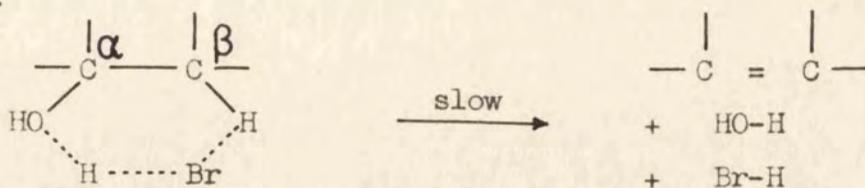


the xanthate pyrolyses. Elimination appears to depend upon the number of hydrogens available.¹³²

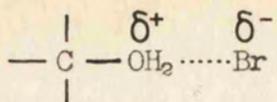
There are many other examples of reactions giving olefins which could or do follow an E.1 type mechanism in the gas phase. Various phosphorus containing compounds¹³³ including the Wittig reaction¹³⁴ probably involve intramolecular transition states.



Alcohols¹³⁵ also follow this mechanism and indeed an example of homogeneous acid catalysis has been observed for the dehydration of t-butanol.¹³⁶ The rate of dehydration is proportional to the acid concentration, in this case HBr, and is believed to be caused by strong hydrogen bonding between the t-butanol and the HBr, where the bromine attacks the β -C nucleophilically and the hydrogen (of HBr) protonates the oxygen.



If, as appears likely, the protonation occurs preferentially then an "intimate" ion pair structure may have a transient existence.



Sufficient data have not been accumulated to show whether the mechanism of decomposition of certain sulphur¹³⁷ and nitrogen¹³⁸ containing compounds, of β -keto acids¹³⁹ and of borates¹⁴⁰ is unequivocally an E.1 process although it is possible that a multi-centre type intermediate is involved.⁷³

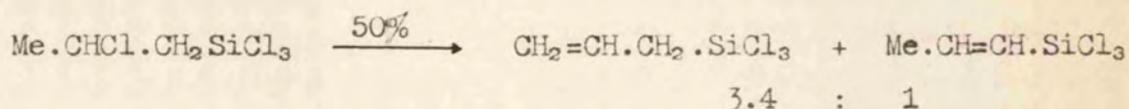
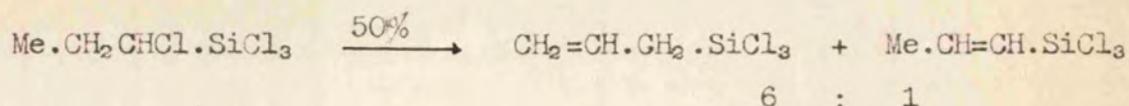
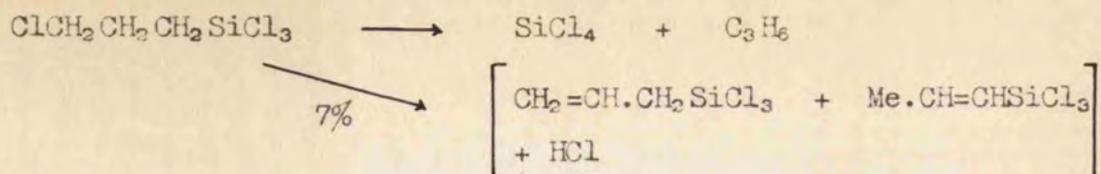
CHAPTER THREE

REACTIONS OF 2-CHLOROALKYLSILANES IN THE GAS PHASE

There have been very few gas phase reactions of these compounds studied kinetically although much information has been provided, particularly by Russian workers, on the general mode of reaction without detailed analysis of the mechanism or measurement of the velocity. Many of the reactions studied have been under heterogeneous conditions either involving a particular catalyst or utilizing the parent silane at high temperature and pressure in an autoclave.

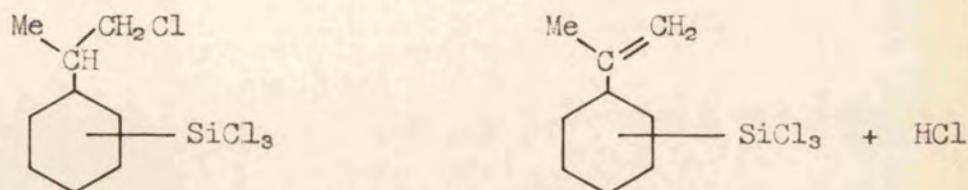
Passage of the chloroalkylsilanes through a heated tube containing a small percentage of FeSi has been used to study the decomposition products. β -chloroethyltrichlorosilane decomposes at about 400°C to yield SiCl_4 , C_2H_4 and also, rather surprisingly, some MeSiCl_3 . The isomeric α -chloro compound does not yield ethylene until the temperature is raised to 500°C and it is assumed in this case that rearrangement of $\alpha \rightarrow \beta$ occurs.¹⁴¹ However, the main reaction at 400-450°C is dehydrochlorination where shortening of the chloroalkyl chain from chloropropyl to chloroethyl reduced the extent of dehydrochlorination.¹⁴² The rate of removal of HCl depends upon the length of the alkyl chain and, in short chains, on the position of the chlorine atom. Under these conditions, possibly rather drastic, the position of the double bond in the resulting unsaturated compound does not appear to depend upon the position of the chlorine in the side chain. However, if chlorine on silicon is substituted by methyl then the dehydrochlorination is more difficult. Some results obtained are outlined schematically

below.



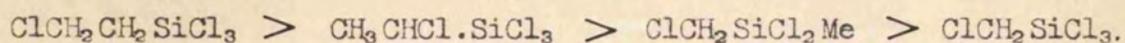
In the case of $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Me}$ the reactant is apparently unchanged apart from the production of 2% MeSiCl_3 and $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ gives no dehydrochlorination. No mention is made of the β -elimination of these compounds which seems surprising as the inductive release from silicon would be enhanced by the presence of methyl substituents and the chance of olefin elimination occurring even in the presence of FeSi would be expected to be high and to outweigh the dehydrochlorination.

When the chlorine atom on the alkyl chain is well removed from silicon as in monochloroisopropylphenyltrichlorosilane then pyrolysis yields the corresponding dehydrochlorination product, trichlorosilyl- α -methylstyrene, in high yield¹⁴³ as would be expected from a normal alkyl halide.



Passage of α - and β -chloroalkylsilanes over 80:20 Si:Cu at 370 - 400°C gives a great many products by analogous reactions to those already discussed and by disproportionation. A second chlorosilyl group

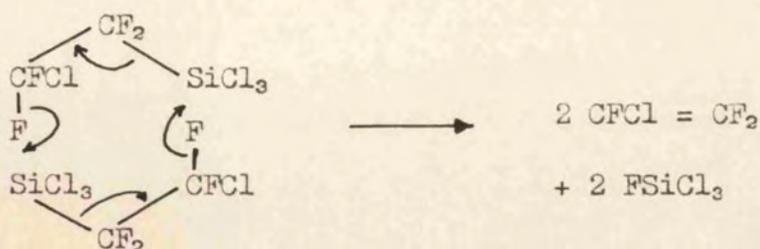
was often substituted for the alkyl chlorine atom, the yield of products decreasing in the order:¹⁴⁴



The complexity of the product mixtures obtained under these conditions can be illustrated by consideration of α - and β -chloroethyldichloroethylsilane.¹⁴⁵

<u>ClCH₂CH₂SiEtCl₂</u>		<u>CH₃CHCl.SiEtCl₂</u>
10%	CH ₂ =CH.SiCl ₃	8%
17%	CH ₂ =CH.SiEtCl ₂	10%
1%	SiCl ₄	1%
5%	EtSiCl ₃	5%
6%	Et ₂ SiCl ₂	15%
6% Cl ₂ EtSiCH ₂ CH ₂ SiHCl ₂		7.5% Cl ₂ EtSiCH(CH ₃)SiHCl ₂
13% Cl ₂ EtSiCH ₂ CH ₂ SiCl ₃		11% Cl ₂ EtSiCH(CH ₃)SiCl ₃
5% (Cl ₂ EtSiCH ₂ CH ₂) ₂ SiCl ₂		7.5% (Cl ₂ EtSiCH(CH ₃)) ₂ SiCl ₂
37%	LOSSES	35%

The pyrolysis of β -chlorotetrafluoroethyltrichlorosilane, ClCF₂CF₂SiCl₃, at 220°C is suggested to occur by a bimolecular cyclic mechanism³⁴ in which fluorine is transferred to silicon.

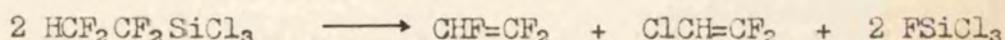


No C₂F₄ was found in the products showing that fluorine and not chlorine was eliminated with the trichlorosilyl group. However, some disproportion-

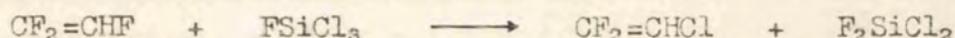
-ation of the FSiCl_3 occurred. It seems surprising that in view of the reactions of β -halogenoethylsilanes proceeding via a unimolecular mechanism that this particular compound reacts bimolecularly.

It has been suggested by Batuev¹⁴⁶ that decomposition of β -chloroethyltriethylsilane may involve a bimolecular intermediate rather than a unimolecular one. Hence it does not seem imperative that all analogous compounds react via an intermediate of the same structure.

Tetrafluoroethyltrichlorosilane, $\text{HCF}_2\text{CF}_2\text{SiCl}_3$, although stable at 150° , decomposes at 220°C by the following scheme:³⁴

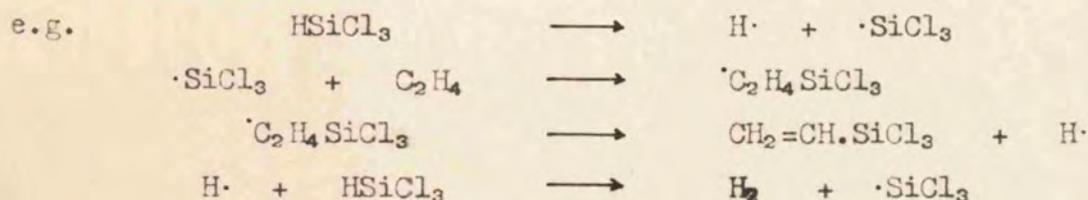


The formation of trifluoroethylene, $\text{CHF}=\text{CF}_2$, was expected by analogy with the above reaction and the formation of the unexpected $\text{ClCH}=\text{CF}_2$ is attributed to a reaction between the normal products.



Although $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ and $\text{ClCH}_2\text{CHCl}\cdot\text{SiCl}_3$ are relatively stable to heat the alkyl substituted compounds, $\text{ClCH}_2\text{CH}_2\text{SiEt}_3$ and $\text{ClCH}_2\cdot\text{CHCl}\cdot\text{CH}_2\text{SiMe}_3$, decompose on attempted distillation.^{28,29,30}

The reaction of ethylene with trichlorosilane in a flow system at 600°C gives the expected addition product, EtSiCl_3 , relatively large quantities of polymer and surprisingly some vinyltrichlorosilane is formed.¹⁴⁷ This would occur either by the prior formation of trichlorosilyl radicals:



or, rather less likely, by the dehydrogenation of the ethyltrichlorosilane formed.

The pyrolysis of β -chloroethyltrichlorosilane has also been carried out in a flow system at 610°C, the main concern in the work being from a synthetic point of view.¹⁴⁸ The main products were ethylene and silicon tetrachloride. Pyrolysis was also carried out in the presence of quinoline and high yields of vinyltrichlorosilane were obtained.

The only gas phase work on these compounds from the kinetic point of view has been carried out by Davidson¹⁴⁹ on β -chloroethyltrichlorosilane at 394°C. It was found in this preliminary study, continuation of which forms the major part of this thesis, that equimolar quantities of ethylene and silicon tetrachloride were formed. Also some hydrogen chloride was produced indicating that dehydrochlorination also occurred. The reaction appeared to be homogeneous and unimolecular as the half-life remained constant for changes in the initial pressure and the surface area to volume ratio.

CHAPTER FOUR

KINETICS OF THE GAS PHASE THERMAL DECOMPOSITION OF 2-CHLOROETHYL-
TRICHLOROSILANE

Following on from the preliminary study¹⁴⁹ it was decided to try to obtain accurate kinetic and mechanistic information on the decomposition of 2-chloroethyltrichlorosilane. No previous work in the gas phase had been reported from this point of view although much general information on the chemical behaviour in the gas phase, see pages 50 - 54, and on similar compounds in solution, see Chapters One and Two, had been accumulated. This suggested that, as well as its intrinsic interest, the pyrolysis reaction might provide a useful operator for the investigation of substituent effects in organosilicon chemistry and enable comparison with similar results obtained in the condensed phase.

(A) THE OVER - ALL REACTION

(i) RATES OF REACTION AND EFFECT OF CONCENTRATION CHANGES

2-chloroethyltrichlorosilane was pyrolysed in a static system between 356 and 417°C. At constant temperature and volume an increase in pressure occurred with the final pressure being just less than twice the initial pressure. There was no induction period observable and a plot of $\log(p_0 - \Delta p)$ against time, where p_0 and Δp are the initial pressure of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ and the increase in pressure at time, t , respectively, was linear to at least 60% decomposition. After this the rate of reaction decreased. This decrease in rate at later stages in the reaction has been shown to be because of secondary reactions. (see page

The initial pressure, p_0 , was evaluated by extrapolation of the total pressure - time curve to zero time. From numerous experiments it was shown that, on average, the pressure at infinite time, p_{∞} , was 1.93 times p_0 . However, the values of p_{∞}/p_0 varied between 1.88 and 2.02 and no great difference nor serious error in rate constants was introduced by equating $\log(p_0 - \Delta p) \equiv \log(2p_0 - P)$, where P is the total pressure at time t , against time instead of $\log(p_{\infty} - P)$ against time. The reaction is therefore predominantly first order and some typical rate plots are shown in Figure 6.

The initial concentration of 2-chloroethyltrichlorosilane was varied from 12 mm. to 138 mm. and the first order rate constant was independent of this variation. The results obtained for the over-all rate constants at different temperatures and initial pressures are shown in Table XIX. Also included are the values of the pressure after more than 10 half-lives (p_{∞}) and the ratio of p_{∞}/p_0 .

TABLE XIX

T°C	p_0	p_{∞}	p_{∞}/p_0	$10^4 k \text{ sec.}^{-1}$	Run
356	45.70	92.00	1.93	0.384	121
356	37.50	72.70	1.94	0.371	125
369.2	69.75	135.6	1.94	0.783	5
376.4	32.50	62.00	1.91	1.15	48
377.6	37.50	-	-	1.22	110
377.6	47.40	-	-	1.14	111
378.5	32.10	63.00	1.96	1.29	47
379.3	40.85	-	-	1.37	107
379.3	29.25	-	-	1.31	108

TABLE XIX (continued)

T°C	P _o	P _∞	P _∞ /P _o	10 ⁴ k sec. ⁻¹	Run
379.7	32.25	61.10	1.90	1.38	41
380.6	34.80	67.90	1.95	1.42	53
380.6	36.50	71.90	1.97	1.43	54
380.6	37.70	72.40	1.92	1.49	71
381.6	80.10	157.9	1.95	1.50	1
382.8	43.50	85.65	1.97	1.62	13
382.8	63.10	122.5	1.94	1.62	49
382.8	41.40	81.50	1.97	1.63	50
382.8	43.80	84.50	1.93	1.59	52
382.8	32.40	-	-	1.60	72
382.8	28.10	54.50	1.94	1.49	73
382.8	21.45	42.60	1.99	1.57	74
382.8	26.20	51.60	1.97	1.60	75
382.8	41.20	79.90	1.94	1.56	76
382.8	41.10	-	-	1.58	77
382.8	33.10	-	-	1.52	112
382.8	99.00	185.6	1.88	1.595	113
383.3	35.50	66.10	1.87	1.76	35
383.3	12.40	-	-	1.67	36
383.3	50.50	-	-	1.60	37
383.3	49.10	93.70	1.91	1.57	63
383.3	29.90	58.30	1.95	1.68	64
383.3	22.40	-	-	1.62	65
383.3	50.50	-	-	1.68	66
383.3	36.80	70.60	1.92	1.57	67

TABLE XIX (continued)

T°C	P ₀	P _∞	P _∞ / P ₀	10 ⁴ k sec. ⁻¹	Run
383.3	27.00	-	-	1.71	68
383.3	45.80	-	-	1.65	118
383.3	46.60	91.80	1.97	1.69	119
384	33.40	65.90	1.97	1.73	12
385	138.3	279.4	2.02	1.84	6
385	29.85	58.70	1.96	1.86	7
385	39.80	81.65	2.05	1.88	9
385	31.30	62.40	1.99	1.79	10
385	29.50	-	-	1.82	14
385	27.40	52.60	1.92	1.77	15
385	18.70	37.30	1.99	2.31	59
385	51.65	99.00	1.91	1.76	60
385	56.40	106.0	1.88	1.76	61
385	37.80	73.15	1.93	1.88	62
385	12.15	23.55	1.94	1.79	69
385	26.00	51.20	1.97	1.63	70
385	31.00	59.00	1.90	1.75	114
385	29.55	58.20	1.97	1.88	115
385	55.00	106.4	1.94	2.00	116
387.1	61.25	120.9	1.95	2.02	16
389.8	51.90	-	-	2.32	8
389.8	55.00	-	-	2.24	11
389.8	21.00	-	-	2.20	29
389.8	31.30	-	-	1.94	32

TABLE XIX (continued)

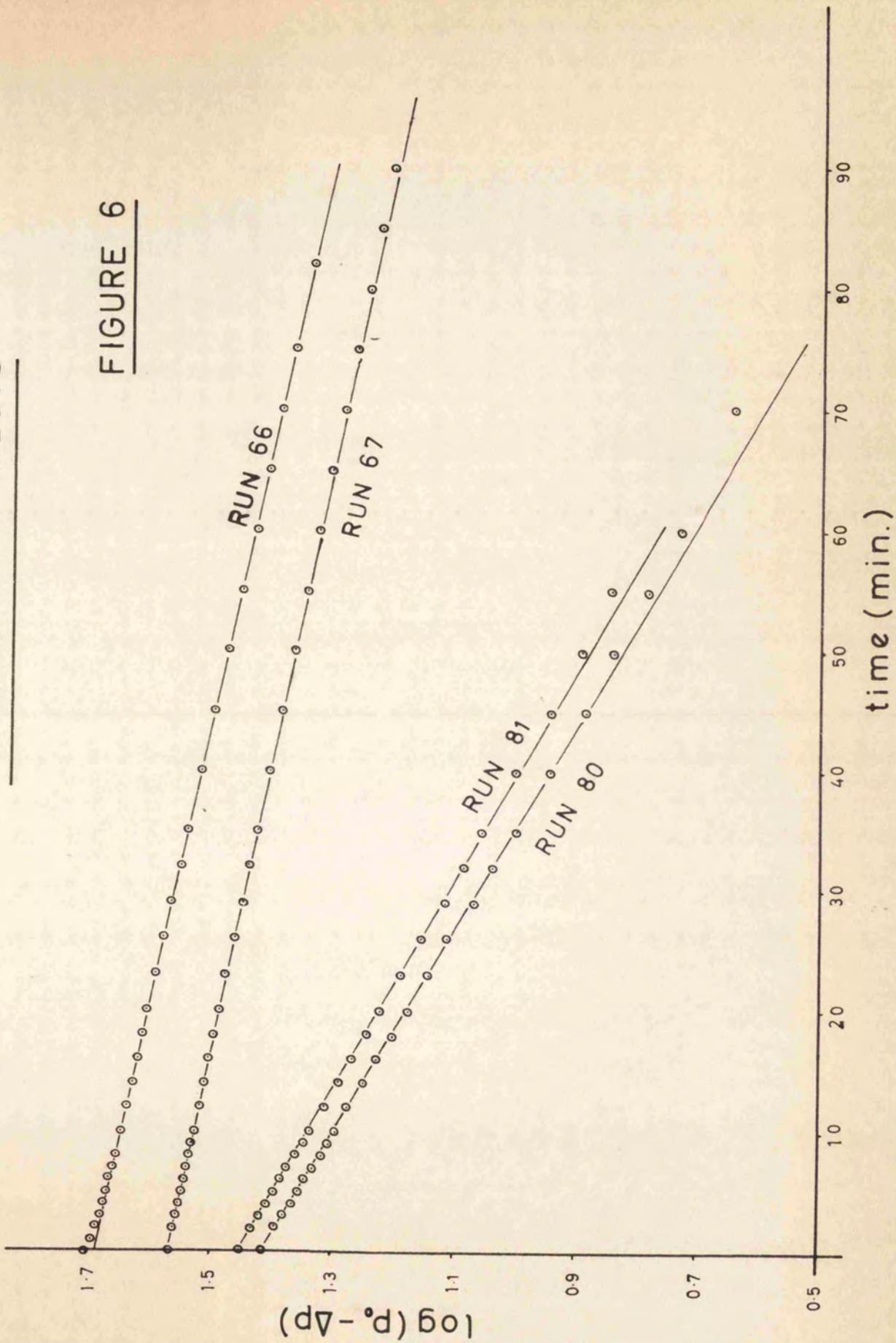
T°C	P ₀	P _∞	P _∞ / P ₀	10 ⁴ k sec. ⁻¹	Run
389.8	45.00	86.40	1.92	2.52	33
391.5	52.40	109.0	2.08	2.64	21
391.5	29.00	-	-	2.55	22
391.5	50.00	-	-	2.62	23
393.7	21.25	40.85	1.92	2.94	17
393.7	29.80	57.70	1.93	2.84	18
393.7	42.30	85.50	2.02	2.94	19
393.7	38.20	74.75	1.96	2.76	20
398	30.20	60.00	1.98	3.56	24
398	43.00	87.15	2.02	3.65	25
398	24.80	48.00	1.94	3.35	26
398	31.25	63.40	2.02	3.71	27
398	27.20	51.60	1.92	3.72	28
399.3	100.6	190.4	1.89	3.73	2
399.3	45.00	-	-	3.84	85
401.2	42.50	82.90	1.95	4.23	55
402.6	16.40	32.25	1.96	4.38	78
402.6	34.30	66.50	1.94	4.36	79
402.6	26.00	-	-	4.52	80
402.6	28.20	-	-	4.40	81
402.6	28.25	-	-	4.20	82
402.6	33.20	-	-	4.45	83
402.6	17.50	-	-	4.45	84
402.6	23.00	-	-	4.36	86

TABLE XIX (continued)

T°C	P ₀	P _∞	P _∞ /P ₀	10 ⁴ k sec. ⁻¹	Run
402.6	29.95	-	-	4.36	94
406.4	82.10	163.4	1.98	5.18	4
407.3	27.00	-	-	5.75	97
407.3	20.40	40.05	1.96	5.65	98
407.3	52.00	99.40	1.91	5.24	99
407.3	36.20	-	-	6.03	100
407.3	27.15	52.90	1.95	5.80	101
407.3	40.70	-	-	5.65	104
407.3	40.00	-	-	6.08	105
407.3	11.50	-	-	6.10	106
408.1	35.85	66.25	1.85	5.98	3
409.5	37.40	72.70	1.94	6.20	95
410.9	12.90	-	-	6.75	96
417	49.40	95.00	1.92	9.22	120

TYPICAL RATE PLOTS

FIGURE 6



(ii) ARRHENIUS EQUATION

The effect of temperature on the over-all reaction rate was evaluated using the Arrhenius equation;

$$k \text{ (sec.}^{-1} \text{)} = A e^{-E/RT}$$

from the linear plot of $\log k$ against $10^3/T^{\circ}\text{K}$. The Arrhenius plot is shown in Figure 7 although this figure is much condensed from the graph that was drawn to evaluate the over-all activation energy (E) and the pre-exponential factor (A) and does not contain all the experimental results. The over-all reaction was represented by the equation,

$$k \text{ (sec.}^{-1} \text{)} = 10^{11.40 \pm 0.16} e^{-45,500 \pm 500/RT}$$

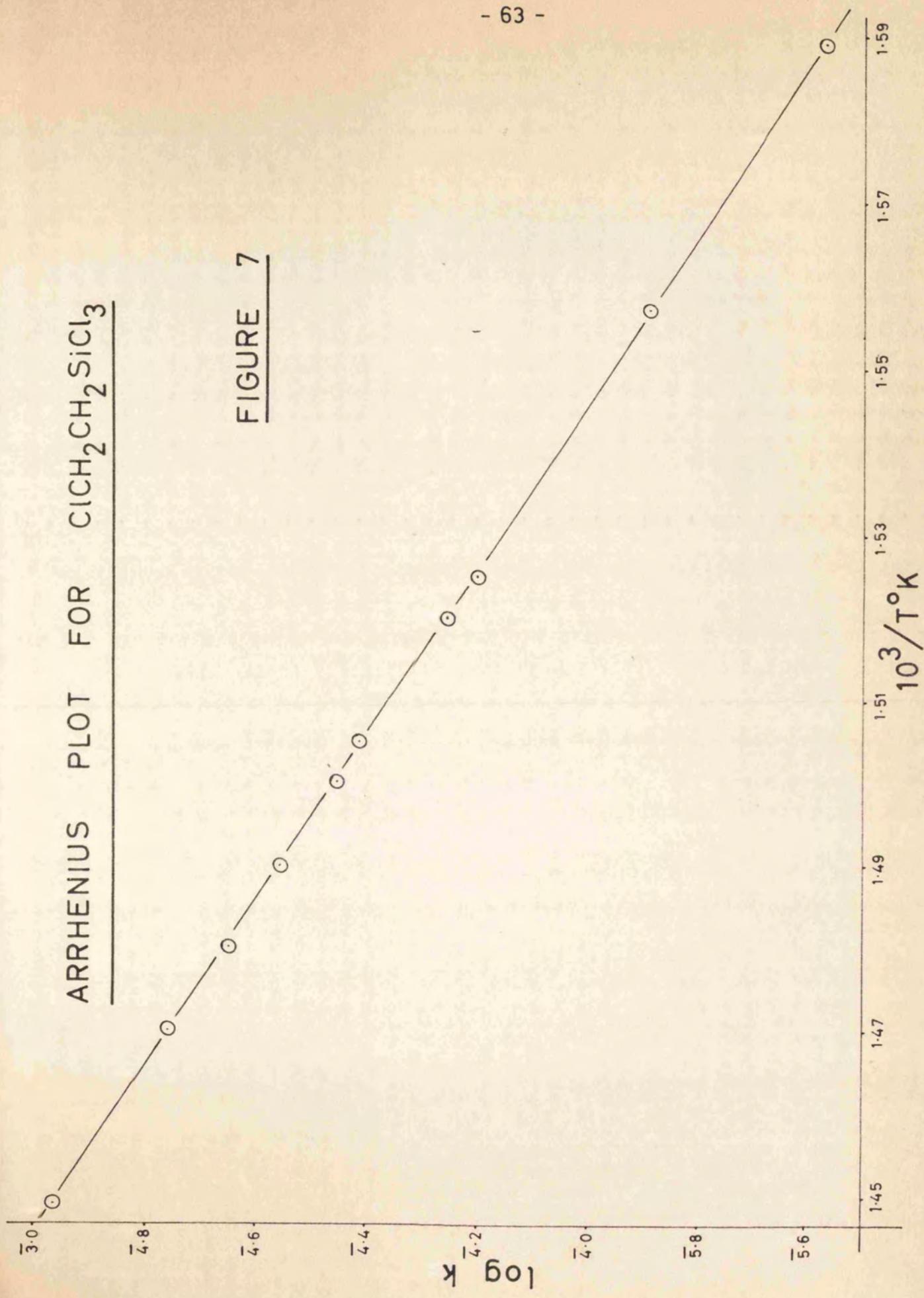
over the temperature range 356 - 417°C. Further discussion of the Arrhenius parameters will be deferred until later, when the individual steps contributing to the over-all kinetics will be considered.

(iii) EFFECT OF INHIBITORS

A number of runs were carried out in the presence of nitric oxide or cyclohexene to test whether radical chains played a part in the mechanism. The effect on the over-all rate of reaction was small but a slight acceleration of the reaction rate did occur. However, reduction of the relative amount of "inhibitor" did not reduce the rate below that of the "uninhibited" reaction. Results obtained in the presence of inhibitors are shown in Table XX together with some results without inhibitors present to enable comparison to be made. Graphs of the rate constants against relative concentrations of inhibitor and 2-chloroethyl

ARRHENIUS PLOT FOR $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$

FIGURE 7



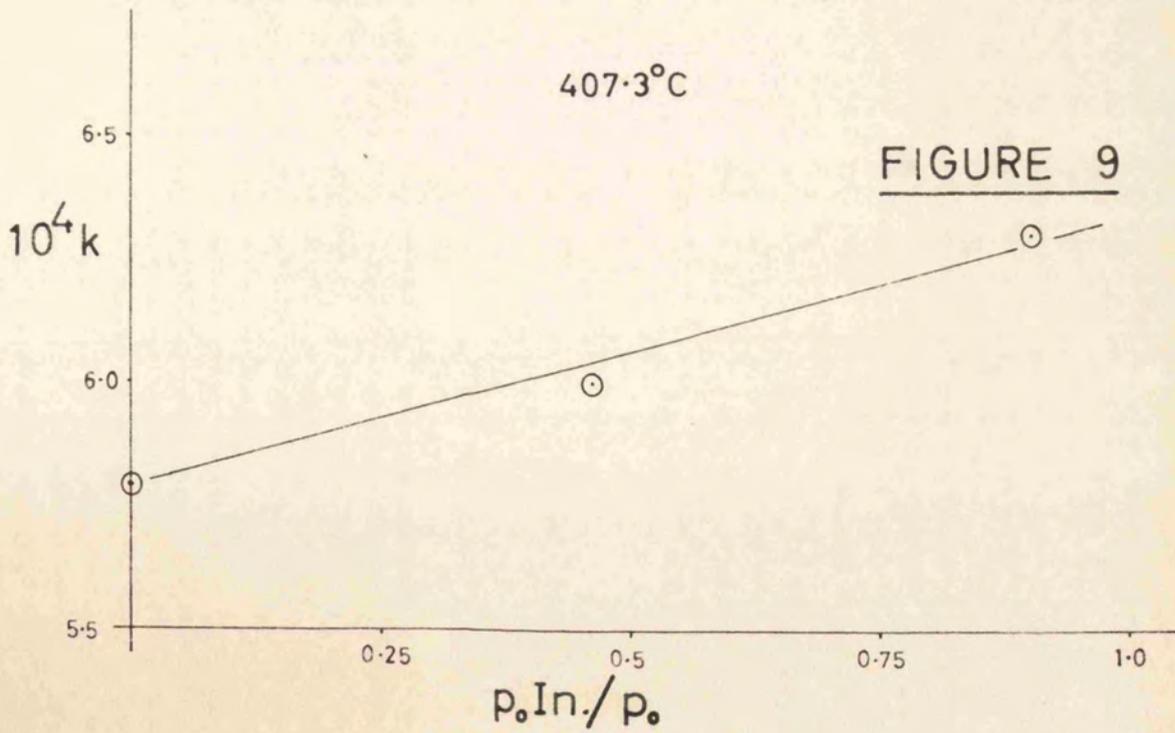
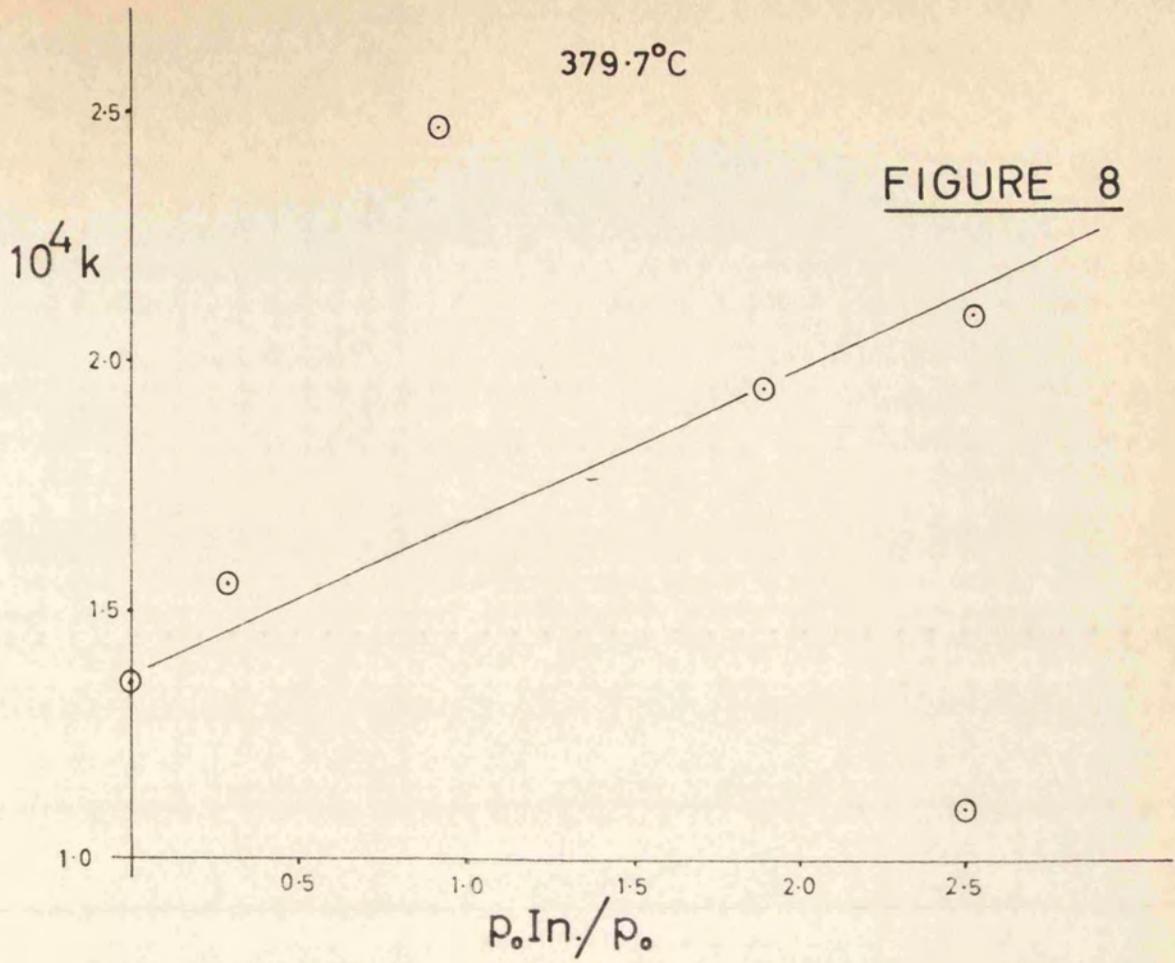
-trichlorosilane are shown in Figure 8 for nitric oxide at 379.7° and in Figure 9 for cyclohexene at 407.3°C.

TABLE XX

T°C	p _o	p _o In.	Inhibitor	p _o In/p _o	10 ⁴ k	Run
356	43.00	20.40	NO	0.475	0.416	122
356	39.20	18.80	NO	0.48	0.397	123
356	36.20	4.40	NO	0.121	0.371	124
356	-	-	-	-	0.377	Mean
375.5	13.85	10.35	C ₆ H ₁₀	0.75	1.09	38
375.5	39.50	9.80	C ₆ H ₁₀	0.25	1.11	39
379.7	35.60	10.10	C ₆ H ₁₀	0.28	1.56	40
379.7	12.15	30.30	NO	2.50	1.09	42
379.7	41.70	37.80	NO	0.91	2.47	43
379.7	24.60	46.10	NO	1.88	1.95	44
379.7	21.95	55.30	NO	2.52	2.10	45
379.7	-	-	-	-	1.38	41
382.8	41.70	31.20	C ₆ H ₁₀	0.75	1.46	51
382.8	-	-	-	-	1.58	Mean
383.3	20.60	12.00	NO	0.58	1.74	117
383.3	-	-	-	-	1.65	Mean
407.3	20.90	9.70	C ₆ H ₁₀	0.465	6.00	102
407.3	23.40	21.20	C ₆ H ₁₀	0.90	6.30	103
407.3	-	-	-	-	5.79	Mean

The significance of these results will be discussed with the subsidiary reactions, see pages 88-96

EFFECT OF INHIBITORS ON REACTION RATE



(iv) EFFECT OF SURFACE

To investigate the possibility of some surface reaction(s) taking place, the ratio of surface area to volume of the reaction vessel was changed. This was achieved both by the employment of reaction vessels of different capacities and also by packing the 1510 ml. reaction vessel with glass tubes. There was no observable difference in the rate of the over-all reaction. Results outlining this are shown in Table XXI.

TABLE XXI

T°C	$10^4 k \text{ sec.}^{-1}$	S/V cm.^{-1}	Run
380.6	1.42	0.42	53
380.6	1.43	0.42	54
380.6	1.45	2.39	56
380.6	1.49	2.39	57
382.8	1.52	0.38	112
382.8	1.595	0.78	113
385	1.84	0.28	6
385	1.86	0.28	7
385	1.88	0.28	9
385	1.79	0.42	10
385	1.77	0.42	15
New vessel cleaned with warm concentrated HNO ₃			
385	2.31	0.38	59
385	1.76	0.38	60
385	1.76	0.38	61

This investigation of surface effects was interesting in that virtually no conditioning of the surface was needed at all. In fact before Run 59 a new reaction vessel was treated with warm concentrated nitric acid before insertion into the furnace and reproducible runs were obtained almost immediately, see Table XXI. It does seem that here is a rare example of the absence of heterogeneous behaviour at any stage in the investigation. As has been already mentioned, pages 29 - 33, the usual requirement for reproducibility of kinetics of decomposition of organic compounds is a "seasoned" surface. The behaviour of 2-chloroethyltrichlorosilane becomes even more interesting when it is observed that the decomposition of 2-chloroethyldimethylphenylsilane possesses substantial heterogeneous character, see Chapter Six. It may be that $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ is more "Inorganic" than $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ and the organic compounds usually studied pyrolytically and that this has some bearing on the behaviour.

(B) THE INDIVIDUAL REACTIONS

(i) GENERAL

By gas chromatographic analysis supplemented by infra-red and mass spectra it was found that the reaction products were mainly ethylene and silicon tetrachloride with smaller quantities of hydrogen chloride, vinyltrichlorosilane, vinyl chloride, trichlorosilane and ethyltrichlorosilane. The vinyl chloride and trichlorosilane concentrations rose to a maximum during a run and then declined; the former to a small value and the latter to zero. No other products of the decomposition of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ were detected. In some runs with

large initial pressures a small peak appeared on the chromatogram after more than 10 half-lives. This unidentified peak had a retention time of 18 min. The same peak appeared on heating vinyltrichlorosilane alone, the vinyltrichlorosilane has a retention time of 9 min., and was presumably due to some polymerization, see following section. Ethyl chloride, 1,2-dichloroethane, acetylene and hydrogen were shown to be absent by gas chromatography and the latter also by the complete condensation of the products at -196°C . Later the absence of any other substances of molecular weight less than 100 was substantiated by mass spectrometry.

The main objects of this investigation were firstly, to find out if ethylene and silicon tetrachloride were formed by a unimolecular elimination and if so to use this reaction to investigate substituent effects on the silicon atom. Secondly, to elucidate the mechanism of the other reactions and then to find the effect of replacing the Si-Cl bonds by Si-alkyl or Si-aryl groups. It was not realized at first that the product mixture was as complex as stated above and the presence of vinyl chloride, trichlorosilane and ethyltrichlorosilane was not proved until after Run 39. For the first runs the products were thought to be ethylene, silicon tetrachloride, vinyltrichlorosilane and hydrogen chloride. At that time it was not possible to take many samples during a run and analyses at infinite time were concentrated upon. The results obtained are shown in Table XXII where E, S and V are ethylene, silicon tetrachloride and vinyltrichlorosilane respectively and the percentages are calculated with respect to the initial pressure, p_0 , so that comparison may be made with the more recent, more accurate, work.

TABLE XXII

Final product analysis for early runs

T°C	p _o	%E	%S	%V	Run
369.2	69.75	-	89	18	5
381.6	80.10	-	87	19	1
382.8	43.50	79	85	13	13
384	33.40	80	89	16	12
385	29.85	87	87	15	7
385	39.80	75	86	12	9
385	31.30	79	91	17	10
385	29.50	62	68	13	14
385	27.40	65	88	23	15
387.1	61.25	72	81	14	16
389.8	51.90	83	93	16	8
391.5	52.40	80	-	20	21
391.5	50.00	70	84	16	23
398	30.20	70	79	12	24
398	43.00	65	91	8	25
398	24.80	82	-	12	26
398	31.25	76	85	16	27
399.3	100.6	-	-	29	2
406.4	82.10	-	67	13	4
408.1	35.85	-	72	18	3

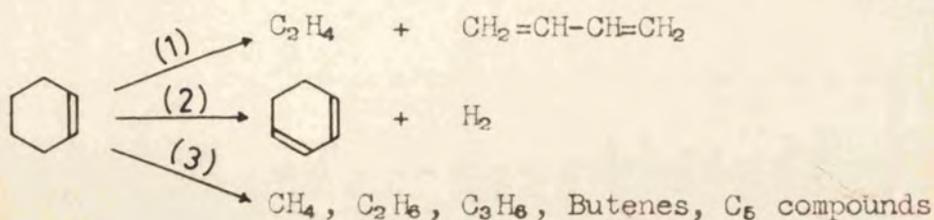
It was obvious from these results that the kinetic scheme did not merely involve ethylene elimination and dehydrochlorination and that efficient separation of the constituents on the column probably was not occurring especially with respect to the "silicon tetrachloride" peak. The analytical system was therefore improved to incorporate a sampling valve¹⁵⁰ and a more efficient gas chromatography column and detection system.

(ii) STABILITY OF PRODUCTS AND INHIBITORS INDIVIDUALLY

HCl, C₂H₄, NO, CH₂=CHCl, SiCl₄, HSiCl₃, CH₂=CH.SiCl₃,
C₂H₅SiCl₃, C₆H₁₀ and ClCH₂CH₂SiCl₃.

At the temperature these experiments were carried out it was shown, by gas chromatographic analysis, that with one exception, possibly two, these compounds were stable. The exception was cyclohexene which at the higher pyrolysis temperatures used did decompose slightly. Also there was an indication of a minute amount of decomposition, polymerization, with vinyltrichlorosilane.

Smith and Gordon¹⁵¹ have investigated the thermal decomposition of cyclohexene and found that the reaction followed the following scheme between 425 - 535°C.



Reactions (1) and (2) are homogeneous and unimolecular with approximately the same activation energy. Reaction (3) is free radical and comprises less than 10% of the total reaction. The over-all reaction rate is

governed by the Arrhenius equation:

$$k \text{ (sec.}^{-1} \text{)} = 7.7 \times 10^{15} e^{-67,600/RT}$$

To show the extent of the above reactions at the temperatures used in the pyrolysis of 2-chloroethyltrichlorosilane, some cyclohexene was left in the reaction vessel at 400°C for 12 hrs. The pressure increased from 48.8 to 49.4 mm. and chromatographic analysis showed that ca. 0.3 mm. of ethylene had been produced. Hence the rate acceleration observed manometrically in the presence of cyclohexene may be partly due to the occurrence of the above reactions in addition to the action of trichlorosilane on cyclohexene producing hydrogen chloride.

Despite the experimental evidence that none of the other products underwent any decomposition a few points need to be made.

With vinyltrichlorosilane a very small amount of polymerization has been found to occur in the vapour phase at the temperatures used for this work. At moderate pressures extensive polymerization of vinyltrichlorosilane has been shown to occur¹⁵² between 280 and 400°C and the results are shown in Table XXIII. These reactions do not seem to take place, except to a negligible extent, at low pressures in the vapour phase.

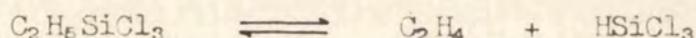
TABLE XXIII

Polymerization of vinyltrichlorosilane at moderate pressures

T°C	chlorosilanes	(Cl ₃ SiCH ₂) ₂	dimer	polymer [CH ₂ -CH(SiCl ₃)]
280	35%	2%	4%	59%
300	3	8	10	79
400	17	26	24	33

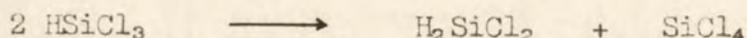
Vinyl chloride is said to decompose by a mechanism varying from three-halves to second order as the reaction proceeds.¹⁵³ Decomposition occurs between 551 - 618°C with an activation energy of 53 kcal./mole. The main products are hydrogen chloride and polymer with small amounts of ethylene, acetylene and methane. Pyrolysis of 21 mm. vinyl chloride at 380°C for 15 hrs. did not show any decomposition.

Since dehydrosilylation can occur on pyrolysis of 2-chloroethyltrichlorosilane it seems possible that a similar process could occur with ethyltrichlorosilane making the reaction below reversible.



A very small quantity of ethylene was produced on heating ethyltrichlorosilane at 400°C for 10 hrs. Hence it appears that the reaction goes effectively right - left as shown above and any small amount of decomposition of ethyltrichlorosilane would be well within the experimental error in its determination.

Trichlorosilane is known to disproportionate under certain circumstances. At temperatures over 550°C mainly hydrogen and silicon tetrachloride are formed whereas at lower temperatures some dichlorosilane is produced.¹⁵⁴ It was extremely difficult to obtain chromatographically pure trichlorosilane and if a large quantity, ca. 100 mm., of trichlorosilane was left in the reaction vessel for some time then some silicon tetrachloride was formed. There seems little reason to doubt that the reaction:



would occur in the study of the

pyrolysis of 2-chloroethyltrichlorosilane were it not for the preferential reaction of the trichlorosilane formed with the vinyl chloride and ethylene as outlined below.

Freshly distilled 2-chloroethyltrichlorosilane often contained a small quantity of ethylene impurity. However, this was easily removed by degassing and no further decomposition occurred in the heated, 200°, injection bulb. This also indicated that decomposition of the parent molecule was not occurring on the chromatography column.

(iii) INITIAL RATES OF FORMATION OF PRODUCTS

(a) Without inhibitor

The concentrations of ethylene (E), silicon tetrachloride (S), vinyl chloride (VC), and vinyltrichlorosilane (V) in the reaction mixture were determined at intervals during the kinetic runs. The silicon tetrachloride was determined using the thermistor detector whereas the organic components were determined by hydrogen flame ionization. It was not found possible to accurately determine the trichlorosilane and hydrogen chloride in this way. The quantity of hydrogen chloride was found to be equal to that of vinyltrichlorosilane by mass spectrometry. Ethyltrichlorosilane did not appear in the products until more than 60% reaction and the quantity was so small that to measure the rate of its formation was impossible. The most convenient and illustrative method of showing the results was by plotting the experimentally determined pressure of the particular product against $1 - e^{-kt}$. The value of k was determined from the $\log (p_0 - \Delta p)$ versus time plots as previously described.

As shown in Figures 10 and 11 and also in Figure 42 on page 187 in the experimental section; the partial pressures of ethylene (pE) and silicon tetrachloride (pS) show good linear behaviour indicative of a first order reaction.

Similarly the initial rates of formation of vinyltrichlorosilane, Figure 12, and vinyl chloride, Figure 13, are linear. As the reaction proceeded the amount of vinyltrichlorosilane produced increased to greater than the initial rate would predict, whereas the opposite occurs with vinyl chloride. The trichlorosilane concentration also reached a maximum, like vinyl chloride, and then declined to zero at the end of a run. Some vinyl chloride remained at infinity.

The gradient of the linear portion of the graphs shown in Figures 10 - 13 is, taking ethylene as example, given by:-

$$\text{gradient} = \frac{kE \cdot p_0}{k_{\text{over-all}}}$$

Hence for each curve the ratio of the rate of formation of the particular component, in this case ethylene, and the over-all reaction rate can be calculated. The values of the initial rates obtained by this procedure are given in Table XXIV.

TABLE XXIV

Rates of formation of products in the absence of inhibitors

T°C	p ₀	10 ⁴ k	kE/k	kS/k	kVC/k	kV/k	Run
356	37.50	0.371	0.67	-	0.15	-	125
376.4	32.50	1.15	0.75	-	0.11	-	48
377.6	37.50	1.22	0.74	-	-	0.20	110
377.6	47.40	1.14	0.70	-	-	-	111

TABLE XXIV (continued)

T°C	p _o	10 ⁴ k	kE/k	kS/k	kVC/k	kV/k	Run
380.6	34.80	1.42	0.69	-	0.18	-	53
380.6	36.50	1.43	0.67	-	0.16	-	54
382.8	41.40	1.63	0.68	-	0.16	-	50
382.8	43.80	1.59	0.69	-	0.14	-	52
382.8	32.40	1.60	0.70	-	0.20	-	72
382.8	28.10	1.49	0.72	-	0.16	-	73
382.8	26.20	1.60	0.70	-	0.21	-	75
382.8	41.20	1.56	0.65	-	0.16	-	76
382.8	41.10	1.58	0.74	-	0.16	-	77
382.8	99.00	1.59	0.70	-	-	-	113
383.3	49.10	1.57	0.75	0.72	-	-	63
383.3	29.90	1.68	0.70	0.71	-	-	64
383.3	36.80	1.57	0.75	0.71	-	-	67
383.3	27.00	1.71	0.78	0.75	-	-	68
385	18.70	2.31	0.69	-	-	-	59
385	51.65	1.76	0.74	-	0.13	-	60
385	56.40	1.76	0.71	-	0.15	-	61
385	37.80	1.88	0.70	-	0.16	-	62
385	12.15	1.79	0.78	0.76	-	-	69
385	26.00	1.63	0.74	0.72	0.12	-	70
399.3	45.00	3.84	0.70	0.69	-	0.10	85
401.2	42.50	4.23	0.72	-	0.12	-	55
402.6	16.40	4.38	0.74	0.73	-	-	78
402.6	34.30	4.36	-	0.67	-	-	79

TABLE XXIV (continued)

T°C	p ₀	10 ⁴ k	kE/k	kS/k	kVC/k	kV/k	Run
402.6	26.00	4.52	-	0.69	-	-	80
402.6	28.20	4.40	0.73	0.71	-	-	81
402.6	28.25	4.20	0.73	0.71	-	0.12	82
402.6	33.20	4.45	0.77	-	-	0.12	83
402.6	17.50	4.45	0.76	0.72	-	0.11	84
402.6	23.00	4.36	0.75	0.70	-	0.14	86
402.6	29.95	4.36	0.72	-	-	-	94
407.3	27.00	5.75	-	-	-	0.11	97
407.3	20.40	5.65	0.83	-	-	0.13	98
407.3	52.00	5.24	0.70	-	-	0.09	99
407.3	36.20	6.03	0.74	-	-	0.11	100
407.3	27.15	5.80	0.88	-	-	0.14	101
409.5	37.40	6.20	0.74	-	-	0.11	95
410.9	12.90	6.75	0.77	-	-	0.13	96
417	49.40	9.22	0.69	-	-	-	120

Also one run with increased surface to volume ratio

380.6	36.20	1.49	0.73	-	0.17	-	57
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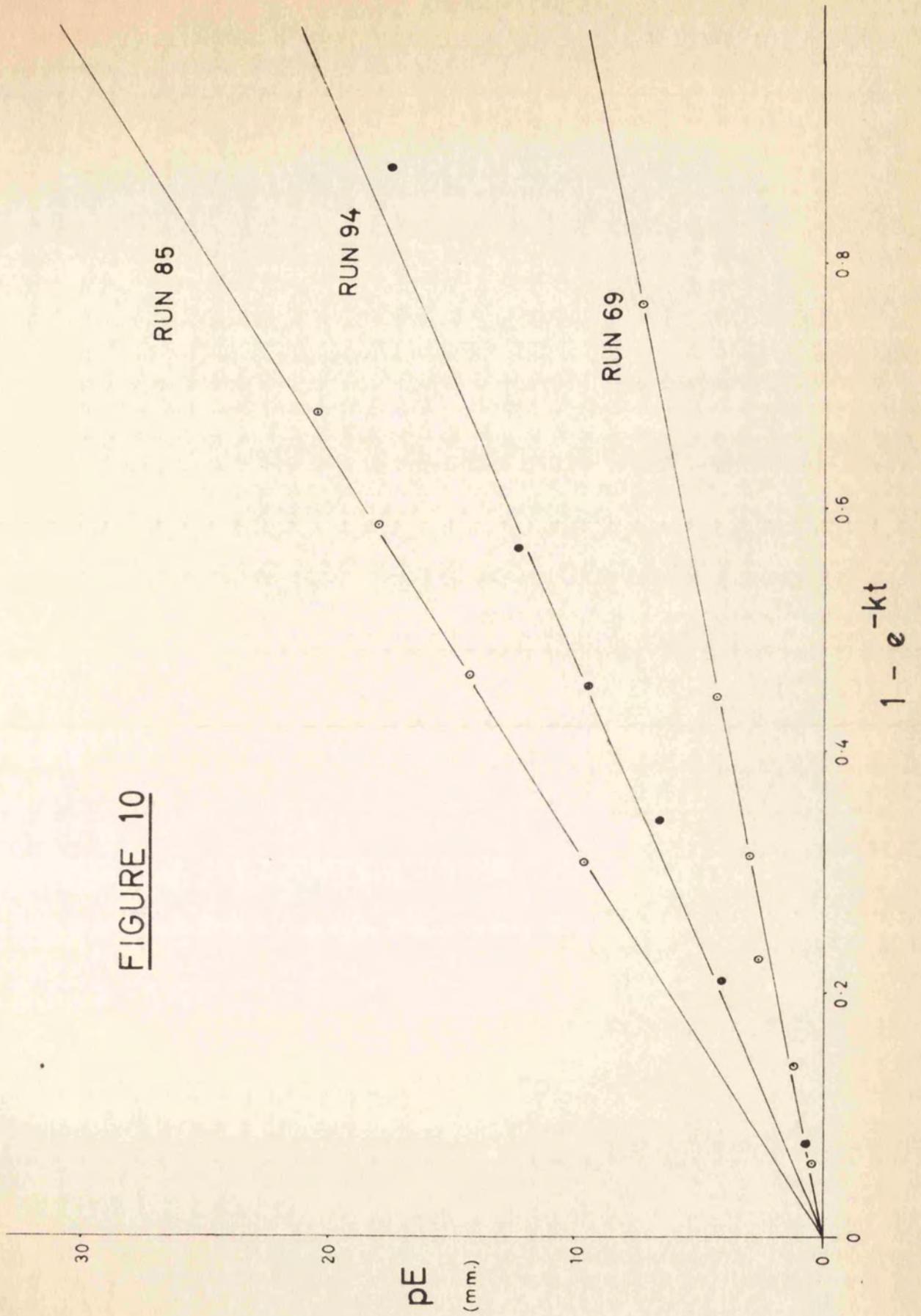
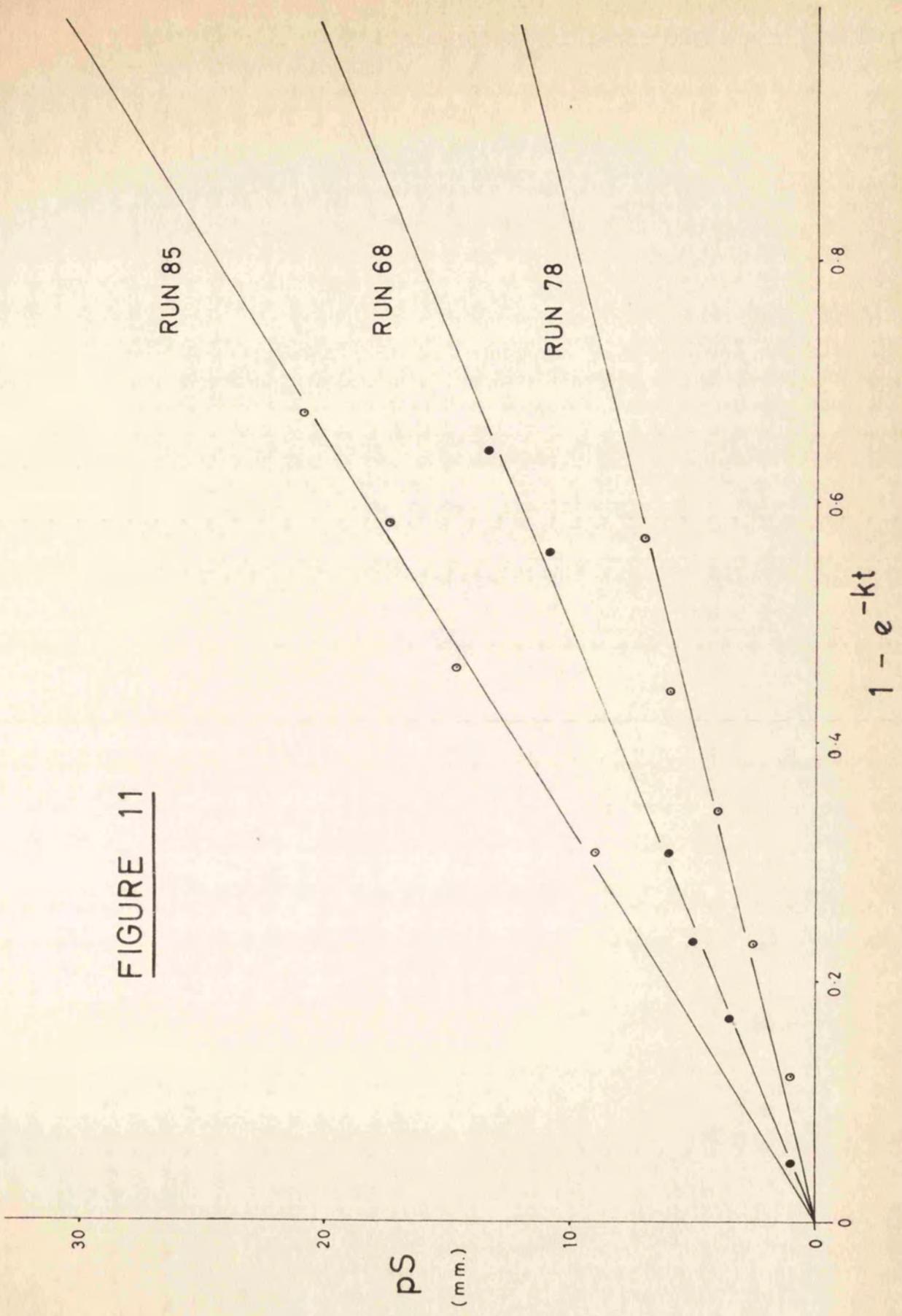


FIGURE 11



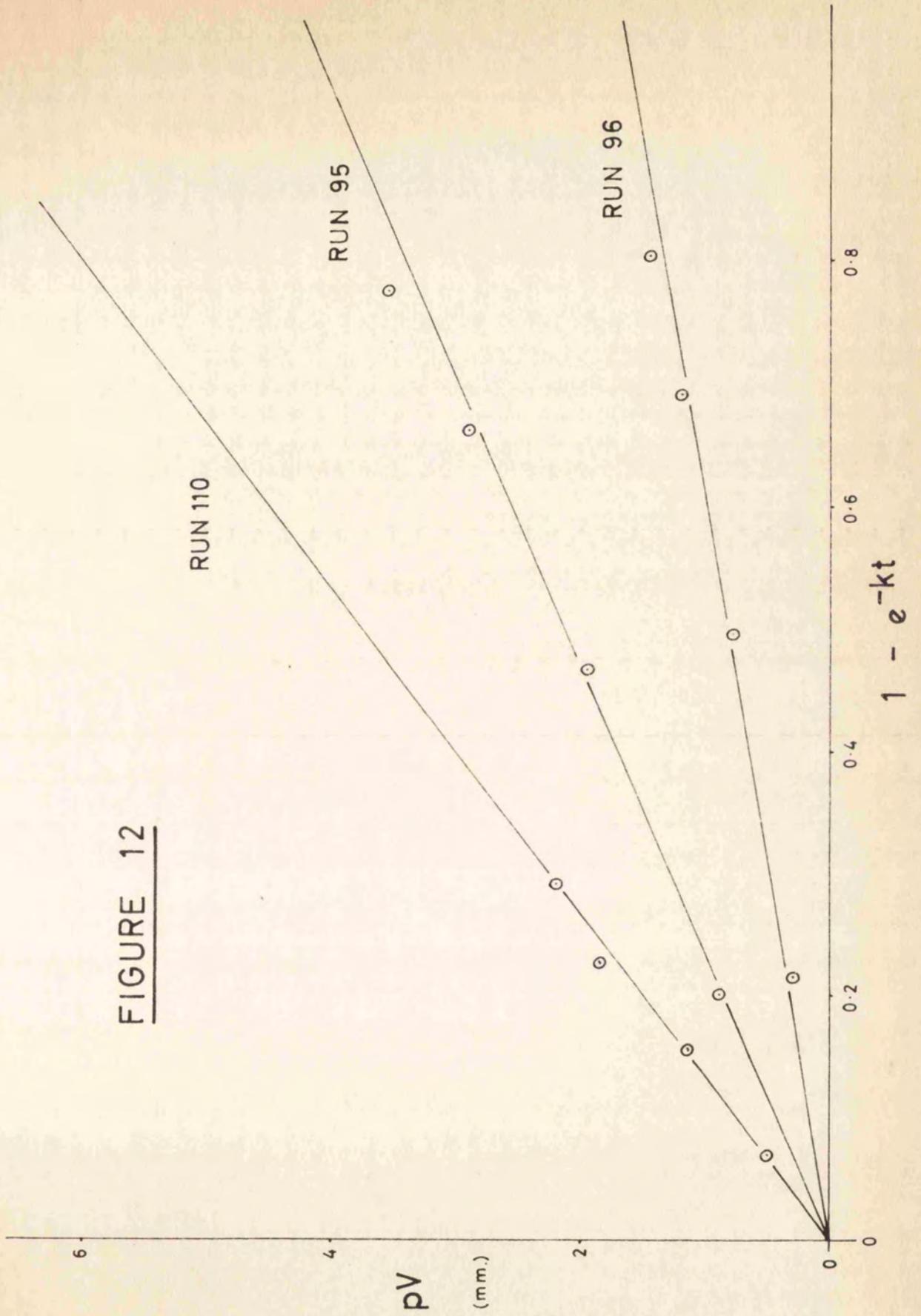
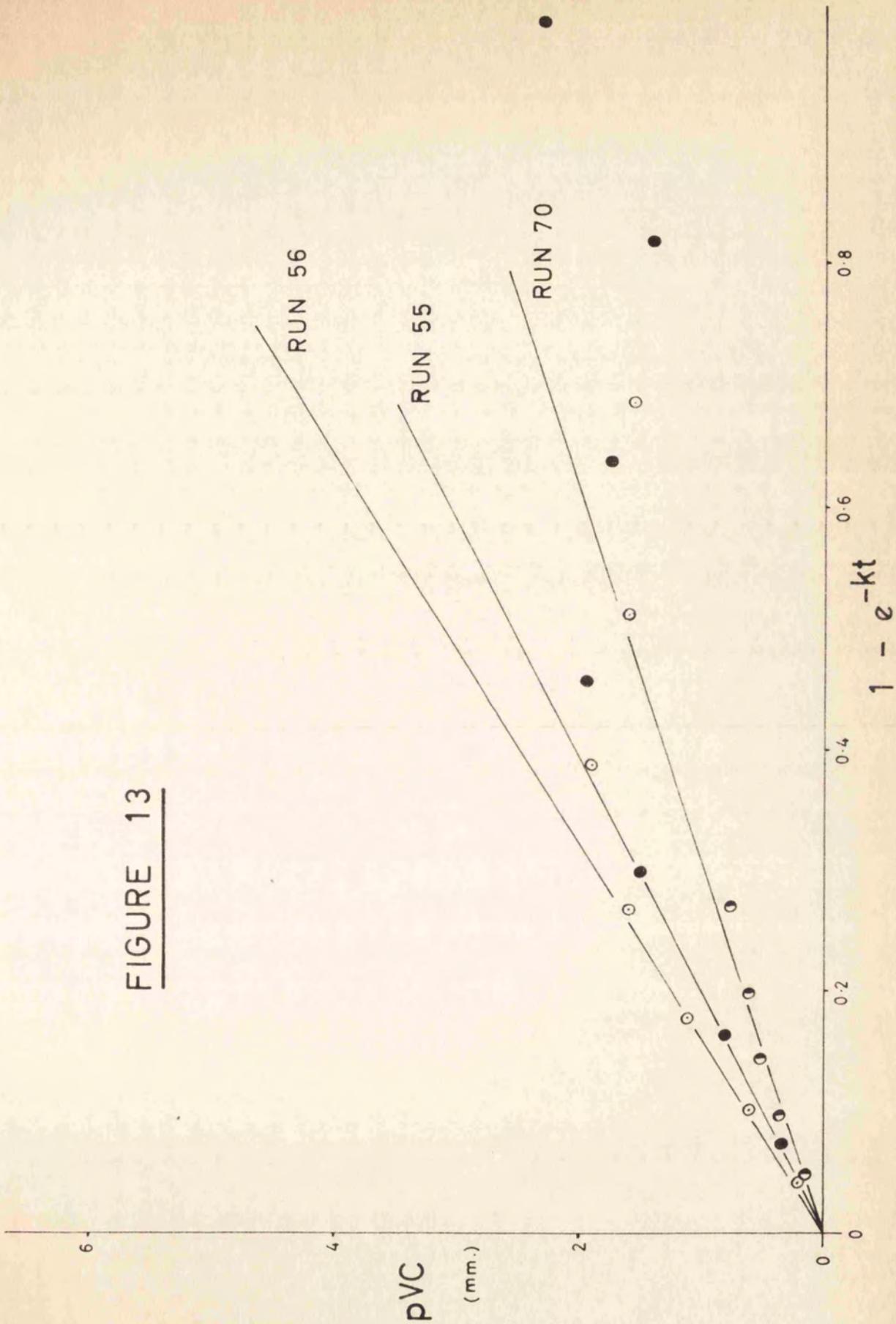


FIGURE 12

FIGURE 13



(b) In the presence of inhibitors

When nitric oxide or cyclohexene were present the initial rates of formation of the products remained the same within experimental error, although the experimental error was rather high for slight changes to be observed. However, the plots of pV and pVC versus $1 - e^{-kt}$ remained linear until the reaction had proceeded to a greater extent. The results are illustrated by Figures 14 and 15 and are tabulated in Table XXV. The rate of formation of vinyltrichlorosilane could not be measured in the presence of cyclohexene because they had approximately the same retention times.

TABLE XXV

Rates of formation of products in the presence of inhibitors

T°C	p ₀	p ₀ In.		10 ⁴ k	kE/k	kVC/k	kV/k	Run
356	43.00	20.40	NO	0.416	0.75	0.12	0.15	122
356	39.20	18.80	NO	0.397	0.73	-	-	123
356	36.20	4.40	NO	0.371	0.72	0.16	-	124
379.7	12.15	30.30	NO	1.09	0.74	0.16	-	42
379.7	21.95	55.30	NO	2.10	0.68	-	0.10	45
382.8	41.70	31.20	C ₆ H ₁₀	1.46	0.75	0.14	-	51
407.3	20.90	9.70	C ₆ H ₁₀	6.00	0.74	-	-	102
407.3	23.40	21.20	C ₆ H ₁₀	6.30	0.72	-	-	103

Also one run in the presence of ethylene

379.3	30.45	11.60	C ₂ H ₄	1.35	0.74	0.18	-	109
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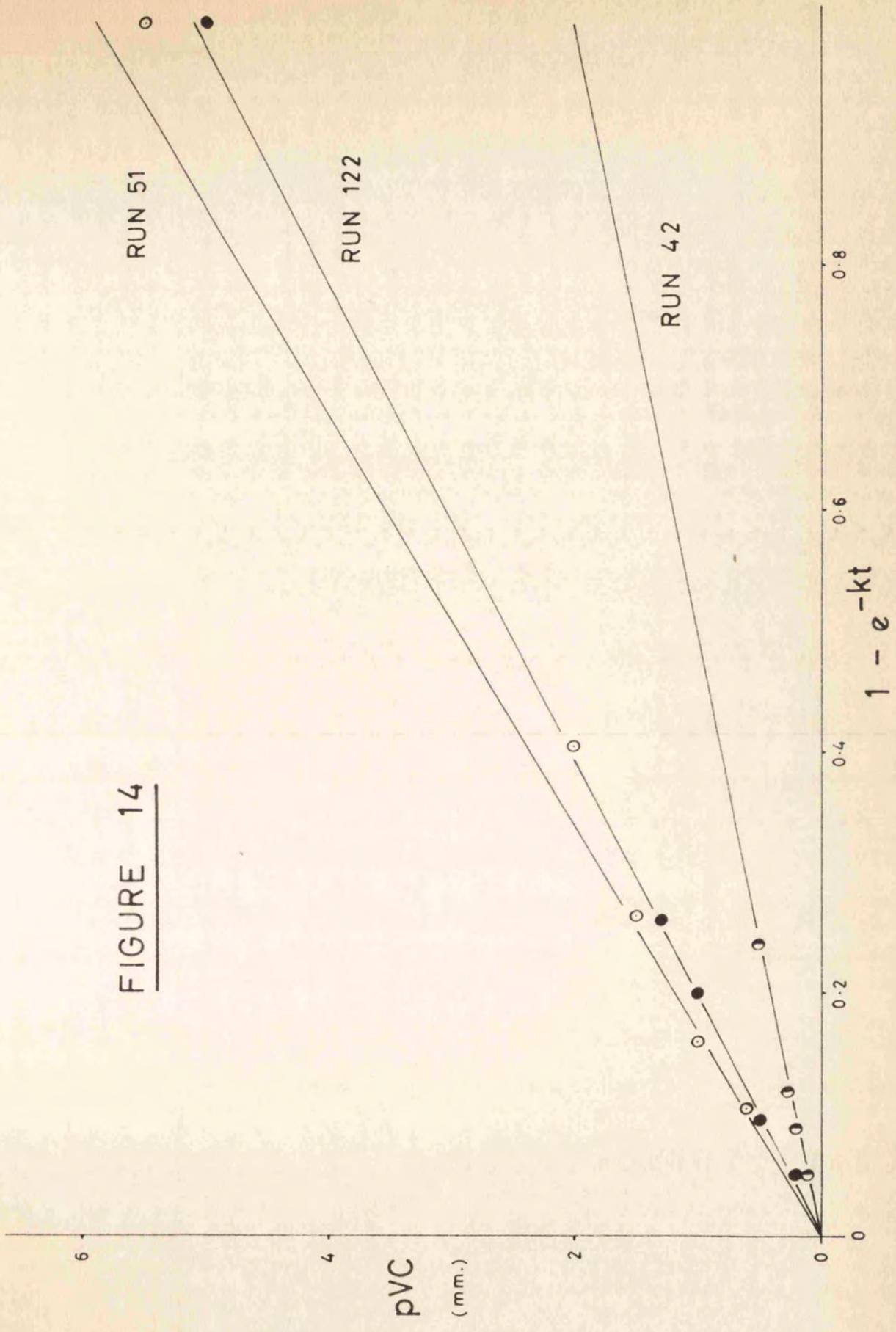
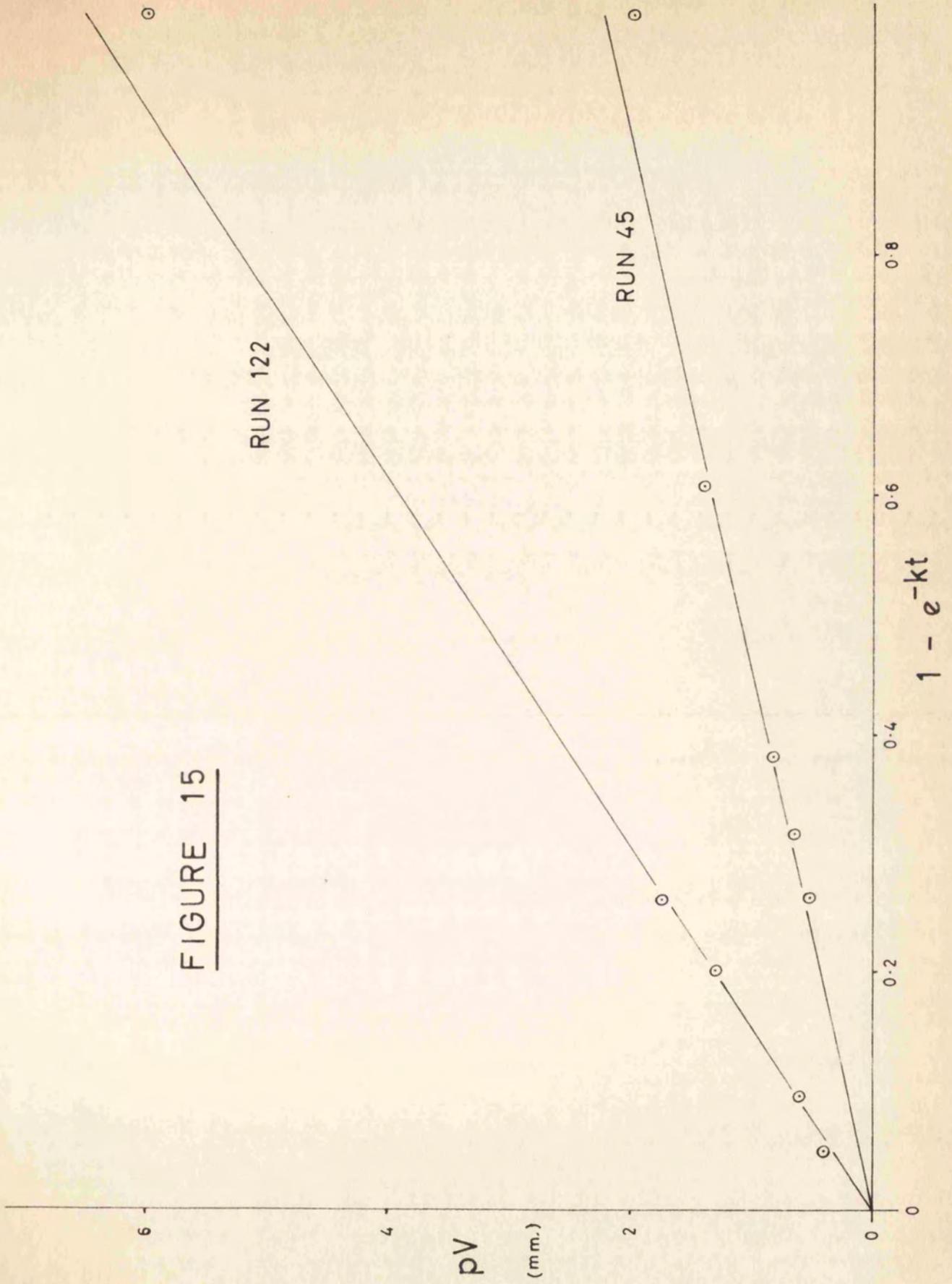


FIGURE 14

FIGURE 15



(iv) CONCENTRATIONS AT INFINITY

Gas chromatographic analysis was also carried out after more than 10 half-lives to substantiate the evidence obtained during the runs.

(a) Without inhibitor

In the absence of nitric oxide and cyclohexene the results at infinity for ethylene and silicon tetrachloride agreed with the initial rates obtained during a run to within $\pm 10\%$. In the cases of vinyl chloride and vinyltrichlorosilane the quantities remaining were substantially different from what the initial rates would predict although the sum of the pressures, $pV_{\infty} + pVC_{\infty}$, was approximately the same as predicted from the sum of the initial rates. It will be shown, section (vi), that the larger amount of vinyltrichlorosilane and the correspondingly smaller amount of vinyl chloride are due to the subsidiary reaction between vinyl chloride and trichlorosilane to produce vinyltrichlorosilane and hydrogen chloride. The results obtained are shown in Table XXVI, the percentages being with respect to the initial pressure, p_0 , of 2-chloroethyltrichlorosilane so that comparison with Tables XXIV and XXV may be made.

TABLE XXVI

Final product analysis in the absence of inhibitors

T°C	p_0	%E	%S	%VC	%V	Run
356	37.50	71	-	3	26	125
376.4	32.50	69	-	7	-	48
378.5	32.10	-	70	7	-	47
380.6	34.80	-	-	6	20	53
380.6	36.50	68	-	5	25	54

TABLE XXVI (continued)

T°C	Po	%E	%S	%VC	%V	Run
380.6	37.70	73	-	-	21	71
382.8	63.10	74	-	5	22	49
382.8	41.40	70	-	8	19	50
382.8	43.80	65	-	7	-	52
382.8	28.10	72	76	-	22	73
382.8	21.45	75	75	-	23	74
382.8	26.20	-	76	-	26	75
382.8	41.20	-	-	-	25	76
383.3	49.10	69	80	-	-	63
383.3	29.90	67	67	-	23	64
383.3	36.80	70	67	-	20	67
383.3	46.60	71	-	4	25	119
385	18.70	69	-	-	-	59
385	51.65	77	-	6	19	60
385	56.40	68	-	7	16	61
385	37.80	75	-	9	16	62
385	12.15	68	73	-	27	69
385	26.00	67	72	-	24	70
401.2	42.50	78	-	5	20	55
402.6	16.40	76	72	-	25	78
402.6	34.30	-	70	-	18	79
417	49.40	69	-	3	26	120

Also one run with increased surface to volume ratio

380.6	36.20	69	-	6	22	57
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(b) In the presence of inhibitors

The effects of nitric oxide, and cyclohexene, on the reactions producing vinyl chloride and vinyltrichlorosilane compared with the "uninhibited" reaction were to reduce the quantity of vinyltrichlorosilane and increase the amount of vinyl chloride in the analyses after more than 10 half-lives. The experimental results were reasonably close to those for the initial rates of reaction. The ethylene elimination reaction was unaffected. The results obtained are shown in Table XXVII where the percentages are again calculated with respect to the initial pressure, p_0 , of 2-chloroethyltrichlorosilane.

TABLE XXVII

Final product analysis in the presence of inhibitors

T°C	p_0	p_0 In.		%E	%VC	%V	Run
356	43.00	20.40	NO	72	12	14	122
356	39.20	18.80	NO	71	15	16	123
356	36.20	4.40	NO	72	11	20	124
379.7	24.60	46.10	NO	-	18	-	44
379.7	21.95	55.30	NO	-	11	9	45
382.8	41.70	31.20	C ₆ H ₁₀	-	13	-	51

No ethyltrichlorosilane was observed in the products when an inhibitor was present. It is noteworthy that when a small amount of nitric oxide is present, 4.40 mm., then complete inhibition of the reaction:



does not take place and this is reflected in the final product analysis, see Run 124.

(v) STOICHIOMETRY OF THE REACTION

Although no decomposition of 2-chloroethyltrichlorosilane occurred on the chromatography column the retention time for this compound was about 55 min. and the peak broad under the conditions necessary for separation of the products. The measurement of the rates of appearance of products and the concentrations of products at infinity were concentrated upon. The results obtained by final product analysis are shown in Table XXVIII where the percentages are calculated with reference to p_0 . The column $\%C_2$ is the sum of the percentages of the C_2 fragments, viz.:- ethylene (E), vinyl chloride (VC), vinyltrichlorosilane (V) and ethyltrichlorosilane (Et). If the experimental results shown in Table XXVIII are utilized with the additional information that $p_V = p_{HCl}$, this identity is assumed to be correct in the presence of nitric oxide, any additional hydrogen chloride being formed solely from the reaction between trichlorosilane and nitric oxide, then the ratio of final to initial pressure can be calculated to be approximately equal to 1.93 and in agreement with experiment. Also the condition:- $p_S - p_E = p_{Et} = p_{VC}$ should hold for the uninhibited reaction; this may in fact be the case as the values given for p_{Et} are subject to large experimental error and must only be considered as an estimate. However, it was of course possible to tell when no ethyltrichlorosilane was present.

TABLE XXVIII

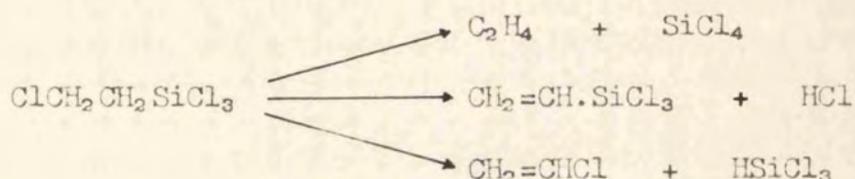
Final product analyses used for stoichiometry of the reaction

T°C	p _o	p _o NO	pE _∞	pVC _∞	pV _∞	pEt _∞	%E	%VC	%V	%Et	%C ₂	Run
356	43.00	20.40	30.9	5.0	6.0	0	72	12	14	0	98	122
356	39.20	18.80	27.6	6.0	6.4	0	71	15	16	0	102	123
356	36.20	4.40	25.9	4.0	7.2	0	72	11	20	0	103	124
356	37.50	-	26.7	1.2	9.7	0.7	71	3	26	2	102	125
380.6	36.50	-	24.7	2.0	9.3	-	68	5	25	-	98	54
380.6	36.20	-	25.1	2.0	8.0	-	69	6	22	-	97	57
382.8	63.10	-	46.5	3.0	14.0	-	74	5	22	-	101	49
382.8	41.40	-	29.0	3.2	8.0	-	70	8	19	-	97	50
383.3	46.60	-	33.2	2.0	11.5	0.5	71	4	25	1	101	119
385	51.65	-	40.0	3.3	10.0	-	77	6	19	-	102	60
385	56.40	-	38.0	3.8	9.2	-	68	7	16	-	91	61
385	37.80	-	28.3	3.5	6.0	-	75	9	16	-	100	62
417	49.40	-	34.0	1.5	13.0	0.5	69	3	26	1	99	120

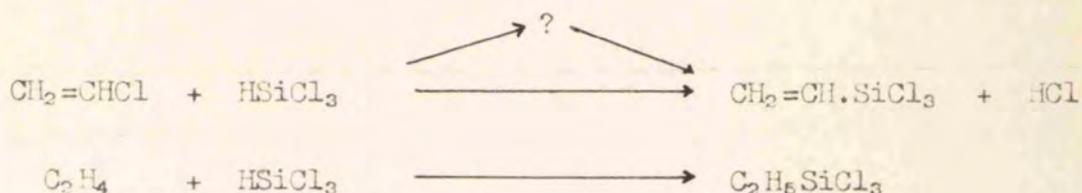
(vi) SUBSIDIARY REACTIONS

Before considering the subsidiary reactions individually it will perhaps be useful here to briefly summarize the evidence in the preceding pages. Ethylene and silicon tetrachloride are formed at equal rates by a first order reaction which is unaffected by inhibitors. Also the final product analysis for these compounds agrees with their rate of formation. This reaction is therefore kinetically simple and in all probability involves a cyclic transition state. The initial rate

of formation of vinyl chloride and of vinyltrichlorosilane was independent of the presence of inhibitors. Also, when large amounts of nitric oxide were present then the final product analysis agreed with the appropriate rate ratios. Hence these reactions are initially first order eliminations. Therefore it seemed likely that the 2-chloroethyltrichlorosilane decomposed initially by three simultaneous unimolecular eliminations.

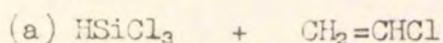


From the infinity results without inhibitor present the total reaction scheme was not as simple as this and the following subsidiary reactions are known to occur.



Reactions of this type are well known and have been extensively studied, the addition of silicon hydrides across a double bond being a common synthetic route in organosilicon chemistry.¹⁵⁵ In the absence of catalysts the reactions are usually carried out in a flow system at 550-650°C; addition to chloro-olefins giving high yields of vinyl - silicon products.^{156,157,158,159,160,161} Alternatively the reactions are carried out between 300-350°C in an autoclave at high pressures.¹⁶² Catalytic addition of silicon hydrides to olefins is achieved at low temperature using chlorplatinic acid, platinum-SiO₂ or platinum-carbon¹⁶³ or more commonly with peroxides,^{164,165} reaction with chloro-olefins giving some

addition compounds but mainly vinyl compounds.^{51,166} The vinyl compounds may arise from normal addition followed by elimination. The mechanisms have been suggested to be free radical in character where the addition of Si - H is similar to radical additions of CHCl_3 and HX in that a secondary or a tertiary rather than a primary radical is formed. Therefore terminal addition of the SiCl_3 radical occurs. The SiCl_3 radicals are efficient chain transfer agents and, with simple olefins, little telomerization occurs. 1:1 addition products are usually obtained in high yield. Reaction of trichlorosilane with ethylene at 270 - 390°C under pressure^{167,168} gives rise to telomerization products of the formula $\text{Cl}_3\text{Si}(\text{CH}_2\text{CH}_2)_n\text{H}$ where $n = 1 - 5$ but this reaction would not be very likely to occur at low pressures.



This reaction was studied at 402.6°C in the same system as was used for the pyrolysis of 2-chloroethyltrichlorosilane. There was found to be no pressure change in the reaction and the only products were vinyltrichlorosilane and hydrogen chloride, except when the products were left in the reaction vessel for a long time, more than 24 hrs., when a very small quantity of ethylene was detectable. The results obtained are outlined in Table XXIX where k is the average second order rate constant.

It will be noted that provided the concentration of trichlorosilane is less than that of the vinyl chloride that the reaction is reasonably accurately described by a second order rate law, the reaction being approximately first order with respect to each reactant. However, if the

amount of trichlorosilane was greater than that of vinyl chloride then the reaction could not be described by a simple rate law.

TABLE XXIX

Reaction between trichlorosilane and vinyl chloride
at 402.6°C

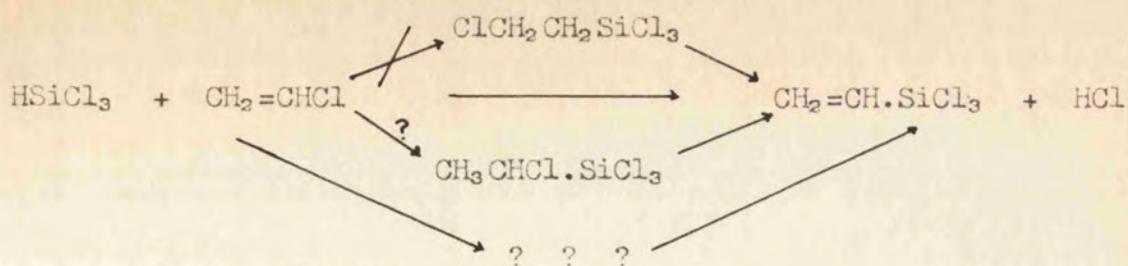
Run	p_0 VC	p_0 HSiCl ₃	$10^5 k$ mm. ⁻¹ sec. ⁻¹
87	11.3	5.1	1.70
88	6.9	3.3	0.95
89	7.0	4.05	1.73
91	11.0	18.9	0.39 - 0.97
92	11.6	16.7	0.53 - 1.76
93	24.6	4.5	1.50

It seems likely that in the decomposition of 2-chloroethyltrichlorosilane the conditions will be such as to make the trichlorosilane concentration less than or equal to that of vinyl chloride and so the reaction will be approximately second order.

It might be expected that addition should precede elimination in this reaction. However, if this did occur under these experimental conditions then the addition product had a transient existence and was not the expected 2-chloroethyltrichlorosilane because no ethylene or silicon tetrachloride was formed in the reaction. Reaction of vinyl chloride and trichlorosilane at high pressures in the presence of a platinum catalyst does produce 2-chloroethyltrichlorosilane.¹⁶⁹

Alternatively the addition product could be 1-chloroethyltrichlorosilane

which does not however decompose until higher temperatures.¹⁴¹



In the presence of nitric oxide this reaction does not occur to any measurable extent. Only a minute trace of vinyltrichlorosilane being formed after more than 24 hrs. It would seem therefore that the reaction is a radical one, see, however, Section (c) below.



At 402.6°C this reaction occurs at a slower rate than the corresponding reaction with vinyl chloride. Only one kinetic run was carried out in the absence of inhibitor and the results are given in Table XXX.

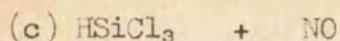
TABLE XXX

Reaction between trichlorosilane and ethylene at 402.6

Run	p ₀ E	p ₀ HSiCl ₃	10 ⁵ k mm. ⁻¹ sec. ⁻¹
90	8.60	8.60	0.09

The reaction is at least 10 times slower than with vinyl chloride and again appears to be second order. The reaction is completely inhibited by nitric oxide. The occurrence of this reaction accounts for the decline of the manometrically measured over-all rate constant and for the observation that the final pressure of ethylene is slightly less

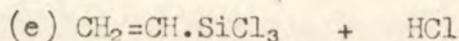
than that of silicon tetrachloride in runs without added inhibitor.



This reaction has been studied by Mr. C. J. Wood¹⁷⁰ in this laboratory on the mass spectrometer. It was found that at 420°C the rate constant was about $10^{-3} \text{ mm.}^{-1} \text{ sec.}^{-1}$. A large amount of hydrogen chloride was formed in the reaction. It does seem probable that the inhibitory action of nitric oxide on the reactions between trichlorosilane and vinyl chloride or ethylene is merely to remove the trichlorosilane by some preferential reaction rather than to inhibit the formation of free radical chains. In other words, the reactions discussed in Sections (a) and (b) above may not in fact be radical in character under the conditions operative in this study.

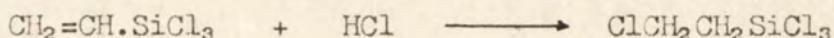


This reaction was also studied in this laboratory by Mr. C. J. Wood¹⁷⁰ and he found that the reaction rate was about one third of that between trichlorosilane and nitric oxide. Hydrogen chloride was also formed in this reaction. No further results are at present available but the production of hydrogen chloride was not expected as the addition of trichlorosilane to cyclohexene at 280°C¹⁷¹ and at 50°C in the presence of benzoyl peroxide¹⁷² gives high yields of cyclohexyltrichlorosilane.



The addition of HX across a vinyl double bond in organosilicon chemistry is a common synthetic method. Anti - Markovnikov addition to unsubstituted vinyl groups attached to silicon normally occurs to

give the β -halogenated compound. In the presence of aluminium chloride, hydrogen chloride adds to vinyltrichlorosilane to give 2-chloroethyltrichlorosilane.^{28,46} It might be expected therefore that the reaction:-



would be reversible and would thus form ethylene and silicon tetrachloride, the major products of decomposition of 2-chloroethyltrichlorosilane. The equilibrium does however seem to be very much over to the left hand side as the results shown in Table XXXI below indicate.

TABLE XXXI

Reaction between vinyltrichlorosilane and hydrogen chloride
at 380.6°C

Time(min.)	pHCl	pV	pE	pVC
0	38.8	39.7	-	-
40	-	39.7	0	0
90	-	39.7	0.015	0.015
125	-	39.7	0.02	0.015



The above reactions were carried out during the course of this work to find out whether any inhibition occurred due to the formation of olefinic products. With added ethylene or vinyl chloride no detectable ^{variation} in the rate of the over-all reaction was observed. The results obtained, together with comparative data on $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ alone,

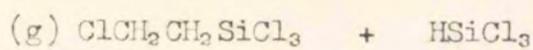
are shown in Table XXXII.

TABLE XXXII

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ in the presence of added olefinic products

T°C	p_0	$p_0\text{E}$	$p_0\text{VC}$	$10^4 k$	$k\text{E}/k$	$k\text{VC}/k$	Run
379.3	30.45	11.60	-	1.35	0.74	0.18	109
379.3	29.25	-	-	1.31	-	-	108
380.6	23.45	-	7.25	1.42	-	-	58
380.6	36.20	-	-	1.49	0.73	0.17	57

It appears therefore that the presence of these substances does not inhibit nor accelerate the reaction.



This reaction was carried out to substantiate the other evidence for the behaviour of trichlorosilane in the reaction scheme. When 2-chloroethyltrichlorosilane was decomposed in the presence of trichlorosilane the plot of $\log (p_0 - \Delta p)$ was not linear, see Figure 16, and the reaction obviously was complicated. The relevant data shown in Table XXXIII indicates that all the vinyl chloride has been used up and a substantial amount of ethylene converted into ethyltrichlorosilane. There seems little doubt that the action of trichlorosilane accounts for the decline of the experimentally determined over-all rate constant.

TABLE XXXIII

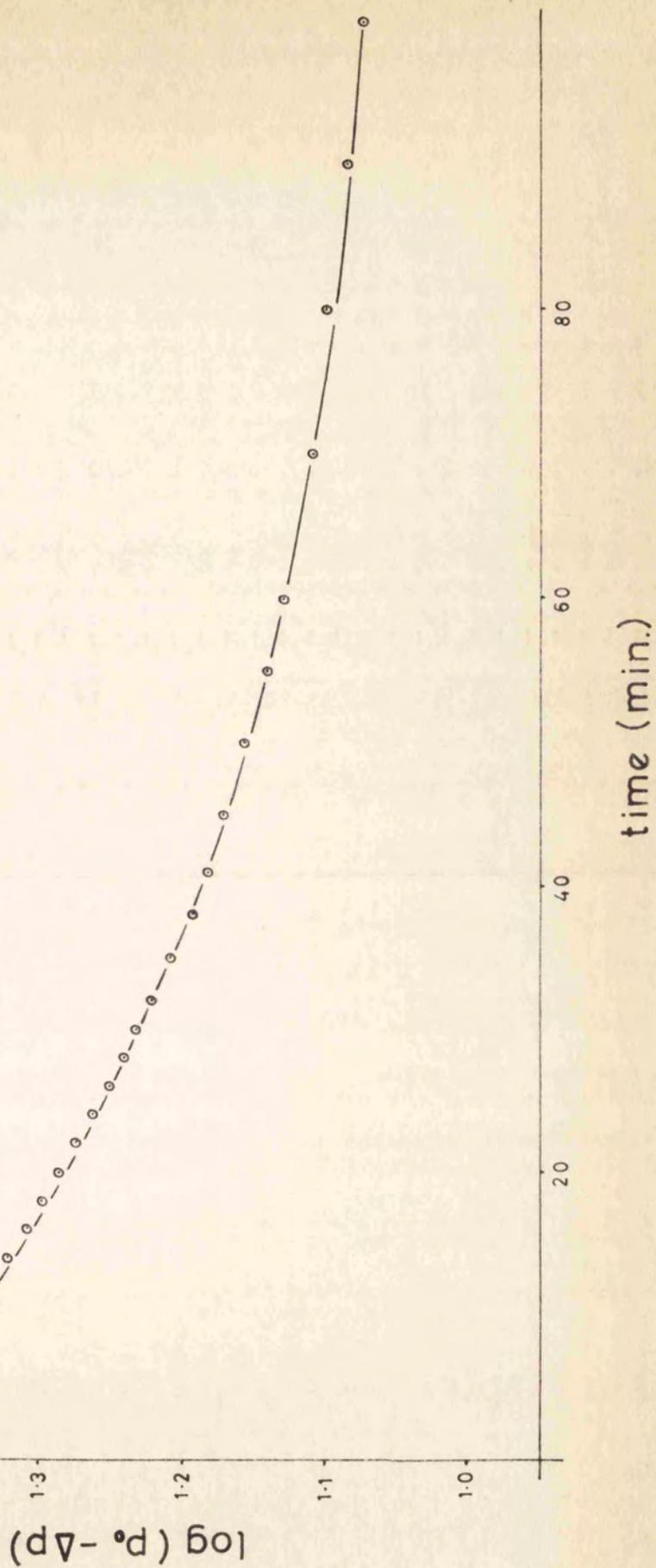
Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ in the presence of trichlorosilane

T°C	p_0	$p_0\text{HSiCl}_3$	p_{00}/p_0	%E	%VC	%V	%Et	Run
380.6	27.50	27.60	1.57	40	0	23	v. large	58A

PYROLYSIS OF $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ IN THE PRESENCE OF HSiCl_3

RUN 58A

FIGURE 16



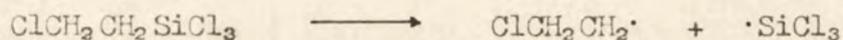
(C) MECHANISM OF THE REACTION

The evidence provided in the preceding pages gives a strong indication of the mechanism of decomposition of 2-chloroethyltrichlorosilane being molecular in nature. The slight rate acceleration in the presence of nitric oxide or cyclohexene is satisfactorily and adequately explained by the reactions of these substances with trichlorosilane. However, the other evidence against a radical mechanism will be discussed briefly followed by a discussion of possible ionic processes and a final discussion of what is considered to be the most probable course of reaction from the evidence obtained.

(i) RADICAL REACTIONS

(a) Initial dissociation of 2-chloroethyltrichlorosilane

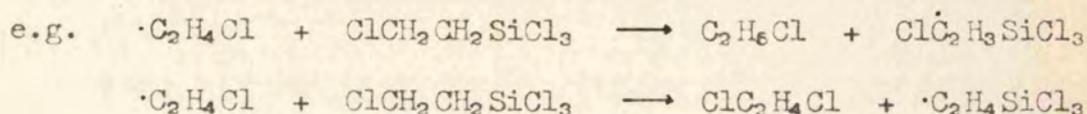
In the gas phase the 2-chloroethyltrichlorosilane molecule breaks at C-Cl and Si-C as expected from solvolysis experiments. The $-\text{SiCl}_3$ and C_2 structures are found intact in the products and there is no evidence for $-\text{SiCl}_2$ or C structures. Most recent dissociation energy studies show that Si-X bonds, where X is any group, are of about the same strength as C-X bonds.¹⁷³ Therefore the Si-C bond is probably stronger than the C-Cl bond, the latter having a dissociation energy of about 80 kcal./mole. The Si-C bond in $\text{C}_2\text{H}_5-\text{SiCl}_3$ has a dissociation energy of 95 kcal./mole and for the Si-Cl bond in SiCl_4 the value is 106 kcal./mole.¹⁷⁴ Hence the reaction:-



seems unlikely to occur and this

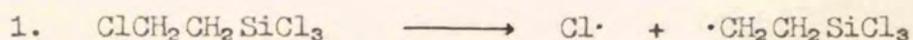
is borne out by the small effect of nitric oxide on the reaction rate

whereas trichlorosilane reacts rapidly with nitric oxide, probably by a chain process with SiCl_3 radicals as chain carriers. Although ClC_2H_4 radicals normally react bimolecularly¹⁷⁵ if they were formed in the pyrolysis of 2-chloroethyltrichlorosilane then they would be expected to react further with the original compound, this being more likely on concentration considerations at the beginning of a run.



Neither ethyl chloride nor 1,2-dichloroethane are found in the products. Chloroethyl radicals do not take part in the chain decomposition of 1,2-dichloroethane.¹⁷⁶

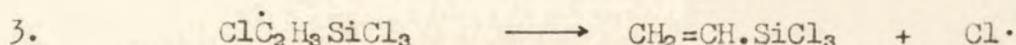
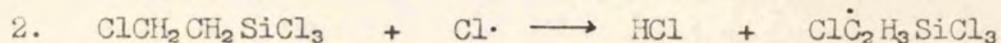
On dissociation energy considerations and since there is no chemical evidence for the homolysis of the Si-C bond then the only possible homolytic dissociation process for 2-chloroethyltrichlorosilane is:-



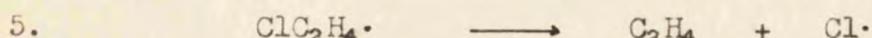
(b) Formation of products

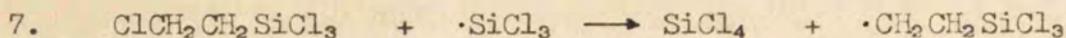
If the initiation step was 1. above then propagation of the reaction could reasonably be expected to follow the following scheme.

Formation of hydrogen chloride and vinyltrichlorosilane:

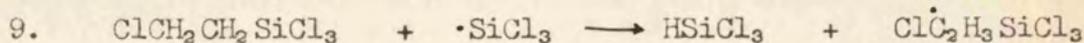


Formation of ethylene and silicon tetrachloride:

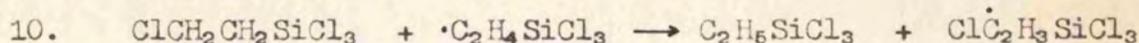




Formation of vinyl chloride and trichlorosilane:

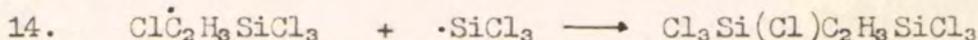
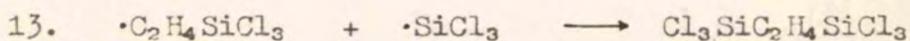
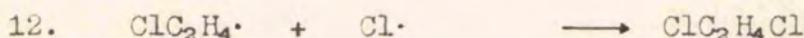
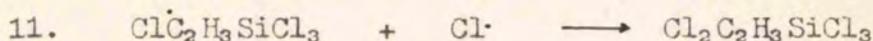


Formation of ethyltrichlorosilane:



Termination steps:

The pyrolysis of 2-chloroethyltrichlorosilane is kinetically first order, therefore the termination steps will involve the reaction between two unlike radicals and the following appear the most probable.



Considering these reactions then it would be expected that the rate of the reaction, k_3 , would be greater than k_6 and k_8 because of the C-Cl bond being the weakest bond. Also, since there are more hydrogen atoms available than chlorine atoms in the parent molecule, hydrogen abstraction would be a preferred reaction. Hence k_2 would be greater than k_4 and k_7 and also k_9 would be greater than k_7 .

In this case therefore one would expect that the predominant products would be hydrogen chloride and vinyltrichlorosilane, and that more dehydrosilylation products would be formed than ethylene and silicon tetrachloride. The most obvious objection to this scheme is that

vinyltrichlorosilane and hydrogen chloride are not the major reaction products but in fact ethylene and silicon tetrachloride account for more than 70% in the product analysis. Large quantities of dehydrochlorination products are produced in catalysed, benzoyl peroxide or chlorplatinic acid, reactions of 2-chloroalkylsilanes presumably by production of Cl radicals by the catalyst.

There are also some other points with respect to this reaction scheme which have to be considered.

(1) Although the limit of detection by the gas chromatography apparatus was about 0.01 mm., no indication was obtained for the presence of any of the products of the termination reactions.

(2) If the dissociation energy of the C-Cl bond in 2-chloroethyltrichlorosilane is about 80 kcal./mole then at the highest temperature used in this study, 417°C, k_1 would be approximately 10^{-12} sec.⁻¹ This might be expected to give rise to very long chains and be indicated by an induction period. No induction period was observed experimentally.

(3) Cyclohexene is known to inhibit reactions involving Cl radicals. Also nitric oxide would probably inhibit reactions involving SiCl₃ radicals. Nevertheless only the rate of formation of hydrogen chloride was increased by nitric oxide and this is explained by the reaction between trichlorosilane and nitric oxide.

(4) Will an α or a β radical be formed in reactions 2., 9. and 10.? For the formation of vinyltrichlorosilane the odd electron would have to reside on the α -position whereas to produce vinyl chloride it would reside on the β -position. It is not known whether an α - or a β - radical would be formed in this case although in addition of

trichlorosilane across vinylsilanes the odd electron is suggested to reside on the β -position.

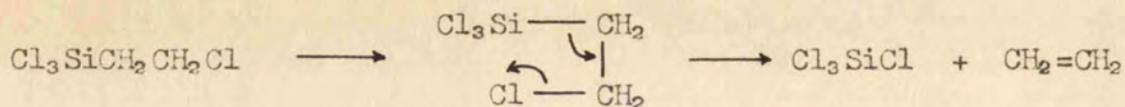
In view of the foregoing discussion it is apparent that the three simultaneous decomposition reactions of 2-chloroethyltrichlorosilane are molecular. The parent molecule possesses no bonds which are weak enough to be easily broken homolytically and therefore an intramolecular reaction becomes favourable energetically. Because of the large amount of energy required for homolysis of the C-Cl bond and the tendency for the silicon atom to attain a fractional positive charge leads to the strong possibility of "quasiheterolytic" processes and these will now be discussed.

(ii) IONIC PROCESSES

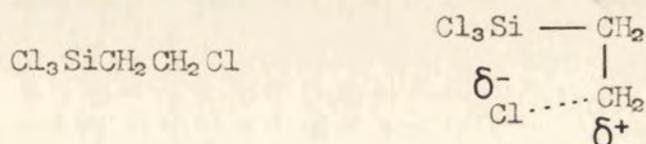
From the evidence presented in the preceding pages the reaction would conventionally be considered as molecular in nature. However, in view of the present-day ideas on similar reactions of alkyl halides and esters (see Chapter Two) and of the mechanism of solvolysis of 2-chloroethylsilanes (see Chapter One) some brief discussion of possible ionic or "quasiheterolytic" processes is necessary. Insufficient evidence is available from present investigations to make any definite conclusions in this respect but it does seem likely that further information on these compounds could indicate some heterolytic character considering the electron releasing capacity of silicon.

The possible processes, considering the main, ethylene elimination, reaction only, would be:-

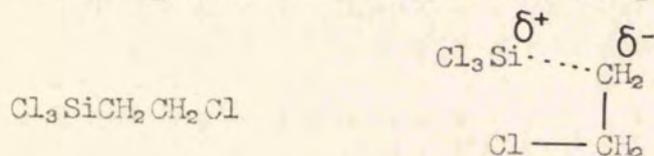
1. Intramolecular



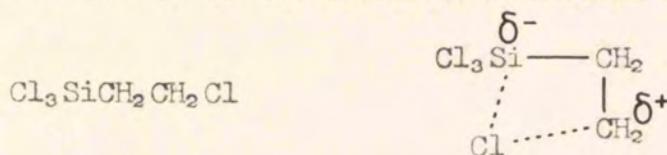
2. Breaking of the C-Cl bond exceeding Si-Cl bond formation



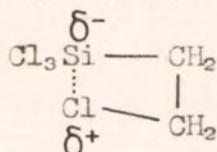
3. Breaking of the Si-C bond exceeding Si-Cl bond formation



4. Formation of the Si-Cl bond exceeds Si-C bond breaking



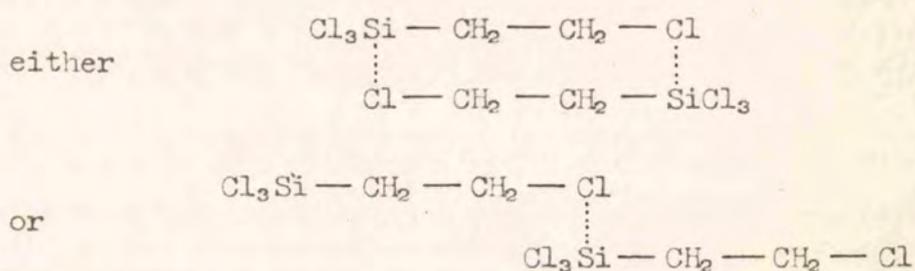
5. Formation of the Si-Cl bond exceeds both C-Cl and Si-C bond breaking



Although they cannot be rejected until further evidence is available it would seem that mechanisms 4. and 5. would be less likely to occur. The pyrolysis reaction of 2-chloroethylsilanes bears some resemblance to the neutral solvolysis of these compounds. However, when a pentacovalent intermediate does occur, in the solvolysis of silicon hydrides, then the function ρ^* is positive¹⁷⁷ and indicates that the electron density on silicon is opposite to that in the 2-chloroethylsilane pyrolysis. It would seem that a fractional positive charge would tend to reside on the silicon atom.

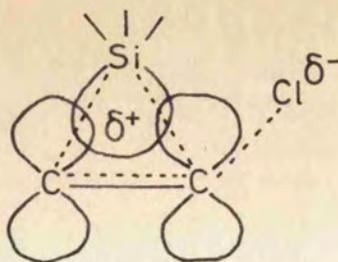
Mechanism 3. would be most unlikely because the weakest bond is the C-Cl bond.

Hence the most probable process involves either a concerted intramolecular reaction, 1., or a quasiheterolytic intermediate, 2., of similar structure to that proposed in the dehydrohalogenation of alkyl halides. Both mechanisms 1. and 2. would give rise to a negative entropy of activation as, apart from the degree of electrostatic character in the bonding, the transition states will be similar and more crowded than the parent molecule. Considerations of bond dissociation energies (see page 97) indicate that the C-Cl bond is the weakest linkage. Further evidence for this has been provided by Raman spectra. The C-Cl bonds possess a very high Raman frequency and intermolecular interaction between the Si and Cl atoms is indicated.^{178,179} Similar results showing intramolecular behaviour are obtained with γ -chloro-propyltrichlorosilane. In the liquid state the interaction appears to be bimolecular:

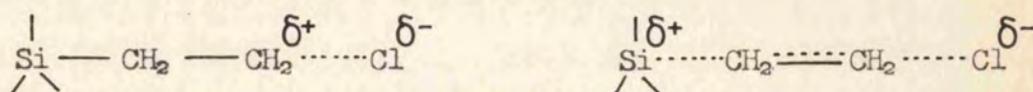


However a cis configuration of the single molecule in the vapour phase would be expected to give rise to the same interaction.

If the mechanism were as in 2. above then at some position on the reaction co-ordinate a structure of the type:



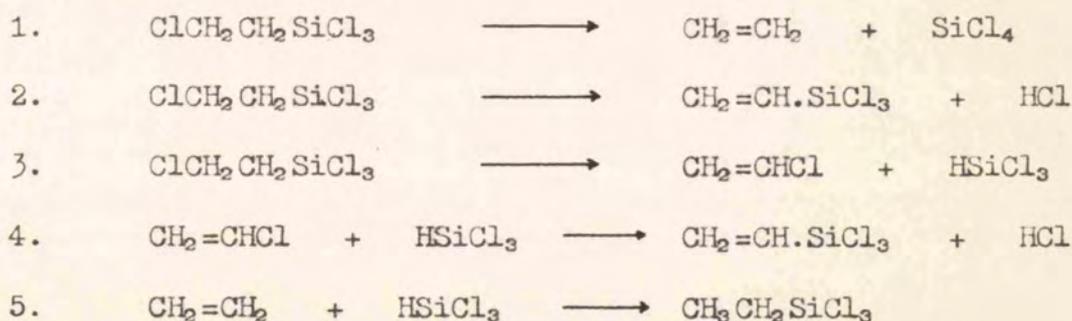
might occur in view of the tendency of silicon to obtain a fractional positive charge, by a type of hyperconjugation.



The large silicon sp^3 hybrid orbital would permit overlap with the developing p-orbitals of the carbon atoms and some contribution to the hybrid orbital may arise from the available d-orbitals of silicon.

(iii) MECHANISM OF THE PYROLYSIS OF 2-CHLOROETHYLTRICHLOROSILANE

From the results and discussion in this chapter it is apparent that the over-all process in the absence of nitric oxide or cyclohexene is:-



Using the following abbreviations for the concentrations of the various components, 2-chloroethyltrichlorosilane (β); ethylene (E); silicon tetrachloride (S); vinyl chloride (VC); trichlorosilane (HSiCl_3); vinyltrichlorosilane (V); hydrogen chloride (HCl) and ethyltrichlorosilane (Et), then the rate equations can be written:

$$- d(\beta)/dt = (k_1 + k_2 + k_3)(\beta)$$

$$d(E)/dt = k_1(\beta) - k_6(E)(\text{HSiCl}_3)$$

$$d(S)/dt = k_1(\beta)$$

$$d(V)/dt = d(\text{HCl})/dt = k_2(\beta) + k_4(\text{VC})(\text{HSiCl}_3)$$

$$d(\text{VC})/dt = k_3(\beta) - k_4(\text{VC})(\text{HSiCl}_3)$$

$$\begin{aligned} d(\text{HSiCl}_3)/dt &= k_3(\beta) - k_4(\text{VC})(\text{HSiCl}_3) - k_6(E)(\text{HSiCl}_3) \\ &= 0 \text{ at infinity} \end{aligned}$$

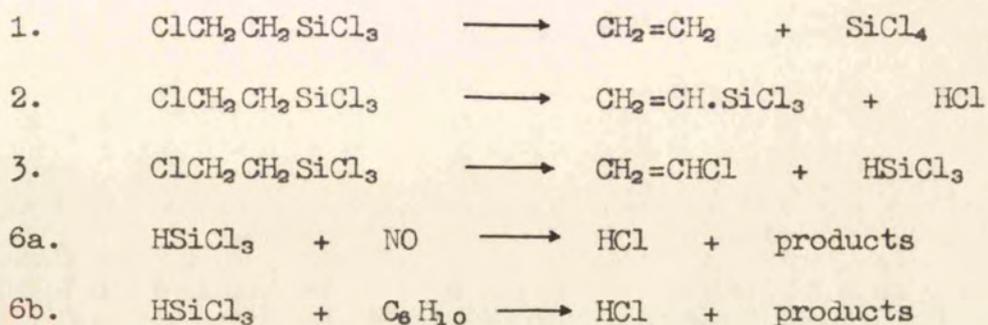
$$d(\text{Et})/dt = k_6(E)(\text{HSiCl}_3)$$

At infinity this requires that;

$$(S) - (E) = (\text{VC}) = (\text{Et})$$

but the analysis was not precise enough to permit accurate indication of this equality other than to suggest that it is not improbable.

In the presence of nitric oxide and cyclohexene the reaction scheme simplifies to:



and reactions 4. and 5. above do not occur. Therefore the rate equations,

using the additional abbreviation (In) for the concentration of nitric oxide or cyclohexene, become:

$$- d(\beta)/dt = (k_1 + k_2 + k_3)(\beta)$$

$$d(E)/dt = d(S)/dt = k_1(\beta)$$

$$d(V)/dt = k_2(\beta)$$

$$d(HCl)/dt = k_2(\beta) + k_6(HSiCl_3)(In)$$

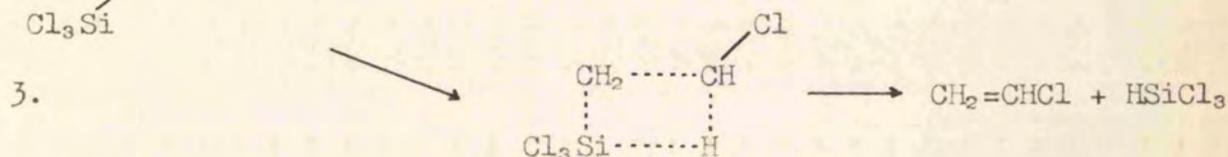
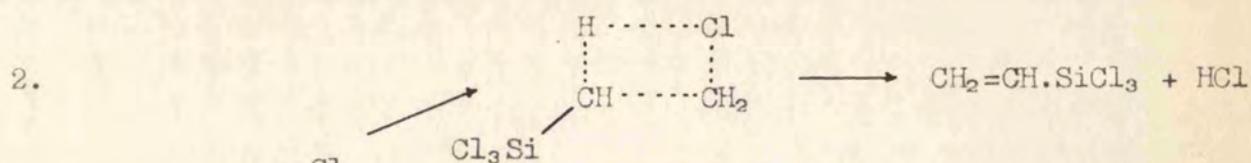
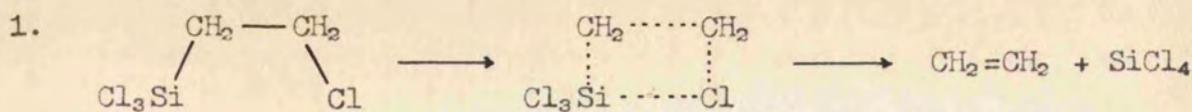
$$d(VC)/dt = k_3(\beta)$$

$$d(HSiCl_3)/dt = k_3(\beta) - k_6(HSiCl_3)(In)$$

The over-all reaction has a rate constant approximately equal to $10^{-4} \text{ sec.}^{-1}$ whereas reactions 4. and 5. have rates of approximately 10^{-5} and $10^{-6} \text{ mm.}^{-1} \text{ sec.}^{-1}$ respectively. Also reaction 6., which effectively removes any trichlorosilane, has a rate of approximately $10^{-3} \text{ mm.}^{-1} \text{ sec.}^{-1}$. Therefore the linear portion of the $\log(p_0 - \Delta p)$ versus time plot corresponds with the disappearance of 2-chloroethyltrichlorosilane by the simultaneous reactions 1., 2. and 3. and hence lend themselves to the kinetic treatment adopted in this work. Reaction 4. may not of necessity be a radical chain process and its inhibition by nitric oxide may be merely because of preferential reaction between trichlorosilane and nitric oxide, which may of course be radical or non-radical.

Cyclic transition states can be written for reaction 1., 2. and 3. and, in fact, 2. and 3. have as their origin the same configuration

of the 2-chloroethyltrichlorosilane molecule.



No variation in the rate of ethylene elimination was detected with temperature and therefore E_1 can be equated with the over-all activation energy. For the over-all reaction the Arrhenius equation is:-

$$k \text{ (sec.}^{-1}\text{)} = 10^{11.40 \pm 0.16} e^{-45,500 \pm 500/RT}$$

Hence if kE/k is taken as the average value of 0.72, and $E_1 = 45,500$ kcal/mole then:

$$k_1 \text{ (sec.}^{-1}\text{)} = 10^{11.26} e^{-45,500/RT}$$

The value of the A-factor is rather lower than the "normal" value for a unimolecular reaction and is indicative of a more crowded transition complex. This can arise with a four-centre transition state or intermediate. If the energy of activation, E_1 , is taken to be equal to the heat of activation, ΔH_1^\ddagger , then the entropy of activation, ΔS_1^\ddagger , can be

calculated.

$$k = \frac{RT}{Nh} e^{\frac{\Delta S^\ddagger}{R}} e^{-E/RT}$$

$$\text{therefore } A = \frac{RT}{Nh} e^{\frac{\Delta S^\ddagger}{R}} = 2.1 \times 10^{10} T. e^{\frac{\Delta S^\ddagger}{R}} \text{ sec.}^{-1}$$

This gives a value of $\Delta S_1^\ddagger = -8.0 \pm 0.7$ cal./deg./mole because of the low A-factor. This is a reasonable value for a cyclic transition state.¹⁸⁰

The results are not of sufficient accuracy to evaluate E_2 and E_3 but they will probably be 40 - 50 kcal./mole.

Under uninhibited conditions reactions 4 and 5 account for the experimental evidence that;

- (1) the concentrations of vinyl chloride and trichlorosilane pass through a maximum;
- (2) some vinyl chloride remains at infinity whereas no trichlorosilane remains;
- (3) the over-all rate of reaction decreases after ca. 60% reaction and the ratio of the final pressure, p_{∞} , to the initial pressure, p_0 , is less than 2.0.

In the presence of inhibitors reactions 4 and 5 do not occur and no ethyltrichlorosilane is observable in the products. The amounts of vinyltrichlorosilane and hydrogen chloride at infinity are reduced; the quantity of vinyltrichlorosilane removed being about 10 times the amount of ethyltrichlorosilane removed. This is in approximate agreement with the rate ratio k_4/k_5 found. Increase in the over-all rate of reaction may be explained by reaction 6 occurring with the formation of hydrogen chloride.

CHAPTER FIVE

STRUCTURAL CHANGES IN 2-CHLOROETHYLSILANES AND THEIR EFFECT

(A) THERMAL DECOMPOSITION OF 2-CHLOROETHYLDICHLOROETHYLSILANE¹⁸¹

Concurrent with the latter part of the work on 2-chloroethyl-trichlorosilane the gas phase pyrolysis of 2-chloroethyldichloroethylsilane was studied in an identical manner by Mr. C. J. L. Metcalfe in this laboratory.

One of the difficulties which occurred and which was not apparent in the study of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ was that on preparing to start a kinetic run, by heating up $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$ to 120°C in a bulb, some decomposition took place giving ethylene and an unidentified product (retention time 57 min.) of relatively low volatility. This substance was not ethyl-trichlorosilane (retention time 15.5 min.) nor the parent molecule (retention time 92 min.). This decomposition at the lower temperatures was not investigated because it did not occur at the higher temperatures, $356 - 397^\circ\text{C}$, used for pyrolysis and could be kept down to approximately 5% by the storage of the material under propene. Hence the majority of the work was carried out in the presence of this inhibitor although some results were obtained in its absence to establish that rate retardation or acceleration did not occur.

(i) THE OVER-ALL REACTION

Increase in pressure occurred on pyrolysis and the ratio of final to initial pressure was approximately 2.0 and varied rather less than in the study of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$; the variation for $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$ being

1.98 - 2.02. A plot of $\log(p_{\infty} - p)$ against time, where p is the experimentally measured total pressure at time t , was linear until about 80% decomposition and then declined. That is, linearity was maintained until a greater extent of reaction in the study of $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$. No change in rate constant was observed on changing the initial concentration at constant temperature and hence the over-all reaction was first order. Results obtained in the presence of propene are outlined in Table XXXIV.

TABLE XXXIV

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$ in the presence of propene

$T^{\circ}\text{C}$	P_0	$P_0 \text{C}_3\text{H}_6$	$10^4 k \text{ (sec.}^{-1}\text{)}$
356	41.40	32.65	1.05
356	53.60	28.1	1.10
366	32.65	63.2	2.29
366	11.65	27.25	2.06
367.5	35.80	34.1	2.02
376	38.40	43.5	3.83
376	23.80	48.0	3.76
376	24.00	48.7	3.75
376	49.00	50.0	3.66
386	27.90	50.1	6.85
386	28.80	47.8	6.80
386	18.25	38.75	6.80
386	44.55	89.75	6.60
386	7.55	34.05	7.10

TABLE XXXIV (continued)

T°C	P ₀	P ₀ C ₃ H ₆	10 ⁴ k (sec. ⁻¹)
391	36.75	47.5	8.81
391	9.10	35.8	8.45
391	34.40	54.0	8.96
391	19.55	35.85	9.01
396.5	26.50	40.85	12.05
396.5	24.85	35.55	12.59
396.5	8.40	24.7	12.92
396.5	61.75	86.0	11.62

As stated above some runs were carried out in the absence of propene and these are shown in Table XXXV.

TABLE XXXV

Pyrolysis of ClCH₂CH₂SiCl₂Et alone

T°C	P ₀	10 ⁴ k (sec. ⁻¹)
366	33.05	2.48
366	19.80	2.32
366	23.85	2.37
367.5	39.10	1.95
367.5	38.90	1.94
392	18.15	6.41 *
392	18.75	7.11 *
393	20.20	8.60

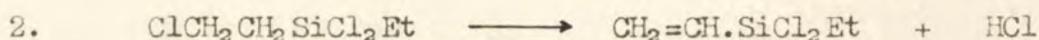
For the two runs marked with a * in Table XXXV the surface area to

volume ratio was increased substantially by the insertion of glass beads into the reaction vessel. Within experimental error, which unfortunately was rather large, no change in reaction rate was observed. These results were utilized in an Arrhenius plot of $\log k$ against $10^3/T^\circ\text{K}$ and this is shown in Figure 17. Because of the difficulties arising from the introduction of the parent substance in company with propene the gradient of the graph was not quite so certain as with $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ (Figure 7, page 63) and it is quite possible that the activation energies for the two decompositions are identical. However, the best line gives an Arrhenius equation for $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$ of:

$$k \text{ (sec.}^{-1} \text{)} = 10^{12.26 \pm 0.50} e^{-46,000 \pm 1,500/RT}$$

(ii) THE INDIVIDUAL REACTIONS

The products obtained in the pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$ were mainly ethylene and ethyltrichlorosilane with some hydrogen chloride and vinyl dichloroethylsilane. In some runs an extremely small quantity of vinyl chloride was detected. Analysis by gas chromatography showed that no other products were produced. After correction for the small quantity of ethylene present on injection into the reaction vessel, the final product analysis showed that reaction 1 accounted for 90% of the products

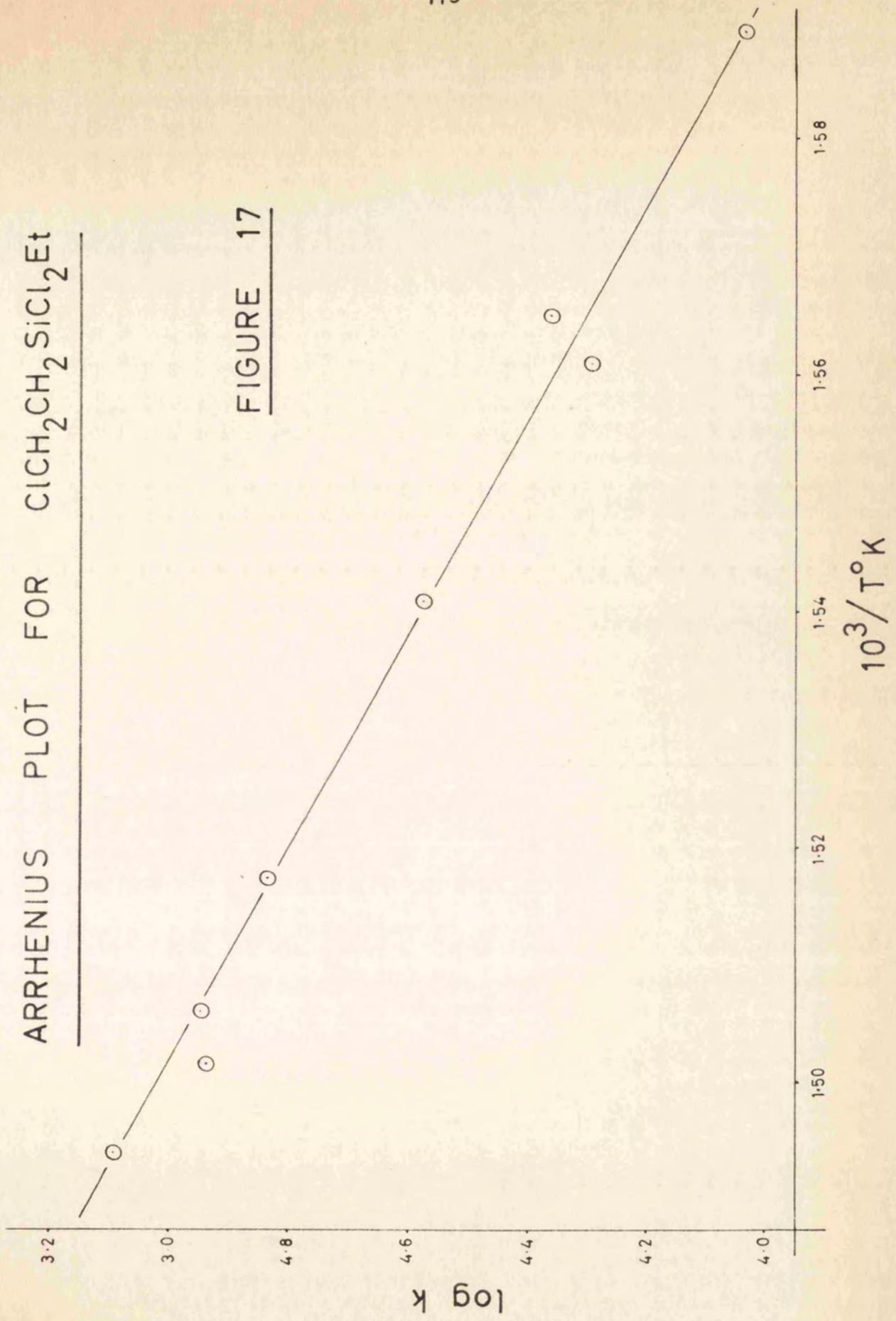


and that vinyl dichloroethylsilane, from reaction 2, accounted for half the remainder. The hydrogen chloride, although not analysed for, was shown to be present by thermal conductivity detection.

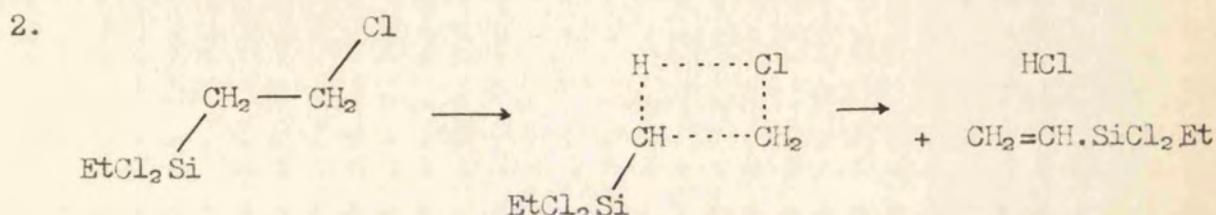
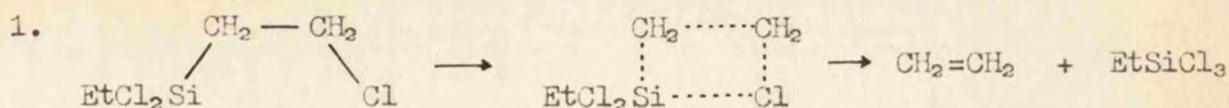
For the ethylene elimination and dehydrochlorination reactions

ARRHENIUS PLOT FOR $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$

FIGURE 17



possible four-centre transition states or intermediates can be suggested as for the same reactions in the pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$, see page 107.



(iii) COMPARISON OF $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ AND $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$

For the over-all decompositions the Arrhenius equations are:

$-\text{SiCl}_3 \quad k \text{ (sec.}^{-1} \text{)} = 10^{11.40} e^{-45,500/\text{RT}}$

$-\text{SiCl}_2\text{Et} \quad k \text{ (sec.}^{-1} \text{)} = 10^{12.26} e^{-46,500/\text{RT}}$

By equating the over-all activation energy with that of the ethylene elimination reactions, and taking these reactions to be 72% of over-all for the $-\text{SiCl}_3$ compound and 90% for the $-\text{SiCl}_2\text{Et}$ compound, the Arrhenius equations become:-

$-\text{SiCl}_3 \quad k_1 \text{ (sec.}^{-1} \text{)} = 10^{11.26} e^{-45,500/\text{RT}} \quad , \Delta S^\ddagger = -8 \text{ e.u.}$

$-\text{SiCl}_2\text{Et} \quad k_1 \text{ (sec.}^{-1} \text{)} = 10^{12.21} e^{-46,500/\text{RT}} \quad , \Delta S^\ddagger = -4 \text{ e.u.}$

As stated previously, page 108, one cannot accurately evaluate the Arrhenius parameters for the dehydrochlorination reaction.

The relation between the rate constants for ethylene elimination, k_1 , and dehydrochlorination, k_2 , can be obtained for the two decompositions.

$$\text{-SiCl}_3 \quad k_1 = \text{ca. } 5 k_2$$

$$\text{-SiCl}_2\text{Et} \quad k_1 = 9 k_2$$

From these rate ratios and the Arrhenius equations it is found that;

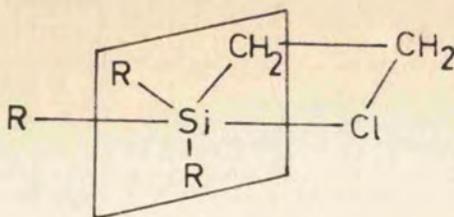
$$k_1 (\text{-SiCl}_2\text{Et}) = 4.5 k_1 (\text{-SiCl}_3)$$

$$k_2 (\text{-SiCl}_2\text{Et}) = 2.5 k_2 (\text{-SiCl}_3)$$

so that replacement of a Si - Cl linkage by Si - Et has the effect of increasing the rate of both reactions. Also, this substitution virtually eliminates the dehydrosilylation reaction. It would be expected that an ethyl group would increase the inductive electron releasing property of silicon and hence render the C - Cl bond weaker. Normally in substitutions of this kind the effect is shown by a decrease in the activation energy with the A-factor remaining effectively constant. However, in this case the rate acceleration on substitution may be steric because of the changes in entropy of activation and the approximately constant activation energy. For the $\text{-SiCl}_2\text{Et}$ compound less entropy is lost in going to the transition state. Whether this is a general state of affairs in 2-chloroethylsilanes or peculiar to this particular comparison can only be decided when more results are available.

The ethylene elimination may be similar to flank substitution in the structure of the intermediate¹⁸² in which case the ethyl group will be free to rotate whereas in the initial state there will be an

interaction between the $\text{ClCH}_2\text{CH}_2-$ and CH_3CH_2- groups.



In this case on going to the transition state one would have an entropy decrease with respect to the chloroethyl group and an increase in entropy with respect to the ethyl group. This could account for the smaller negative entropy of activation for the $-\text{SiCl}_2\text{Et}$ compound.

(B) COMPARISON OF $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$, $\text{ClCH}_2\text{CH}_2\text{SiCl}_2\text{Et}$, $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$
AND $\text{ClCH}_2\text{CH}_2\text{SiMe}_3$

The thermal decomposition of 2-chloroethyldimethylphenylsilane is discussed in the following chapter but because of the heterogeneous nature of the reaction no accurate kinetic results are available for comparison. A study of the pyrolysis of 2-chloroethyltrimethylsilane has been commenced,¹⁸³ although in this case also some difficulty is being experienced with heterogeneous behaviour. The rates of the overall reactions of these compounds would appear to be in the order;



as would be expected from the increasing electron supplying power of the substituents. The only definite conclusions at present available are the relative proportions of products, and hence the relative rates of the individual reactions occurring in each case. These are outlined in Table XXXVI.

TABLE XXVI

Product composition from the pyrolysis of various 2-chloroethylsilanes

Compound	-SiCl ₃	-SiCl ₂ Et	-SiMe ₂ Ph	-SiMe ₃
% ethylene elimination	72	90	99	99
% dehydrochlorination	12	10	0	0
% dehydrosilylation	16	0.1	0.5	-

It was unfortunate that the homogeneous decomposition of the -SiMe₂Ph compound could not be isolated. Improvements in the design of the apparatus may enable this to be done in which case the effect of substituents on the phenyl group and well removed from the reaction site will be most interesting.

CHAPTER SIX

THE GAS PHASE THERMAL DECOMPOSITION OF 2-CHLOROETHYLDIMETHYLPHENYLSILANE

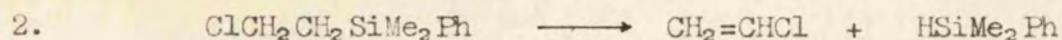
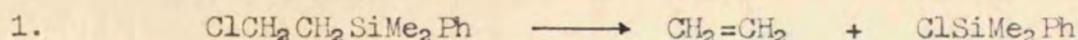
The pyrolysis apparatus had to be altered to enable study of this rather more involatile compound, the details of which are outlined in the experimental section following. Utilizing the heated metal injection valve, Figure 27, and O-ring seals it was found that substantial decomposition occurred prior to introduction into the reaction vessel. Also on removing the heating tape immediately beneath the valve and above the tap to the reaction vessel, see Figure 28, it was apparent that some decomposition was taking place there although experiments showed that it was not a "hot" or "cold" spot.

Later the method of introduction of the sample, in company with a small pressure of oxygen-free nitrogen, was achieved via a rubber serum cap and gas-tight syringe through the hole in the key of a heated vacuum tap. Using this method kinetic determinations could be carried out although at the temperatures used, 230 - 390°C, the reaction rate was generally very fast. The most effective way of plotting the data was by the Swinbourne method¹⁸⁴ as outlined on page 191. Although reasonably good first order rate plots were obtained, see Figure 18, the results at one particular temperature were inconsistent.

Analysis of the products of this reaction indicated that the reaction was almost completely ethylene elimination. This was found whether the parent molecule was substantially decomposed on introduction into the reaction vessel or not. Further analysis on the mass spectrometer did however indicate an extremely small quantity of

vinyl chloride. No hydrogen chloride was detectable in the products.

The reaction scheme therefore was, under all the experimental conditions:



where reaction 1 accounts for more than 99% of the over-all reaction. The presence of trace quantities of dimethylphenylsilane were inferred, not proved, as the quantity was too small to enable detection by gas chromatography and the molecular weight too high for it to be seen on the mass spectrometer.

(A) THE OVER-ALL REACTION

No determination of the rates of the individual reactions was necessary in this case, the quantity of ethylene being very close to the pressure increase in runs using the injection valve (where the parent substance was degassed before injection into the reaction vessel) and close to half the total pressure in runs using the syringe injection technique.

All the pyrolyses were carried out in a 428 ml. cylindrical reaction vessel with a surface to volume ratio of 0.78 cm^{-1} . For runs 24 - 37 inclusive sample injection was using the injection valve and for runs 38 - 101 the sample was introduced via a rubber serum cap. The results obtained are outlined in Tables XXXVII - XXXX and have been put in numerical order in this case because it appears to be important to indicate at what stage greasing of the taps was carried out. This information is included in the tables.

DECOMPOSITION OF $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$

TYPICAL RATE PLOTS

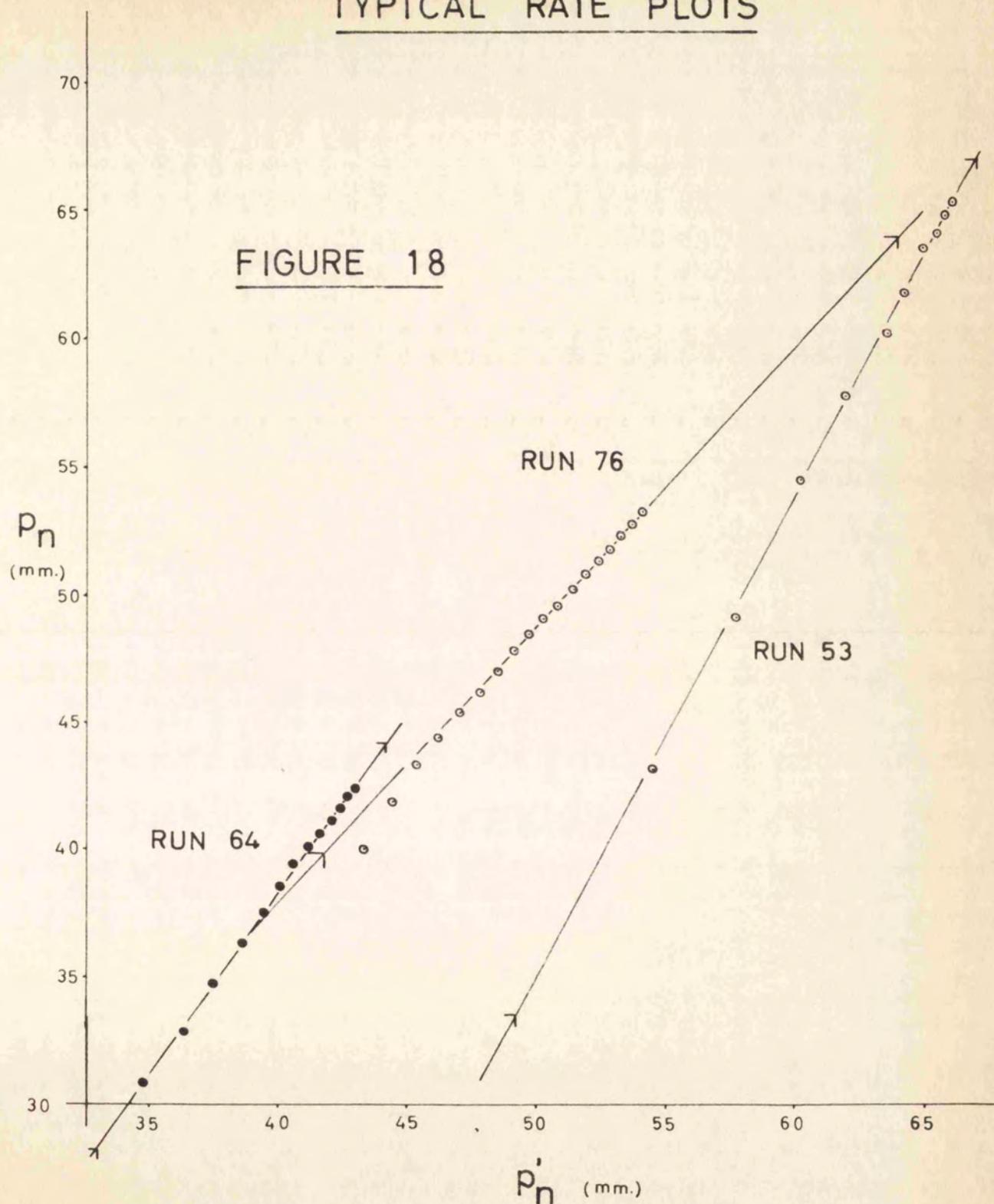


TABLE XXXVII

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ using valve injection

$T^\circ\text{C}$	p_0	p_{∞}/p_0	$10^4 k \text{ sec}^{-1}$	Run
302	36.70	-	4.07	24
302	26.60	-	3.65	25
302	33.60	2.00	5.53	26
302	28.10	-	5.07	27
321	31.00	1.99	6.69	28
Tap to the reaction vessel regreased				
321	32.80	-	3.07	29
321	31.00	-	3.84	30
321	11.2-	1.96	3.07	31
Tap to the reaction vessel regreased				
321	35.50	-	27.3	32
321	32.60	-	27.3	33
290	25.50	-	7.50	34
Tap to the reaction vessel regreased				
290	18.30	-	4.26	35
290	24.50	2.06	12.05(?)	36
290	53.50	-	12.80	37

The values of p_0 in Table XXXVII were obtained by extrapolation to zero time. For the remainder of the kinetic results the values of p_0 were obtained by subtraction of the value of p_0 obtained by a Swinbourne plot from p_{∞} obtained by the same procedure. All runs were carried out in the presence of some dry nitrogen and an approximate

allowance for this was made to obtain the pressure readings. The values of p_{∞} and p_0 quoted in the results section, together with the values of $p_{\infty} - p_0$, hence give some estimation of the extent of decomposition on introduction of the sample.

TABLE XXXVIII

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ using serum cap injection

All runs contain ca. 14 mm. of oxygen-free nitrogen

$T^{\circ}\text{C}$	$p_{\infty} - p_0$	$10^4 k \text{ sec.}^{-1}$	Line temp. $^{\circ}\text{C}$	Run
290	50.9	5.55	190	39
Tap to the reaction vessel regreased				
290	28.0	8.0	190	40
290	33.5	10.2	190	41
290	31.4	9.15	190	42
290	27.1	7.6	190	43
290	25.0	6.65	190	44
Tap greased				
270	37.3	15.0	190	45
270	32.8	8.35	190	46
270	42.5	10.0	175	47
270	33.6	7.6	175	48
270	27.2	6.2	165	49
270	37.5	9.8	205	50
253.5	38.0	9.7	205	51
Tap greased				
289.5	22.2	6.08	190	52

TABLE XXXVIII (continued)

T°C	P _∞ -P ₀	10 ⁴ k sec. ⁻¹	Line temp.°C	Run
289.5	33.5	10.6	190	53
289.5	31.2	11.3	190	54
289.5	34.2	9.05	190	55
266.5	39.4	9.75	205	56
266.5	28.3	9.45	205	58
266.5	29.6	7.65	205	59
250	17.0	11.7	205	60
Tap greased, furnace let down to atmos. with nitrogen				
250	22.4	29.2	205	61
250	23.75	20.5	205	62
320	22.75	40.0	205	63
320	15.95	29.4	205	64
The following run done in presence of 16.0 mm. C ₆ H ₁₀				
320	20.0	22.3	205	65
320	24.3	27.7	205	66
330	18.65	28.0	205	67
330	23.0	21.4	205	68
330	20.05	18.1	175	69
370	19.6	48.0	205	70
370	14.35	29.0	205	71
370	15.55	25.2	205	72
350	28.0	11.5	205	73

Tap greased, furnace let down to atmos. with nitrogen

TABLE XXXVIII (continued)

T°C	$P_{\infty}-P_0$	$10^4 k \text{ sec.}^{-1}$	Line temp.°C	Run
350	16.5	15.6	205	74
350	19.0	16.9	205	75
330	24.2	7.9	205	76
330	21.0	12.5	205	77
330	23.2	14.0	205	78
310	<u>ca.</u> 16.5	5.5	205	80
310	21.75	6.8	205	81
390	25.3	57.0	205	82
390	25.0	64.5	205	83
360	21.3	24.0	205	84
360	22.2	21.3	205	85
236.5	19.5	2.58	205	86
236.5	19.2	2.92	205	87
Tap greased, vessel let down to atmos. with nitrogen				
228.5	21.05	3.19	205	88
266.5	20.5	9.0	205	89

It will be noticed that there is no consistency in these results although each particular decomposition gave a reasonably good first order rate plot. However there is often an increase in the rate constant after regreasing the tap; the possible complications introduced by this are discussed on page 127.

Increase of the temperature of pyrolysis to the point where the

reaction velocity was high and only just measurable did not seem to remove what was undoubtedly a heterogeneous component. In accordance with this, if the results were plotted in the normal manner according to the Arrhenius equation then the spread of values was very large and any probable gradient gave rise to a smaller activation energy than would be expected at these temperatures and also a smaller value for the pre-exponential factor.

In view of these results a few rate determinations were made in the presence of a large amount of nitrogen and in one case, Run 94, air. If the reaction was indeed heterogeneous in the reaction vessel then this might have been expected to reduce the over-all reaction rate somewhat. The results are shown in Table XXXIX and, within a large experimental error, indicate that this did not seem to occur.

TABLE XXXIX

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ with added nitrogen or air, line temp. 205°C

$T^\circ\text{C}$	$p_{\infty} - p_0$	$10^4 k \text{ sec.}^{-1}$	p_0 added gas	Run
267	7.1	16.0	500 N_2	91
267	18.9	6.25	160 N_2	92
267	10.25	11.9	190 N_2	93
267	12.0	14.0	135 Air	94

Increase of the surface area to volume ratio from 0.78 to 2.74 cm.^{-1} and addition of cyclohexene inhibitor had very little effect on the over-all reaction rate. The results are shown in Table XXXX. An unsatisfactory complication was the necessity to open the reaction

vessel to air to insert the glass tubes for increasing the surface area to volume ratio.

TABLE XXXX

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ with added cyclohexene and increased S/V

T°C	$p_{\infty} - p_0$	$10^4 k \text{ sec.}^{-1}$	p_0 added gas	Run
268	7.30	11.3	-	95
268.5	9.35	17.8	-	96
268.5	13.3	19.4	32.0 C_6H_{10}	97
268.5	14.2	19.6	39.0 C_6H_{10}	98

The final experiments carried out on the thermal decomposition of 2-chloroethyldimethylphenylsilane involved sealing off the reaction vessel and carrying out three runs in the lines alone. These results are shown in Table XXXXI.

TABLE XXXXI

Pyrolysis of $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ in the heated lines

Line temp. °C	$p_{\infty} - p_0$	$10^4 k \text{ sec.}^{-1}$	Run
190 - 205	8.7	25.2	99
190 - 205	23.0	27.3	100
165 - 176	47.5	12.5	101

It can be seen by these results that the reaction is very fast, and incidentally still gives a good linear first order plot, at the relatively low temperatures of the lines. Also reduction of the line temperature reduces the rate of the reaction.

(B) POSSIBLE EXPLANATION OF HETEROGENEOUS BEHAVIOUR AND MEANS OF
STUDYING THE HOMOGENEOUS REACTION

From the results obtained it does seem as though the heterogeneous reaction occurs substantially, or possibly completely, in the heated lines connected to the reaction vessel. Also it is apparent that the products are identical from both homo- and hetero-geneous reactions. In view of the results obtained with increase in the surface area to volume ratio, added cyclohexene and added nitrogen it does not seem likely that radical reactions take place or that the reaction is to any appreciable extent heterogeneous in the reaction vessel itself. These tests would not prevent the heterogeneous reaction taking place uninhibited in the heated lines.

Various possibilities can be put forward in explanation of this behaviour. Oxygen may have some effect on the surface condition in this reaction since it involves an appreciably more "organic" substance. Letting down the system to atmospheric pressure with nitrogen is not entirely satisfactory as on removing the one stopcock for greasing there would be no restriction to oxygen entering the lines and the reaction vessel even though the time required for greasing the stopcock could be as short as one minute.

A more attractive explanation of the behaviour would involve the silicone high vacuum grease used for lubrication of the stopcock. Small quantities of silicone grease do find their way into the heated lines and this may provide an active surface for a heterogeneous reaction. The silicone grease is a methyl silicone polymer originating from the

three methylchlorosilanes. It also contains a small quantity of a silica aerogel. It would be most probable that 2-chloroethyldimethylphenylsilane would tend to dissolve in the grease and this may give rise to a heterogeneous component in the reaction.

Therefore to study the homogeneous thermal decomposition of this and similar compounds involves changes in the experimental apparatus. The most probable method would seem to be the complete exclusion of any grease, particularly silicone-based ones. Also all the apparatus would need to be maintained at the same temperature, including the section of the injection system in contact with the reaction vessel. One may in fact be able to achieve this using a metal valve. However, it has very recently been found¹⁸⁵ that the homogeneous thermal decomposition of 2-chloroethyltrimethylsilane can be studied if the reaction vessel is seasoned immediately after regreasing the taps.

Although analysis of the product mixture during a run would not be required in the study of 2-chloroethyldimethylphenylsilane as the reaction is essentially 100% ethylene elimination, difficulties in maintaining a sampling system at a high enough temperature could make the study of similar compounds where the product composition is not so straightforward a troublesome procedure.

CHAPTER SEVEN

EXPERIMENTAL REPORT

(A) PREPARATION AND/OR PURIFICATION OF COMPOUNDS

(i) 2-CHLOROETHYLTRICHLOROSILANE

This compound was prepared essentially by the method of Sommer and Whitmore.³⁶ In a 3 l. round bottomed flask equipped with an efficient condenser and conc. sulphuric acid bubblers 620 g. (3.8 mole) of ethyltrichlorosilane were reacted with 685 g. (5.0 mole) of sulphuryl chloride and 2.7 g. of benzoyl peroxide. The peroxide was added in portions over 30 hrs. and the mixture refluxed for a further 36 hrs. until evolution of HCl and SO₂ had virtually ceased. The sulphuryl chloride was distilled off on a steam bath using a Dufton column and the residue of ethyltrichlorosilane, 1- and 2-chloroethyltrichlorosilane and possibly some more highly chlorinated products was fractionated at 761 mm. Hg pressure. Fractionation of the required product was repeated at 40 - 41 mm. Hg. This gave 104 g. 1-chloroethyltrichlorosilane (0.525 mole), 14% yield, b₇₆₁ 136-9°C. Literature: b₇₃₄ 138°C. and 194 g. (0.98 mole) 26% yield of 2-chloroethyltrichlorosilane, b₇₆₁ 150-3°C, b₄₀₋₄₁ 66-7°C, Literature: b₇₃₄ 152°C.

The fractionated 2-chloroethyltrichlorosilane was transferred to an evacuated flask with a "tree" of break-seals attached and the degassed material was stored here before transfer to a container associated with the vacuum system.

(ii) CHLOROMETHYLDIMETHYLCHLOROSILANE

651 g. (6.0 mole) of trimethylchlorosilane and 405 g. (3.0 mole) of sulphuryl chloride were placed in a 3 l. round bottomed flask fitted with two condensers in series and the top of the condensers connected to a CaSO_4 drying tower and conc. H_2SO_4 bubblers. 2 g. of benzoyl peroxide were then added and the mixture gently refluxed. Further 2 g. additions of benzoyl peroxide were made after successive intervals of 15 hrs. The mixture was refluxed for a total of 70 hrs. until HCl and SO_2 were only being slowly evolved. The liquid was roughly distilled off leaving behind a dark brown fuming residue. Fractionation of the liquid gave unreacted trimethylchlorosilane, a large quantity of what was probably an azeotrope of trimethylchlorosilane and sulphuryl chloride, b_{760} 59 - 62°C, and 200 g. (1.41 mole), 24% yield of chloromethyl-dimethylchlorosilane. b_{760} 112 - 6°C. Literature¹⁸⁶ b_{760} 113 - 6°C.

(iii) CHLOROMETHYLDIMETHYLPHENYLSILANE

In a 1 l. round bottomed three-necked flask equipped with stirrer, dropping funnel and condenser, the tops of the dropping funnel and condenser being taken to conc. H_2SO_4 bubblers, phenyl magnesium bromide was made by addition of 78.5 g. (0.5 mole) bromobenzene to 15 g. (0.625 mole) magnesium in dry ether. The reaction was initiated with 1 ml. of 1,2-dibromoethane. After addition of all the bromobenzene the mixture was refluxed for 45 min. and allowed to stand overnight.

71.6 g. (0.5 mole) chloromethyldimethylchlorosilane in dry ether was coupled slowly with the above Grignard reagent, refluxed for 1 hr. and then hydrolysed with 5% NH_4Cl at 0-5°C. After extraction with ether, drying the ether over Na_2SO_4 and fractionation at reduced pressure

82.6 g. (0.45 mole), 90% yield of chloromethyldimethylphenylsilane was obtained. b_p 97-9°C, n_D^{25} 1.5190. Literature¹⁸⁷ b_{24} 121°, n_D^{25} 1.5186.

(iv) 2-HYDROXYETHYLDIMETHYLPHENYLSILANE

In a 3 l. round-bottomed three-necked flask equipped with stirrer, dropping funnel, condenser and conc. H_2SO_4 bubblers, 82.6 g. (0.45 mole) chloromethyldimethylphenylsilane was reacted with 15 g. (0.62 mole) magnesium in dry ether, the reaction being initiated with 1 ml. 1,2-dibromoethane. The temperature was maintained at about 30°C to ensure continuous reaction. After addition the mixture was refluxed for 2 hrs. and allowed to stand overnight.

The dropping funnel was replaced by a heated tube from a heated 250 ml. round-bottomed flask containing 30 g. paraformaldehyde (1.0 mole as formaldehyde). The formaldehyde was passed into the above Grignard reagent slowly over 1.5 hrs. with cooling of the reaction vessel in ice to control the vigorous reaction. After addition of the formaldehyde the heated tube was replaced by a stopper, the mixture refluxed for 4.5 hrs. and allowed to stand overnight.

The mixture was hydrolysed with 5% NH_4Cl and extracted with ether. The ethereal layer was washed with 10% KOH until free from formaldehyde (shown by Tollen's reagent), dried over K_2CO_3 and after removal of the ether the residue fractionated at reduced pressure. This gave 49.8 g. (0.28 mole), 62% yield of 2-hydroxyethyldimethylphenylsilane, b_{11} 126-8°C, n_D^{25} 1.5195.

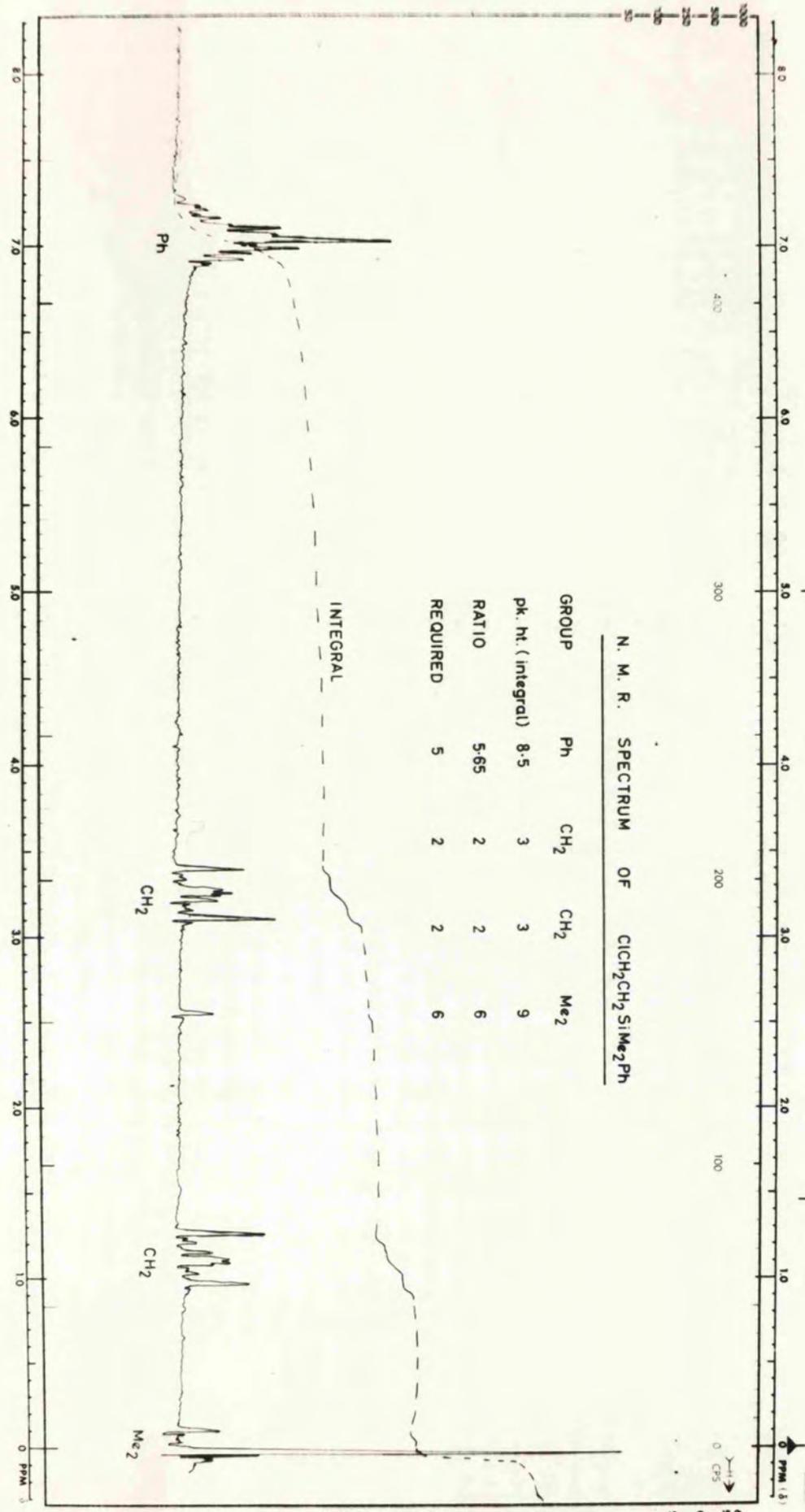
(v) 2-CHLOROETHYLDIMETHYLPHENYLSILANE

In a 250 ml. round-bottomed flask equipped with condenser and dropping funnel, 48.8 g. (0.41 mole) sulphuryl chloride was added dropwise to a mixture of 49.0 g. (0.272 mole) 2-hydroxyethyldimethylphenylsilane and 35.1 g. (0.272 mole) quinoline containing 0.5 g. quinoline hydrochloride. The mixture was cooled in ice during addition. Vigorous reaction gave a yellow solid which after addition of 50 ml. 40-60 pet.-ether and warming changed to a dark brown oil. The resulting oily liquid was transferred into Soxhlet thimbles and extracted with 40-60 pet.-ether. After removal of the ether and sulphuryl chloride the residue was fractionated at reduced pressure. This gave some dimethylphenylchlorosilane, b_{10} 72-6°C, 10 g. (0.06 mole). Literature¹⁸⁸ b_{15} 79°. and 33.9 g. (0.17 mole), 62% yield of 2-chloroethyldimethylphenylsilane, b_9 107-9°C, n_D^{25} 1.5182. Literature⁶⁰ b_3 85-90°C, n_D^{25} 1.5186.

The purity of this substance was determined by titration of the active β -chlorine atom with alkali. In agreement with the structure of the compound, the reaction was very slow and titration was better achieved by addition of excess alkali and back-titrating. This gave: %Cl = 17.30. Calculated for $ClCH_2CH_2SiMe_2Ph$, %Cl = 17.83.

(vi) ETHYLENE

1,2-dibromoethane in dry ether was added to Magnesium in ether using the normal Grignard procedure involving conc. H_2SO_4 bubblers and slow flushing of the system with oxygen-free nitrogen. The evolved gas was passed through an efficient condenser and traps at - 127°C , n-propanol, to remove ether and possibly vinyl bromide, and the ethylene condensed in a liquid nitrogen trap. Pumping and trap to trap distill-



-ation gave chromatographically pure ethylene which also gave the correct infra-red and mass spectrum.

Later a small cylinder of pure ethylene was obtained from I.C.I., Grangemouth. The pure ethylene was stored ready for use in a 5 l. bulb connected to the vacuum line.

(vii) PROPYLENE

Propylene was prepared from 1,2-dibromopropane and Magnesium by the same method as was used for ethylene. Less volatile materials were trapped out in ice-salt traps and the propylene condensed, with a small amount of ether, in a - 78°C, solid CO₂/ ethanol trap. It was purified by trap to trap distillation and the purity established by gas chromatography and mass spectrum. The pure material was stored in a 2 l. bulb.

(viii) VINYL CHLORIDE

12 g. of 1,2-dichloroethane were added to a solution of 30 g. potassium hydroxide in 200 ml. methanol at 60-70°C. High boiling fractions passing the condenser, MeOH and ClCH₂CH₂Cl, were collected in ice traps and the vinyl chloride in a - 78°C, solid CO₂/ethanol trap. The more volatile products, C₂H₄ and C₂H₂, were allowed to escape. After trap to trap distillation of the milky-white liquid on the vacuum system the colourless vinyl chloride gave one peak only on chromatographic analysis and possessed the correct infra-red and mass spectrum. The material was stored ready for use in a 2 l. bulb attached to the vacuum line.

(ix) SILICON TETRACHLORIDE

The commercial material was purified by trap to trap distillation on the vacuum system using "slush" baths at -63°C (chloroform) for the high boiling impurities, -127°C (n-propanol) to collect the silicon tetrachloride and liquid nitrogen to collect the HCl and other lower boiling compounds. Chromatographic analysis showed one peak only and the correct infra-red spectrum was obtained. The pure compound was stored in break-seal containers and a small quantity was transferred as required into a "carrot-shaped" flask attached to the vacuum apparatus.

(x) VINYLTRICHLOROSILANE

The commercial material was purified by trap to trap distillation using traps at 0°C (ice), -78°C (solid CO_2 /ethanol) and -196°C (liquid nitrogen). One peak only observed on chromatographic analysis and correct infra-red spectrum obtained. Pure material was stored in break-seal containers and a small quantity transferred as required into a "carrot-shaped" flask attached to the vacuum apparatus.

(xi) HYDROGEN CHLORIDE

Pure hydrogen chloride was obtained from Dr. J. D. Smith and it possessed the correct mass spectrum.

(xii) ETHYLTRICHLOROSILANE

A small quantity of commercially supplied material, purified by trap to trap distillation and giving a single chromatographic peak was provided by Mr. C. J. L. Metcalfe.

(xiii) TRICHLOROSILANE

The commercial material was fractionated by trap to trap distillation using a variety of "slush" baths. The usual temperatures were -63°C (chloroform), -127°C (n-propanol) and -196°C (liquid N_2). The purified material was found to give a broad peak, sometimes two peaks, on gas chromatographic analysis. It may possibly be that some disproportionation of the trichlorosilane occurs on the column packing. No kinetic determinations were hence possible on the rate of formation of trichlorosilane although its presence was indicated.

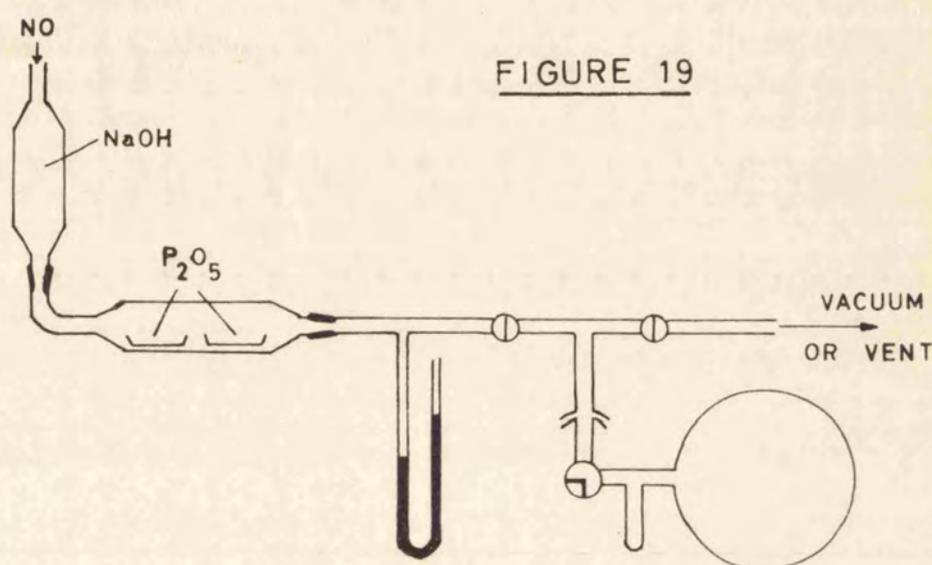
(xiv) NITRIC OXIDE

Attempted preparation by treatment of a mixture of potassium nitrite and potassium iodide solutions, after flushing out the system with oxygen-free nitrogen, with 50% sulphuric acid¹⁸⁹ was not successful. The evolved gas was bubbled through conc. H_2SO_4 and 50% KOH , passed over P_2O_5 and then frozen and pumped from liquid nitrogen. It was found that a blue solid condensed but gave rise to a brown vapour. It appeared from the fact that the blue solid volatilized at about 0°C that it was essentially N_2O_3 .

Nitric oxide prepared as above was passed into a cold concentrated solution of ferrous sulphate and the normal brown complex was obtained. On warming a gas was given off but it was impossible to obtain pure nitric oxide in any quantity.

Using the same preparative method as above with the inclusion of sodium hyposulphite solution in the bubblers at the beginning and end of the system gave a small quantity of nitric oxide but again the product was mainly N_2O_3 .

Nitric oxide was successfully prepared by the method of Blanchard¹⁹⁰ involving the reaction of acidified ferrous sulphate solution with sodium nitrite solution. To enable storage of the pure compound in an evacuated bulb a slight modification was made to the collection end of the apparatus, see Figure 19. The P_2O_5 was included to dry the nitric oxide. The bulb could be evacuated in situ. After



flushing out the apparatus with freshly generated nitric oxide small quantities could be removed into the bulb by control of the tap and observation of the manometer. The prepared nitric oxide was frozen with liquid nitrogen and pumped for a short time. Only one peak was observed on chromatographic analysis although the response was small. Later tests using the mass spectrometer showed that the only impurity was a very small quantity of nitrogen.

(xv) ETHYL CHLORIDE

The commercial material supplied for use as an anaesthetic by Hedley and Co., London was found, after degassing, to be pure chromatographically.

(xvi) CYCLOHEXENE

The commercial material was fractionated using a 4 ft. Vigreux column and after degassing was found to be pure chromatographically.

(B) APPARATUS

(i) FURNACE

This furnace was used for all but a very few runs and was a large one capable of taking up to a 5 l. spherical reaction vessel. The reaction vessel rested on an asbestos ring over an asbestos plate raised some 2 in. from the furnace floor. Surrounding the reaction vessel was an open-ended metal can with a slot cut in the side to allow the line from the vessel, the resistance thermometer and the thermocouple to pass through. Surrounding the can were placed 8 heating strips each with a resistance of 120 ohm. and another 2 identical heating strips were placed underneath the asbestos plate supporting the reaction vessel. The heaters were connected in series pairs and the resultant five pairs connected in parallel to give a combined resistance of 48 ohm. The connections were made with stout nickel wire and insulated with "fish spine" insulators. Surrounding the heaters was a 2 in. thick insulation of KIP 20-26 bricks, supplied by Kingscliffe Insulating Products Ltd., Sheffield, the design being such that two bricks occupied each face of the cube. The side and bottom bricks were cemented together but the top two bricks were left uncemented to enable access to the reaction vessel. The whole was then covered with a layer of asbestos board, the top piece being again easily removable. The final over-all dimensions of the furnace were ca. 18 in. square. The construction is shown diagrammatically in Figure 20. For use with the 5 l. reaction vessel in some of the early runs the metal can had to be removed.

FURNACE

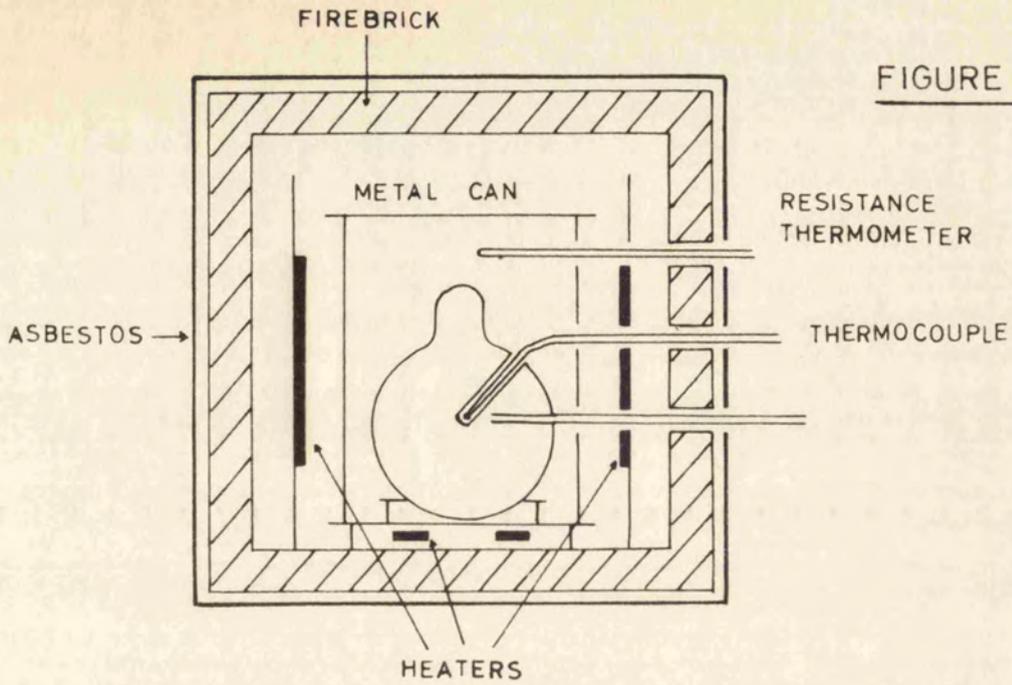


FIGURE 20

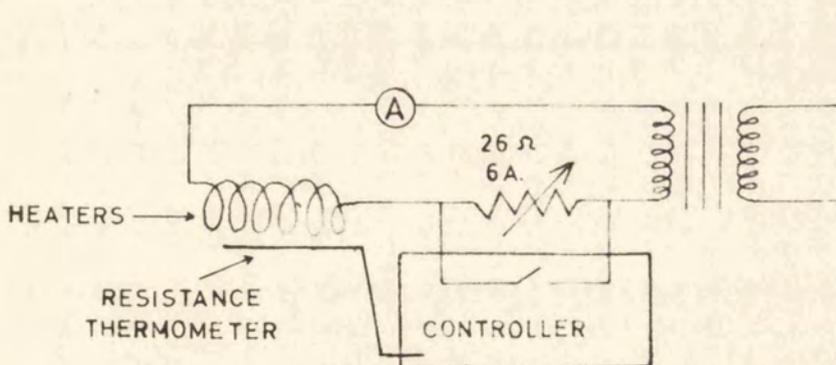


FIGURE 21

FURNACE CIRCUIT

Heating of the furnace was via a heavy duty Variac transformer and control was achieved by switching in and out a 26 ohm., 6 amp. resistance using a Sunvic R.T.2 on-off proportional controller incorporating a platinum resistance thermometer. The circuit diagram is shown in Figure 21.

Using reaction vessels up to a volume of 2 l. the temperature could be controlled to approximately 0.2°C and with the larger vessel control was to 1.0°C.

A few runs were carried out in a 500 ml. cylindrical vessel inserted in an electrically heated tubular aluminium furnace. This furnace was insulated with firebrick and the temperature controlled to 0.2°C by an identical controller to the above.

(ii) TEMPERATURE MEASUREMENT

The temperature of the reaction vessel was determined using chromel - alumel thermocouples, T1 and T2 as supplied by British-Driver-Harris, Manchester, and these were situated either in the pocket provided in the reaction vessel or else on the reaction vessel surface. For reaction vessel volumes up to 2 l. the temperature in the reaction zone was constant to about 0.2°C whereas for the larger vessel, when the metal can had to be removed, the temperature variation in the reaction zone was about 1°C. Each thermocouple used was calibrated periodically against a N.P.L. certificated platinum/ 13% rhodium-platinum thermocouple supplied by Johnson-Matthey Ltd. The temperature was therefore known accurately to about $\pm 1^\circ\text{C}$.

(iii) REACTION VESSELS

A number of "Pyrex" reaction vessels were used of nominal volumes 500 ml., 1500 ml., 2000 ml. and 5000 ml. The 500 ml. and 1500 ml. vessels were of design (1), as illustrated in Figure 22, the 2000 ml. and 5000 ml. vessels were of design (2) and the 500 ml. vessel was later modified to design (3). For designs (1) and (3) the thermocouple was stuck to the upper surface of the reaction vessel with asbestos paper while for design (2) the thermocouple was inserted in the pocket. No difference in temperature was detected for thermocouples placed either in the pocket or on the upper surface for the 2000 ml. vessel.

The actual dimensions of the reaction vessels used, the volume being determined by filling with water and weighing and the surface area by calculation, are given in Table XXXXII.

TABLE XXXXII

Dimensions of the reaction vessels

Nominal volume cc.	Actual volume cc.	Surface area cm. ²	S/V cm. ⁻¹
5000	5400	1497	0.28
2000	1944	744	0.38
1500	1510	634	0.42
500	428	332	0.78

In the study of 2-chloroethyltrichlorosilane the surface area to volume ratio of the 1510 ml. vessel was increased after Run 55 by the addition of 144 "Pyrex" glass tubes of length 10 cm., inside diameter 2 mm. and outside diameter 4 mm. The surface area per 10 cm. tube was

obtained by calculation neglecting the ends and the volume by displacement. Similarly the surface area to volume ratio of the 428 ml. flask was increased after Run 94 in the study of 2-chloroethyldimethylphenylsilane by the addition of 40 tubes identical to the above. The figures are shown in Table XXXVIII.

TABLE XXXVIII

Increase of surface area to volume ratio by addition of glass tubes

	Surface area cm. ²	Volume cc.
1 tube	18.8	0.8
Flask	634	1510
144 tubes	2705	115
Flask	332	428
40 tubes	752	32

Hence the new surface area to volume ratio of the 1510 ml. flask is 2.39 cm.^{-1} and that of the 428 ml. flask is 2.74 cm.^{-1}

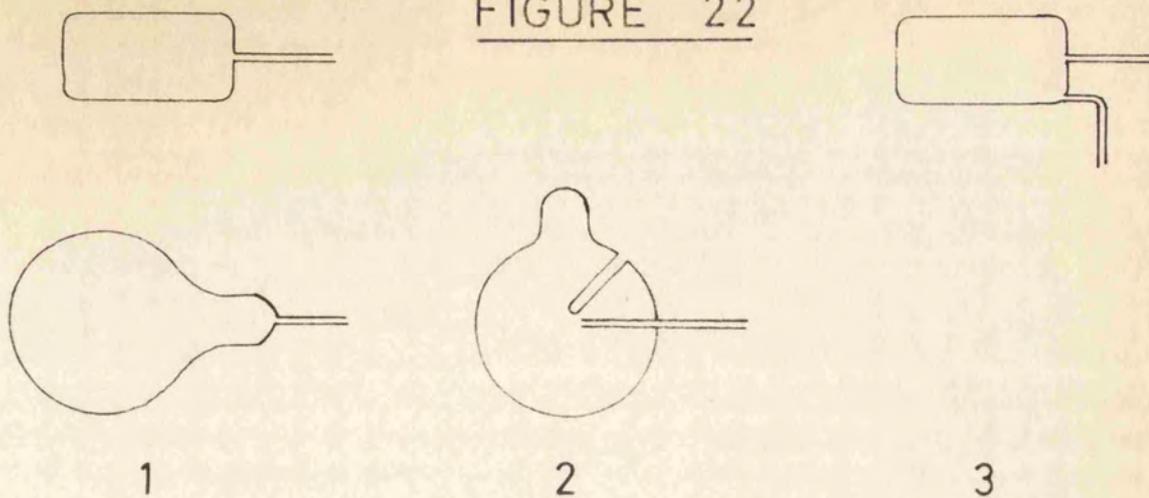
(iii) THE VACUUM SYSTEM

(a) The pumping system

The pumping section was of the conventional type including a by-pass for the mercury diffusion pump to enable rough evacuation using the rotary pump only. A backing volume of 2 l. was included so that the rotary pump could be turned off either if it was giving rise to excessive vibration or if the system was to be left unattended for some time. The rotary pump was a single stage Genevac, Type G.R.S.2.

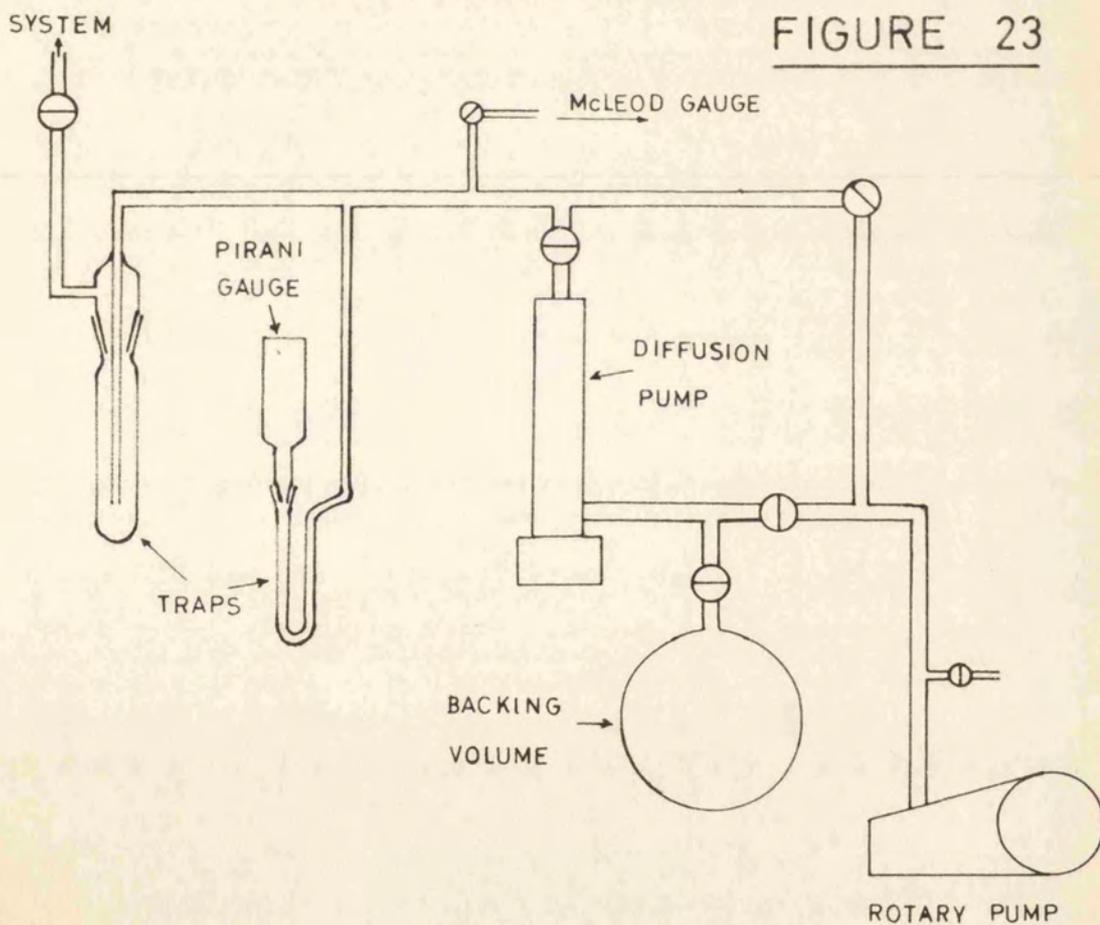
REACTION VESSELS

FIGURE 22



PUMPING SECTION

FIGURE 23



The mercury diffusion pump was made by Jencons, all glass, and heated by a bowl type electric fire element at 110 volt. Water for cooling the diffusion pump was made to flow through a polythene bucket which operated a microswitch to turn off the heating if the water pressure dropped below a certain level. The section was constructed out of 15 mm. diameter tubing and 15 mm. pump-type vacuum taps were used for the main line. All taps in this section were lubricated with "Soft" grade Edwards High Vacuum Ltd. grease. Also included in this section were a main trap, a subsidiary trap for the lead to the Pirani gauge head and a lead to a McLeod gauge. The pumping section is illustrated in Figure 23.

(b) Indication of vacuum

The apparatus and the ancillary equipment, see later, could normally be evacuated to 10^{-5} mm. Hg. Kinetic studies were only made when the pressure was less than 10^{-4} mm. Hg. Indication of vacuum was by means of a Pirani gauge, Edwards High Vacuum Ltd., for a continuous record and particularly useful when removing hydrogen carrier gas from the sample loop after chromatographic analysis. A McLeod gauge was also used intermittently. Both these pressure gauges were used for daily leak testing. The conventional Tesla coil was used for locating major leaks in the glassware.

(c) Reaction section

(1) For the study of 2-chloroethyltrichlorosilane

The reaction section underwent a number of modifications during the course of this work. Only the most important changes with respect to the section from which kinetic determinations were made will be

discussed.

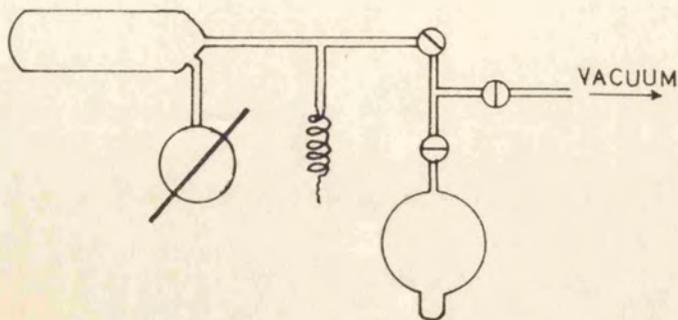
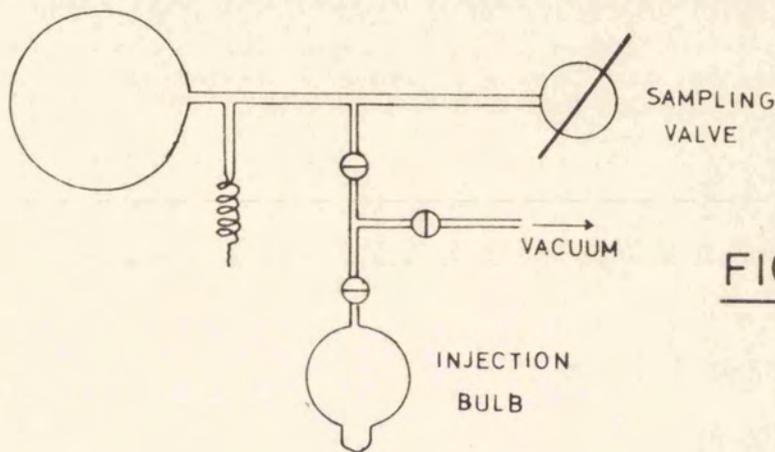
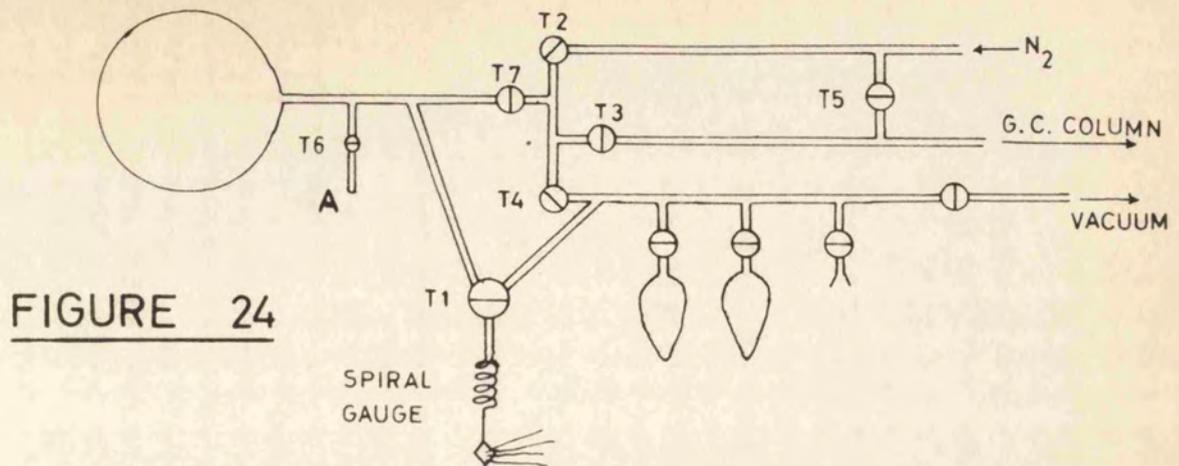
Figure 24 outlines schematically the original system. All the taps shown, with the exceptions of T1 and T6, were Springham diaphragm taps but it was found that the neoprene rubber (later Viton A) of the diaphragm became hardened by contact with chlorosilane vapours and eventually leaked. The taps were therefore replaced by ordinary vacuum taps and taps T2, T3, T4 and T5 by spring-loaded vacuum taps. Tap T1 was a two-way vacuum tap which was later removed, because of the marked tendency of this type of tap to leak after a short time, and the spiral gauge connected solely to the reaction vessel. Taps T6 and T7 were straight-through vacuum taps of 1 mm. and 2 mm. bore respectively.

Introduction of the sample to start a kinetic run was from the tube A into which a small quantity of degassed material had been frozen. The liquid was heated up in A with a cool flame and the tap T6 opened for a short time, ca. 10 sec. The method of removal of a sample was utilizing taps T2, T3, T4, T5 and T7 and is discussed with the chromatography apparatus. This method was used for some preliminary work and for runs 1 - 27.

After Run 27 a mild steel sampling valve¹⁵⁰ was incorporated; some corrosion occurred with this valve and after Run 43 a similar one made from stainless steel was introduced. Also at this time the method of injection of the 2-chloroethyltrichlorosilane was changed. Vapour was now introduced from a heated injection bulb, see Figure 25.

For the $-\text{SiCl}_3$ compound the final modification was to sample the reaction mixture via a separate line from the reaction vessel, see Figure 26.

REACTION SECTION FOR $-\text{SiCl}_3$ COMPOUND



Runs 118 - 125 were carried out on another apparatus very similar to Figure 25 except that the reaction vessel was a 500 ml. cylinder. Use of another apparatus was necessary because of changes made to the system to deal with the less volatile $-\text{SiMe}_2\text{Ph}$ compound, see below.

All vacuum taps in the reaction sections were lubricated with silicone high vacuum grease.

(2) For the study of 2-chloroethyldimethylphenylsilane

The system was originally as shown in Figure 26. However, decomposition of the starting material occurred before injection into the reaction vessel from the heated bulb. The system was therefore modified to include a metal valve, Figure 27, by means of which the sample could be injected as the liquid. The modified reaction section is shown in Figure 28. The liquid 2-chloroethyldimethylphenylsilane was introduced through the stopper, A, frozen into the small tube, B, with liquid nitrogen and degassed from there. Rotation of the valve through 180° allowed the liquid to pass into the reaction vessel.

Inconsistent kinetic results were obtained using this method of injection and, on removal of the heating tape, it appeared that some decomposition was occurring just below the injection valve and before the tap to the reaction vessel. The system was therefore modified so that the pure degassed material could be injected, in company with a small quantity of dry, oxygen-free nitrogen, via a serum cap using a Hamilton gas-tight hypodermic syringe. From the results obtained up to this stage it had been shown that decomposition of this compound yielded more than 99% conversion to ethylene and dimethylphenylchlorosilane and so

LIQUID INJECTION VALVE

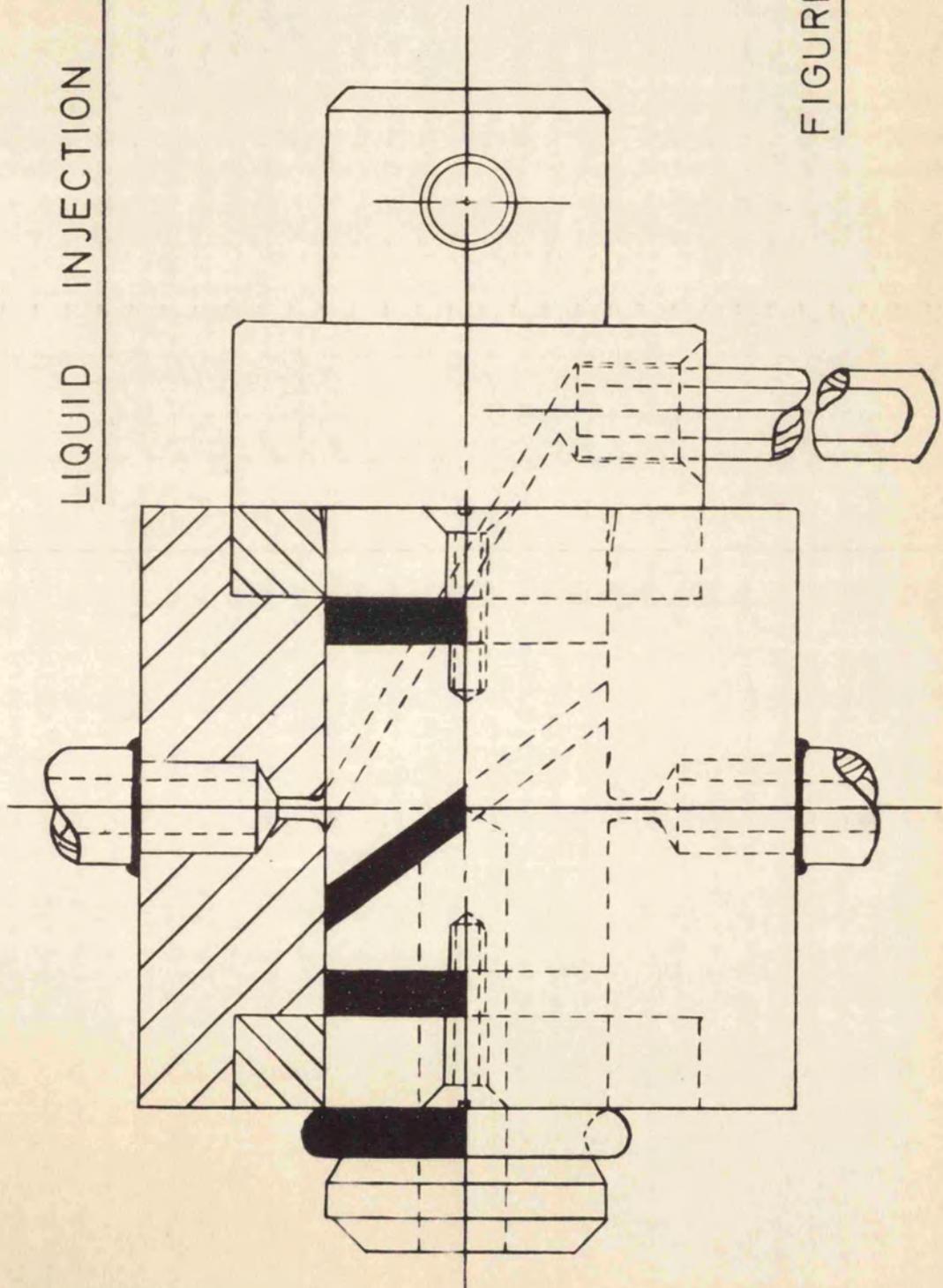


FIGURE 27

REACTION SECTION FOR SiMe_2Ph COMPOUND

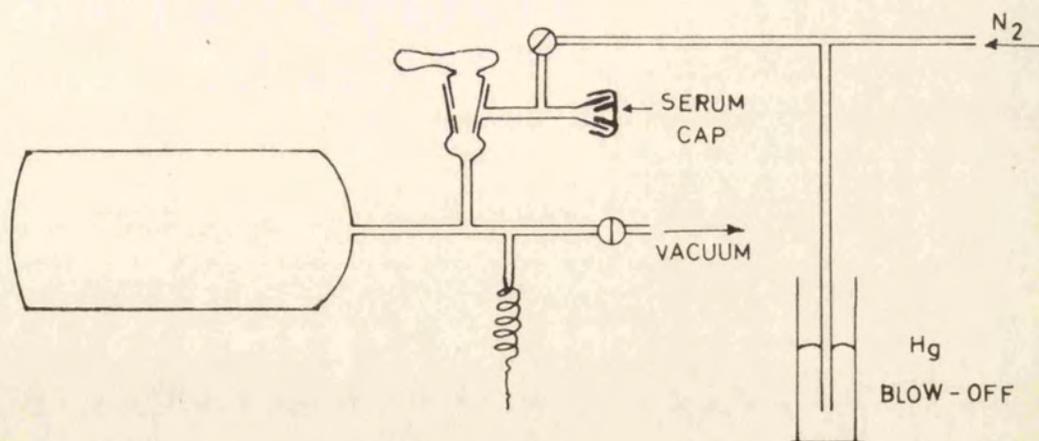
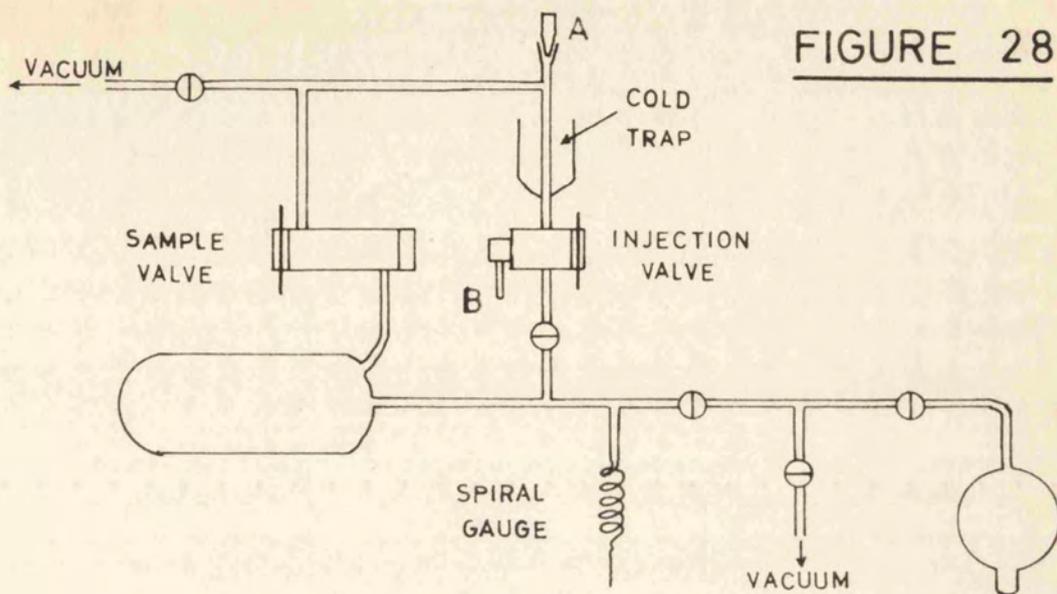


FIGURE 29

the sampling valve for gas chromatography and its associated line from the reaction vessel were removed. Figure 29 shows the final arrangement of the glassware which was used from Run 39 onwards in the study of the $-\text{SiMe}_2\text{Ph}$ compound.

As with the reaction section for study of the $-\text{SiCl}_3$ compound all taps were lubricated with silicone high vacuum grease.

(d) Heating

In all the reaction sections outlined above the lines outside the furnace were electrically heated. For certain sections "Electrothermal" glass-fibre insulated "Heat-by-the-Yard" was used, it being extremely easy to remove in order to make modifications or repairs to the glassware. However the "Heat-by-the-Yard" tended to overheat if wound round stopcocks because of overlapping and so "Vacrom" resistance wire was used wound over asbestos paper and insulated afterwards with a further layer of asbestos paper. The temperature of the lines connected to the reaction vessel and the spiral gauge was maintained at ca. 175°C in the study of the $-\text{SiCl}_3$ compound whereas the gas chromatography sampling valve was maintained at ca. 115°C , this being about the maximum temperature consistent with reasonable life of the butyl rubber O-rings used in the valve. For the study of the $-\text{SiMe}_2\text{Ph}$ compound the lines and spiral gauge were usually maintained at ca. 205°C .

Heating of the sampling valve and reaction section was achieved from Variac transformers whereas any other heated sections were supplied from a multi-tap transformer supplied by the London Transformer Co.

(iv) PRESSURE MEASUREMENT

A glass spiral manometer to which a small plane mirror had been attached (G. Springham Ltd.) and onto which the beam from a galvanometer lamp was shone was used for all this work. The spot reflected from the plane mirror was utilized in three ways to measure the pressure.

(a) The reflected light spot was aligned between two matched photo-cells connected to a spot galvanometer. Increase in pressure caused the glass spiral to twist and the spot was brought back to zero by admission of air into the vacuum jacket of the spiral gauge. The evacuated side of the spiral gauge accommodated a 2 l. bulb so that the null point could be obtained accurately and one arm of a n-butyl phthalate manometer. The pressure was determined by visual reading of the manometer and correction for the density difference between the ester and mercury. This method was changed after the preliminary runs .

(b) The reflected light spot was adjusted visually to a hair-line on a waxed glass slide by controlled admission of air. The pressure was measured on a mercury manometer using a cathetometer. This method was changed after Run 28.

(c) The reflected light spot was shone onto a calibrated curved screen of radius 1 metre situated 1 metre from the mirror. The calibration of the scale was found to be linear. For the spiral gauge used in the majority of runs the calibrations were 1 cm. = 1.63 mm. and later, when inserted in a rebuilt apparatus, 1 cm. = 1.59 mm.; the difference being due to the gauge not being exactly vertical. For some runs Mr. C.J.L.Metcalf's apparatus was used where 1 cm. = 3.41 mm.

(v) ANCILLARY VACUUM EQUIPMENT

(a) Vacuum fractionation unit

The unit is illustrated in Figure 30 and was used for the purification of materials for gas chromatography.

(b) Liquid containers

Large stocks of pure liquids were kept in break-seal containers either with one break-seal or with a "tree" of break-seals. Breakage was achieved by removing a magnet and hence allowing a glass covered iron rod to fall on the seal. On the vacuum apparatus small quantities of pure liquids were kept in "carrot-shaped" flasks of approximately 50 ml. or 100 ml. capacity. When containing liquids they were surrounded by a vacuum jar containing solid CO₂/ethanol to prevent removal of the grease from the stopcock.

Storage of pure 2-chloroethyldimethylphenylsilane under oxygen-free nitrogen for later runs was in a vessel of design A in Figure 31 from which samples could be withdrawn with a gas-tight hypodermic syringe.

(c) Gas containers

Stocks of the pure gases prepared or obtained and the mixtures of pure gases were kept in 2 l. flasks, ethylene was kept in a 5 l. flask, fixed to the vacuum apparatus, see Figure 31, (B), or else in transportable vacuum flasks, see Figure 31, (C), which were attached to the apparatus when required using ball and socket joints.

VACUUM FRACTIONATION UNIT

FIGURE 30

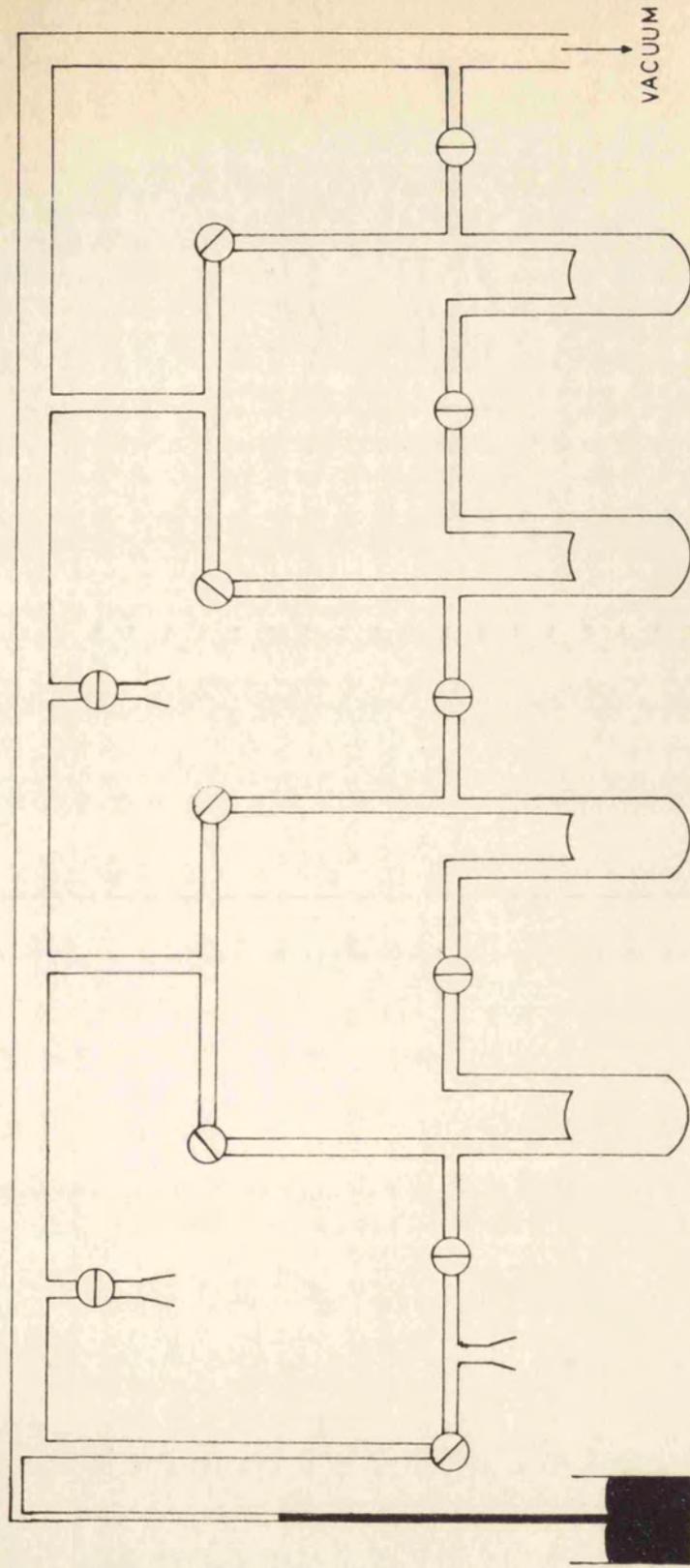
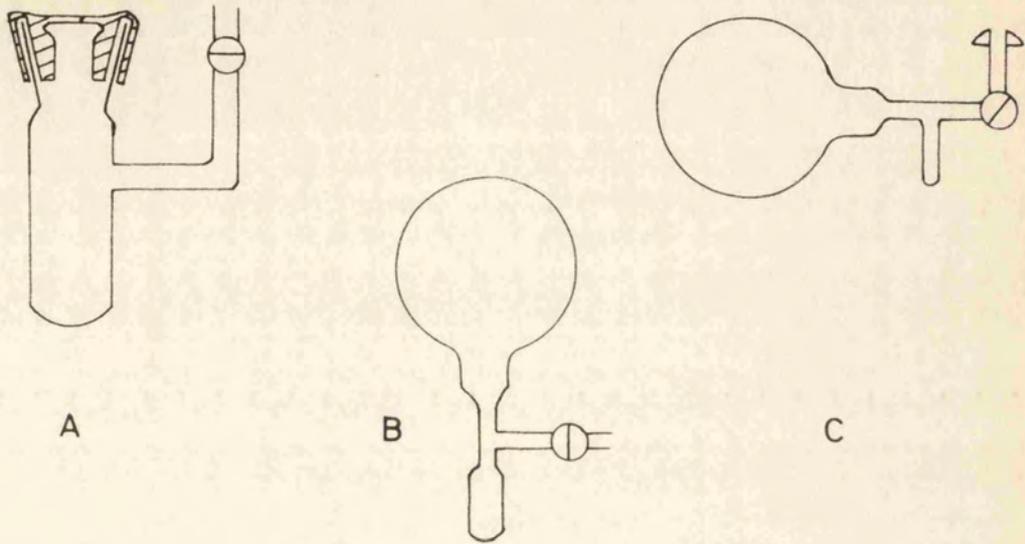
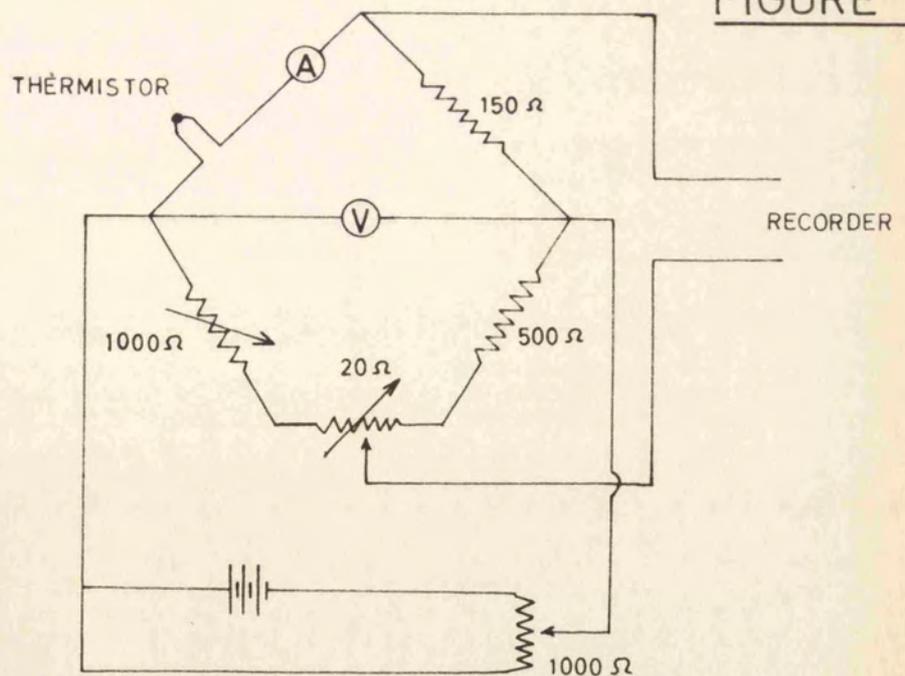


FIGURE 31



THERMISTOR CIRCUIT

FIGURE 32



(vi) CHROMATOGRAPHY APPARATUS

(a) Initial apparatus

The method of sampling was using the apparatus as described in Figure 24 via the short length of heated glass tubing between taps T2, T3, T4 and T7. The volume was varied from about 1 - 5 ml. either by using wider bore tubing or, for the smaller sample volume, by insertion of glass rod into the tubes. The sample volume could be filled from the reaction vessel using tap T7 and the sample passed from there into the column by opening tap T2, closing tap T5, and then opening tap T3. This sequence of manipulations was found to give least interference to the base line and more accurate analyses. The column was a "Pyrex" glass U-tube of internal diameter 3 mm. and length 200 cm. housed in a vapour jacket which was maintained at either 56°C (acetone vapour) or 110°C (toluene vapour). Nitrogen carrier gas was used at an inlet pressure of 12.8 cm. above atmospheric giving a flow rate of 20 ml./min. Detection was by a thermistor detector as one arm of a Wheatstone bridge circuit¹⁹¹ as shown in Figure 32. The bridge was operated at 2.67 volt., 10 mA. these conditions being on the flat portion of the characteristic current - voltage curve of the Stantel Type P23 thermistor used. The column was packed with 10% silicone oil on 44-60 mesh "Embacel" kieselguhr. Ethylene gave a small negative peak under these conditions and the carrier gas was therefore changed to hydrogen at 20 ml./min. The out of balance signal from the thermistor was fed to a Honeywell Brown potentiometric recorder into which was incorporated a range change switch. The retention times for ethylene, silicon tetrachloride and vinyltrichlorosilane were 4, 7 and 13 min. respectively.

(b) Changes in column length, packing, detector and sampling

As the study of this problem progressed it became obvious that the kinetic scheme for the decomposition of 2-chloroethyltrichlorosilane was not a simple one and it seemed likely that the crude method of analysis used might inadequately separate the reaction products.

(1) Column length

The 200 cm. U-tube column was changed for a more compact multiple U-tube glass column from Gas Chromatography Ltd. of length 280 cm. and internal diameter 3 mm. The column was later lengthened to 656 cm. In nearly every kinetic run the column was kept at 56°C by means of refluxing acetone.

(2) Stationary phase

It was thought that better separation of the components might be achieved by using a different stationary phase or support. The following packings were tried. (1) 1 cm. of 4A molecular sieve was inserted at the beginning of the column. There appeared to be no improvement on doing this. (2) 30-40 and 40-60 mesh activated alumina. The coarser alumina gave a reasonable ethylene peak with some tailing but only broad and indistinct peaks were obtained with SiCl_4 and $\text{CH}_2=\text{CH.SiCl}_3$ even after treatment of the packing with a large quantity of chlorosilane to remove surface held OH groups. Change of the packing to 1% silicone oil on 30-40 mesh activated alumina only improved the ethylene peak. (3) 5% silicone oil on 30-40 mesh firebrick gave no improvement on the results. (4) 10% tricresyl phosphate on "Embacel" kieselguhr and 10% liquid paraffin on "Embacel" gave reasonable separations but the peaks

were not as sharp as with the silicone oil packing even at different temperatures and carrier gas flow rates. (5) Separation has been achieved¹⁹² using a mixed stationary phase. However, using 60:20:100, diethylphthalate:silicone oil:kieselguhr; 20:20:100, dinonylphthalate:silicone oil:kieselguhr and 60:20:100, diethylsebacate:silicone oil:kieselguhr packings good separation could not be obtained and appreciable tailing occurred. (6) Similarly a 10% saturated solution of AgNO_3 in triethylene glycol on "Embacel" and 10% of a 10% solution of sodium caproate in silicone oil on "Embacel" did not improve on the analysis. (7) It appeared that the stationary phase originally chosen was the most efficient for quantitative analysis of the reaction mixture. A packing of 0.25% silicone stopcock grease on G.11 glass beads was very resistant to gas flow. 5% silicone oil and 20% silicone oil on "Embacel" were very little different from the original packing.

Hence it was decided to retain the packing for quantitative analysis as 10% silicone oil on 44-60 mesh "Embacel" kieselguhr.

(3) Detector

Detection was changed to a hydrogen flame ionization detector it being less sensitive to slight changes in flow rate and column temperature than the thermistor. A commercial detector involving a normal hypodermic needle and a gauze "collector" was first used but was found most unsatisfactory because of the deposition of silica on the gauze. After a number of tests it was found that platinum wire bent into a loop and situated above the flame and surrounding it was a satisfactory arrangement. The detector was made quite easily and at low cost, the only critical dimension being the distance of the loop from the needle for

maximum sensitivity with stability. The detector is shown in Figure 33. Hydrogen carrier gas was used. The flame ionization detector was very useful in that it did not give a signal for nitric oxide and hydrogen chloride, rarely gave a signal for trichlorosilane and only gave a weak inconsistent signal with silicon tetrachloride (an interesting phenomenon) and hence the chromatogram was clarified appreciably. Later when it was desired to follow these inorganic materials the thermistor detector was reinserted in series with the flame ionization detector. The signal from the thermistor was relayed to a spot galvanometer. Amplification of the signal from the flame ionization detector was using a Gas Chromatography Ltd. amplifier and recorded on a 0-1 mV. Honeywell Brown potentiometric recorder. Later an amplifier giving greater stability and constructed by Mr. J. A. Brivati of this department was substituted.

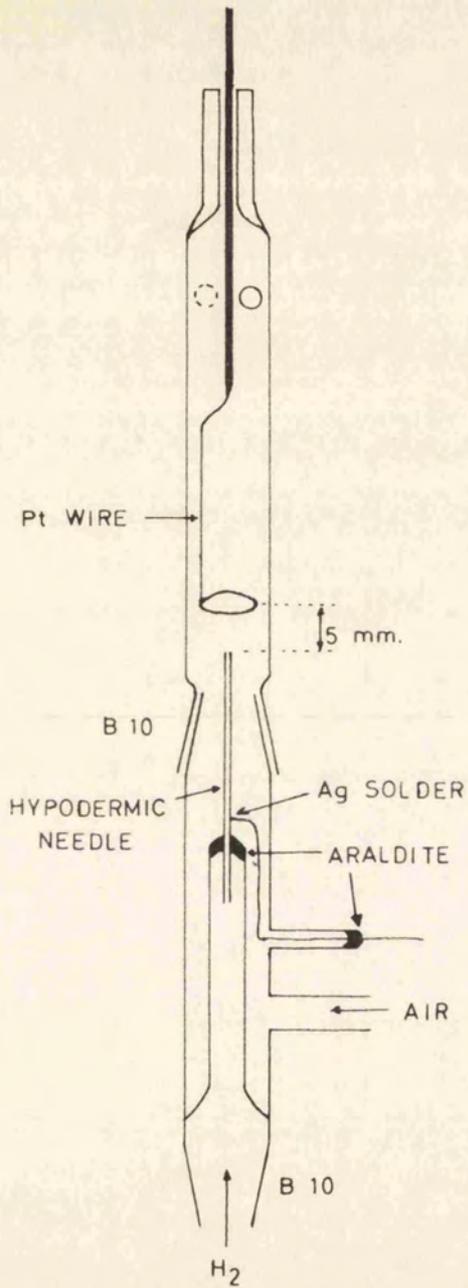
Because of the high sensitivity of the thermal conductivity detector to silicon tetrachloride and the low sensitivity to ethylene and the opposite effect observed on flame ionization detection it was possible to measure the rates of formation of these two compounds quite accurately, probably to better than $\pm 10\%$.

(4) Sampling of the reaction mixture

The method of sampling was changed to include a gas sampling valve modified in only minor details from that of Pratt and Purnell.¹⁵⁰ The valves used, three in all, were constructed by Mr. C. Masters of this department. The first valve was constructed out of mild steel but some corrosion occurred. This was replaced by one of stainless steel construction. Quite a lot of trouble was incurred with this valve because

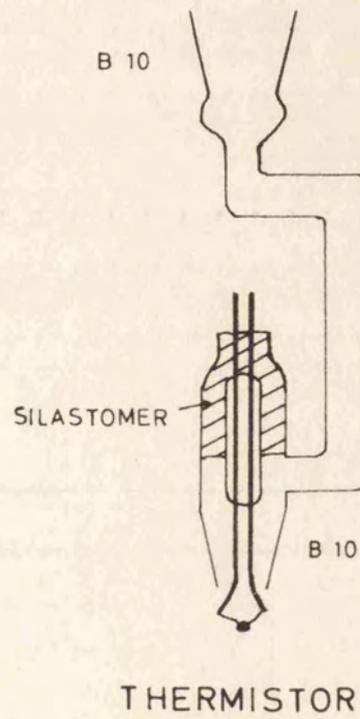
DETECTORS

FIGURE 33



HYDROGEN FLAME
IONIZATION

FIGURE 34



THERMISTOR

of the notorious property of stainless steel to "pick up" when two surfaces are in contact. This property led to scratching on replacing the rubber O-rings and caused leaking. Finally a third valve in stainless steel was constructed as shown in Figure 35 with facility for interchangeable sampling loops.

Before deciding which rubber O-rings to use in the sampling valve samples of butyl rubber, resin-cured butyl rubber, Viton A and fluorosilicone rubber were obtained from Dowty Seals Ltd. and subjected to a number of simple tests to indicate any change in properties on tension and compression at 120°C and also on treatment in an evacuated flask with ca. 560 mm. of the reaction products at 120°C for 10 days. Also tested in the same way were two samples of medium and high acrylonitrile base perbunan rubber. The perbunan rubbers became very brittle on contact with the hot vapours and were discounted. Of the remainder the fluorosilicone rubber became even weaker mechanically. All the rubbers gained weight, 3 - 6%, on treatment with the product mixture but this gain in weight could not be removed by evacuation. The resin cured butyl rubber became brittle. There was little to choose between the Viton A and butyl rubber and the latter were therefore used on the grounds of cost. They were of type VOR 118.

The sample volume used was normally of 2 ml. capacity although for some runs sample volumes of 2.5 ml. and 8 ml. were used. Heating of the valve was by external windings and the temperature was recorded by thermometers placed in the key and on the external surface.

To facilitate insertion and withdrawal of the key it was very lightly lubricated on the end O-rings with a trace of silicone high vacuum grease and to restrict "picking up" of the stainless steel the

SAMPLING VALVE

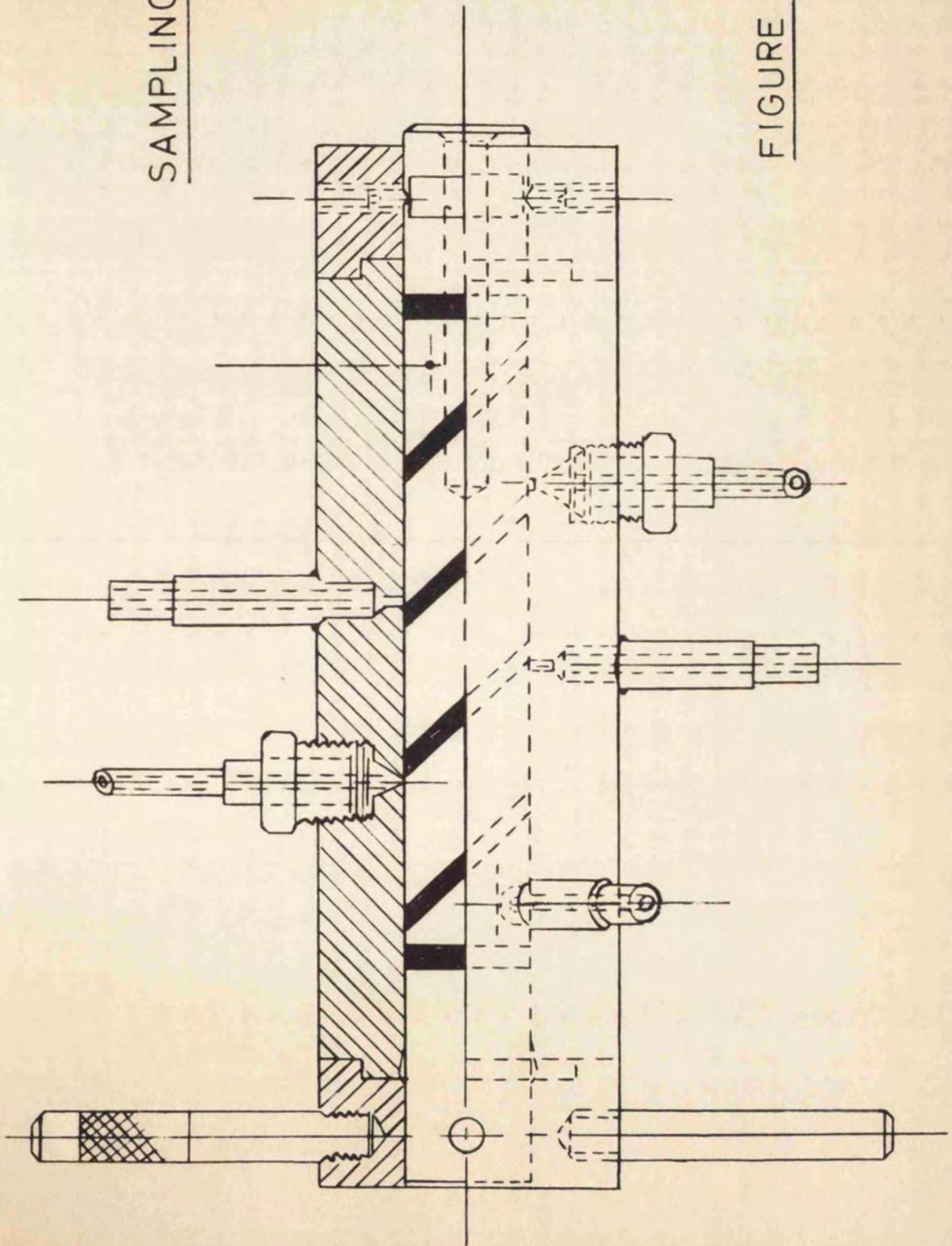
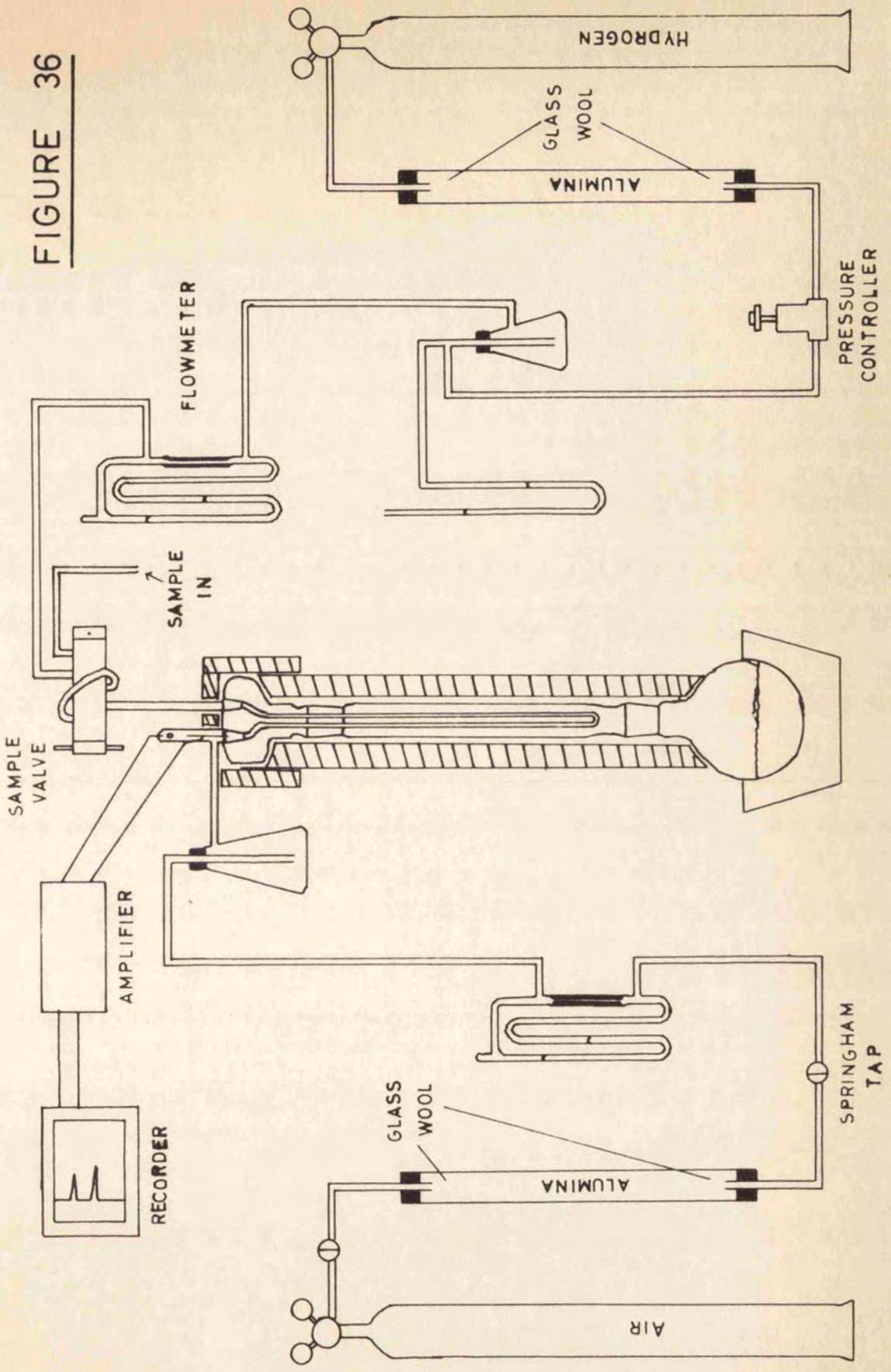


FIGURE 35

FLOW DIAGRAM OF CHROMATOGRAPHY SYSTEM

FIGURE 36



ends of the barrel were covered with a thin film of graphite grease. Later models from the ones used in this work had a copper insert fitted into the ends of the barrel.

By observation of the Pirani gauge after pumping out of the sample loop it was found that ca. 1 min. was required to ensure a pressure of less than 10^{-3} mm. Hg in the sample loop.

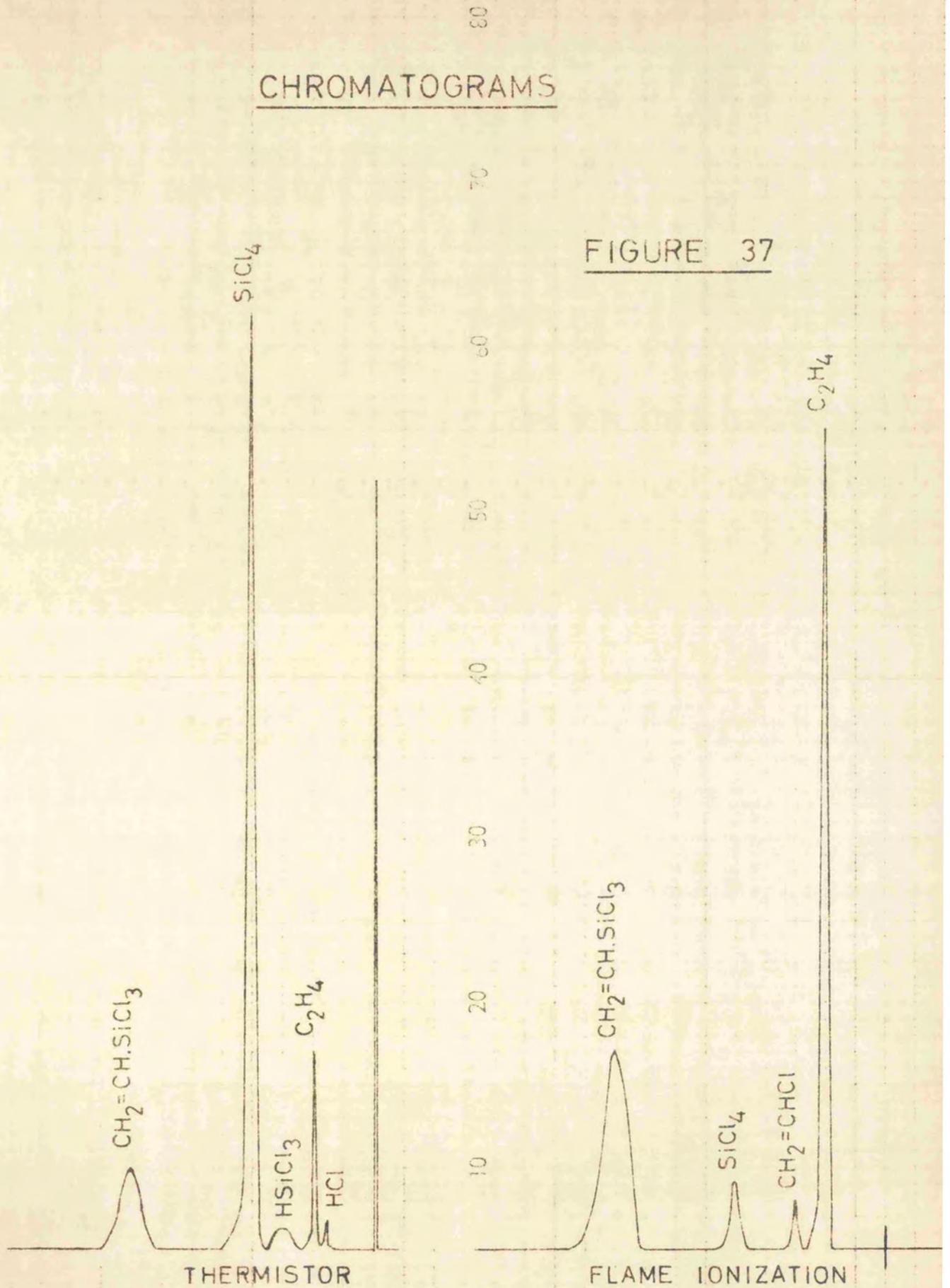
(c) Final apparatus

The arrangement of the gas chromatography apparatus and its ancillary equipment is shown in Figure 36. The normal experimental working conditions were:- 10% silicone oil on 44-60 mesh "Embacel" kieselguhr in a "Pyrex" glass column of dimensions 656 cm. x 3 mm. at a temperature of 56°C. Hydrogen carrier gas at an inlet pressure of 30 cm. above atmospheric giving a flow rate of 40 ml./min. The flow rate of air was 250 ml./min. and the rates of flow of both gases were determined by capillary and/or soap bubble flowmeters. The working voltage of the ionization detector was 400 volt. with the needle positive and the platinum loop negative.

Under these conditions the retention times for the various components were: ethylene 2 min., vinyl chloride 3 min., silicon tetrachloride (irreproducible) 5 min., vinyltrichlorosilane 9 min., cyclohexene 9 min., ethyltrichlorosilane 11 min., and 2-chloroethyltrichlorosilane ca. 55 min. With the thermal conductivity detector nitric oxide and hydrogen chloride gave small responses at 1.5 min. and 1.75 min. respectively whereas trichlorosilane gave a rather broad peak with the apex at about 4 min. A typical chromatogram obtained with the flame ionization detector is shown in Figure 37 and may be compared with

CHROMATOGRAMS

FIGURE 37



the earlier chromatogram using the thermistor detector shown in the same figure.

(d) Calibration of the chromatography apparatus

Calibration for each of the products was achieved in two ways.

(1) The pure component was placed in the reaction vessel and sampled in the same manner as during a run. This was repeated for different pressures of component and a calibration curve plotted.

(2) A mixture was made up in a 2 l. bulb of known pressures of the various products and approximating to that of the probable composition. Analysis was achieved either by injection from the reaction vessel or sometimes via the line normally used for evacuation of the sampling valve. Because of its known reactivity with some of the products trichlorosilane was not included.

It was found on comparing these two methods that some non-representative sampling occurred being indicated by a slightly larger pressure of ethylene and vinyl chloride and a correspondingly smaller pressure of vinyltrichlorosilane during a run. The main reasons for this behaviour appeared to be due to the use of rather wide bore capillary tubing, 2.5 mm., from the reaction vessel to the sampling valve. Non-representative sampling may also have been partly due to the line on earlier forms of the apparatus not being solely for sampling of the reaction mixture. That is, some of the products earlier on the reaction path from the state in the reaction vessel at the time of sampling may have resided in the leads to the spiral gauge or the vacuum tap and been drawn out on sampling. The effect was substantially reduced by the employment of 1 mm. capillary tubing and by making the sampling line discrete. Another contributory factor may have been that the distance

of the valve from the reaction vessel was rather longer than the ideal arrangement. It was thought that some condensation might have occurred on increasing the pressure from ca. 0.1 atmos. to 1.5 atmos. on injection of a sample into the column but, although this might have been a contributory cause of the broad $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ peak, calibrations in the presence of nitrogen showed no change. Finally, it was impossible to use the sampling valve at a higher temperature, which would be desirable, because of the effect of the product mixture on silicone rubber O-rings.

It was found possible to make allowance for the discrepancy in the chromatographic results. During a run, and certainly up to about 60% reaction, the amount of ethylene was too high (for many runs about 15%). Too large a pressure was also indicated for vinyl chloride although the discrepancy was within the experimental error in its determination. The pressure of silicon tetrachloride agreed with the calibrations whereas vinyltrichlorosilane was indicated in too small a pressure although this again was within the experimental error in its determination. With chromatography at infinity the % discrepancy was much less, being less than 5% for ethylene.

It ought perhaps to be mentioned here that the calibrations for the individual components had to be checked each day that kinetic runs were being carried out. The silicon compounds seemed to have some effect on the detector needle in that the sensitivity dropped slightly from day to day and could be restored by cleaning the needle with a fine wire.

The results obtained from chromatographic analysis are not of the

highest accuracy but sufficient data have been accumulated to suggest that the results for ethylene and silicon tetrachloride are accurate to better than $\pm 10\%$ whereas for vinyl chloride and vinyltrichlorosilane the results are within $\pm 20\%$.

(e) Examples of chromatographic analysis

The following are the results of two runs giving the peak heights, pressures of components as given from calibration of the pure components and calculated pressures of these components using the correction factor for the apparatus at that time and found from a synthetic product mixture.

The amplifier used could be increased in sensitivity by knobs reading 1, 3, 10, 25, 50 and 100 although the 100 position was rarely used. The actual factors for interchange between these positions were: $3/1 = 2.97$, $10/3 = 3.47$, $25/10 = 2.42$, $50/25 = 2.08$. Hence calibrations could be carried out with lower sensitivity and larger pressures of components and the conversion factors above gave the calibration for smaller amounts.

(1) Run 62

Ethylene calibration.

p mm.	5.5	7.5	13	19	28.5
peak height	14.3	20.3	39.2	56.0	84.0
sensitivity	3	3	3	3	3

Vinyl chloride calibration

p mm.	4.5	10	16	21.5
peak height	10.6	24.1	40.8	56.3
sensitivity	3	3	3	3

The calibration curves are shown in Figure 38 and the run results are given in Table XXXIV.

TABLE XXXIV

Chromatography results for Run 62 on $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$

Time (min.)	0	10	16	23	35	50
P (mm.)	37.80	42.10	44.35	46.55	50.45	54.30
Δp (mm.)	-	4.30	6.55	8.75	12.65	16.50
pk. ht. E	-	8.2	14.5	20.0	27.7	40.8
sensitivity	-	3	3	3	3	3
pE (mm.)	-	3.3	5.3	7.2	9.65	13.9
0.85pE (mm.)	-	2.8	4.5	6.1	8.2	11.8
pk. ht. VC	-	5.0	8.2	11.7	15.6	4.6
sensitivity	-	10	10	10	10	3
pVC (mm.)	-	0.66	1.01	1.41	1.80	2.20

(2) Run 84

Ethylene calibration

p mm.	8.5	13.5	18	25
peak height	23.0	38.7	50.5	72.1
sensitivity	3	3	3	3

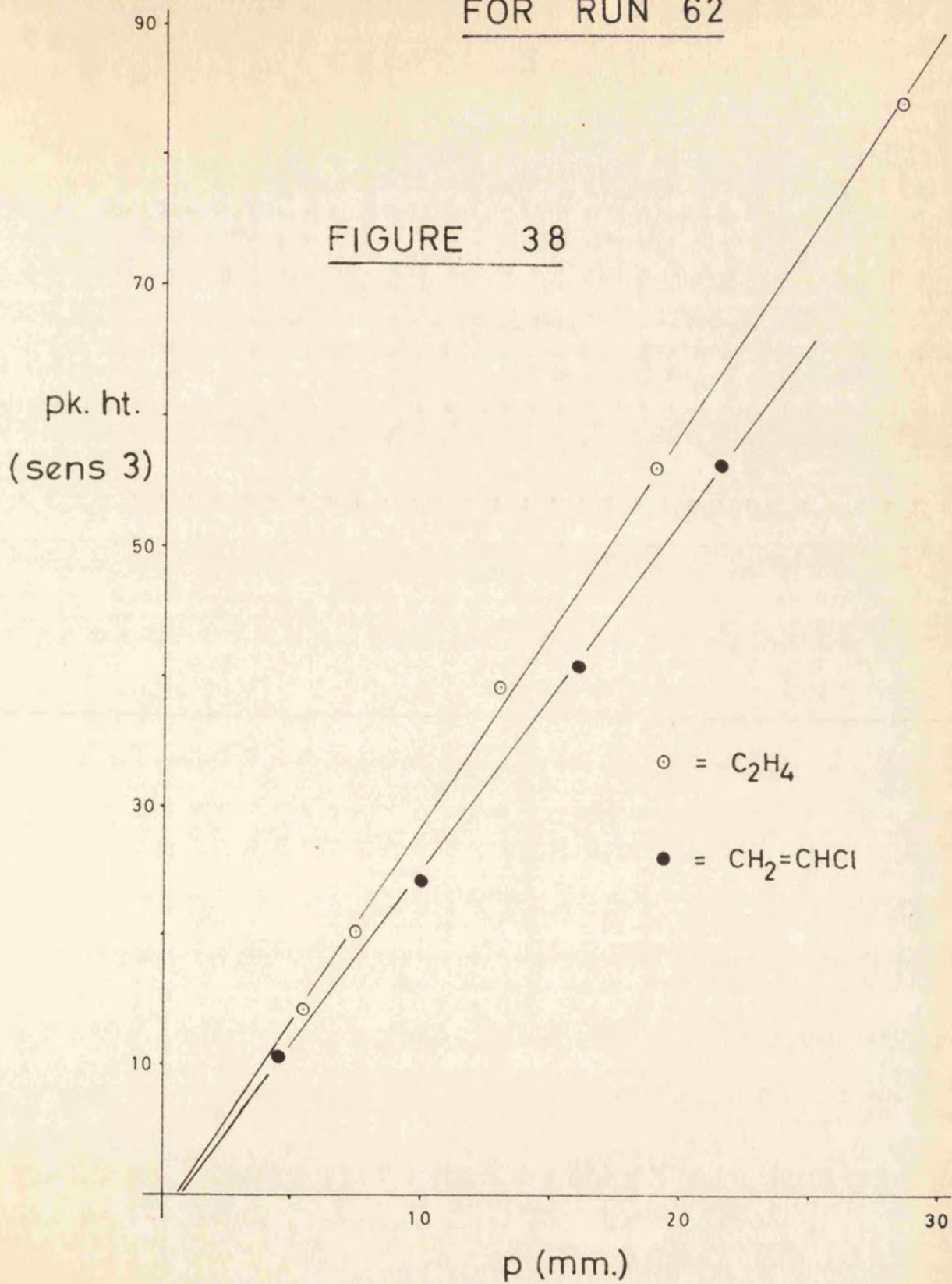
Vinyltrichlorosilane calibration

p mm.	5	8	16	21	34
peak height	9.7	16.3	33.7	38.2	20.1
sensitivity	10	10	10	10	3

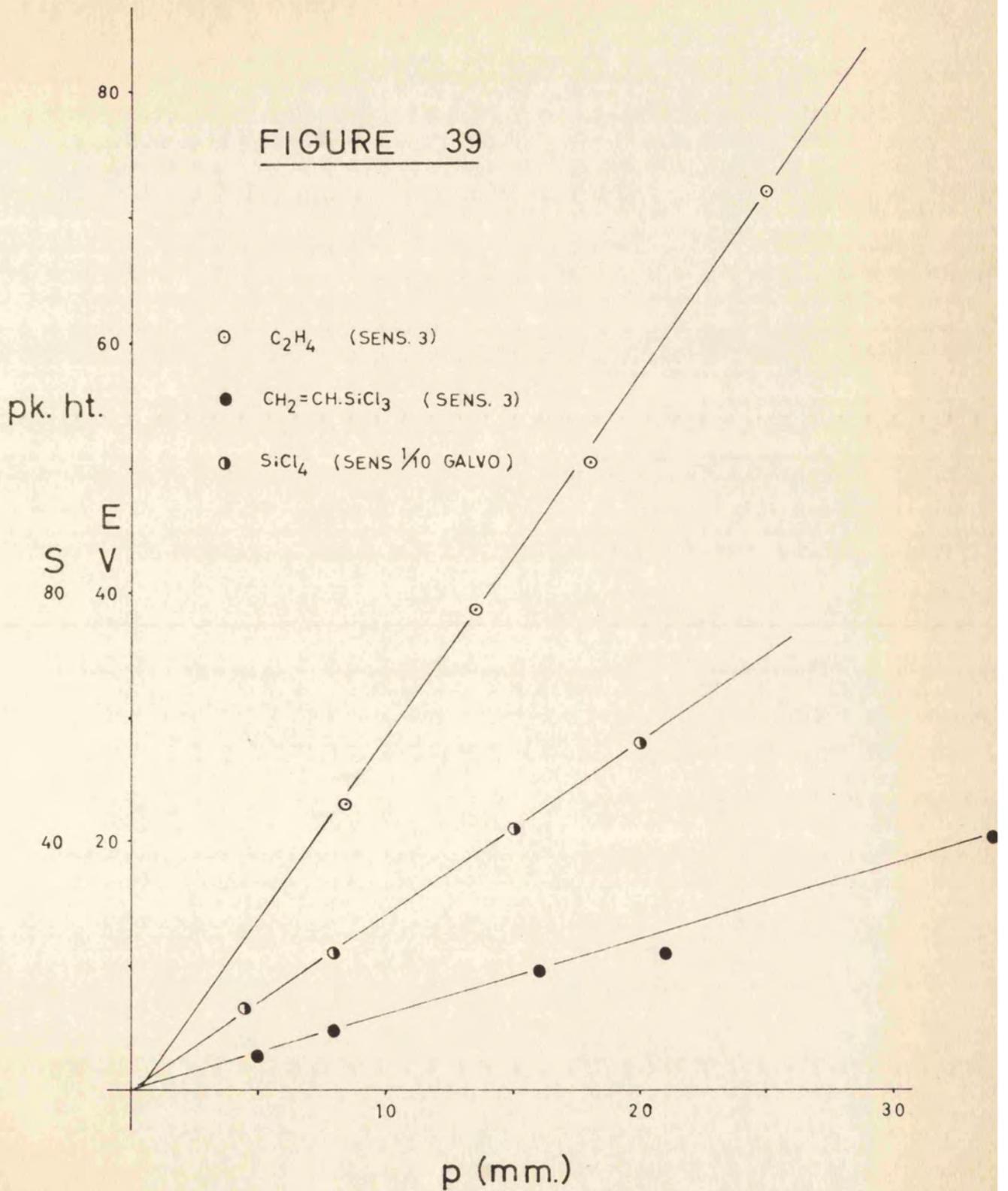
CHROMATOGRAPHY CALIBRATIONS

FOR RUN 62

FIGURE 38



CHROMATOGRAPHY CALIBRATIONS
FOR RUN 84



Silicon tetrachloride calibration (thermistor detector, recorded
on a spot galvanometer)

p mm.	4.5	8	15	20
peak height	13	22	42	56
sensitivity	1/10	1/10	1/10	1/10

The calibration curves are illustrated in Figure 39 and the run results are given in Table XXXV.

TABLE XXXV

Chromatography results on Run 84

Time (min.)	0	16	27	38	49
P (mm.)	17.50	24.00	26.80	28.95	30.45
Δp (mm.)	0	6.50	9.30	11.45	12.95
pk. ht. E	-	12.9	21.5	27.1	30.2
sensitivity	-	3	3	3	3
pE (mm.)	-	5.0	7.9	9.8	11.0
0.85 pE (mm.)	-	4.25	6.8	8.35	9.4
pk. ht. V	-	-	4.7	5.5	7.0
sensitivity	-	-	25	25	25
pV (mm.)	-	-	0.95	1.15	1.43
pk. ht. S	-	10.5	17.5	20.0	25.0
sensitivity	-	1/10	1/10	1/10	1/10
pS (mm.)	-	4.0	6.4	7.4	9.0

(vii) PROOF OF PRODUCTS

For gas chromatographic confirmation the retention of the pure material was compared with that of the product and also by observation of a single enhanced peak on addition of some of the pure material to the run products. Infra-red analyses were carried on a Perkin-Elmer Infracord in gas cells after vacuum fractionation of the products. Mass spectra were carried out on an A.E.I. M.S. 10 spectrometer. Spectra at 70 volt. were compared with data sheets and the ionization^{VOL-TAGE} was also reduced to observe the molecular ions.

(a) Ethylene

Presence of ethylene in the reaction products was confirmed by gas chromatographic analysis, infra-red spectrum and later by mass spectrum.

(b) Vinyl chloride

The presence of vinyl chloride was indicated by gas chromatography retention time. Confirmation was achieved by carrying out 6 runs to ca. 20% reaction, freezing out the products together and fractionating. In this way vinyl chloride containing a small quantity of ethylene was obtained and infra-red analysis proved vinyl chloride present. This was later confirmed on the mass spectrometer.

(c) Vinyltrichlorosilane

Confirmation of vinyltrichlorosilane was obtained by gas chromatography.

(d) Silicon tetrachloride

Silicon tetrachloride was confirmed by gas chromatography, thermal

conductivity, and by infra-red analysis.

(e) Hydrogen chloride

Hydrogen chloride had been shown to be among the products by vapour density measurements and further indication was obtained, although the response was poor, by gas chromatography using the thermistor detector. Confirmation was obtained by the mass spectrum.

(f) Trichlorosilane

Presence of this compound in the kinetic scheme was indicated by gas chromatography using the thermistor detector. Confirmation by its infra-red spectrum was not possible because the small quantity of trichlorosilane in the products at 20% reaction could not be isolated by fractionation. Possibly the trichlorosilane underwent further reaction on fractionation. A fragment at 98 and a smaller one at 100 was observed both from trichlorosilane and the product mixture at 70 volt. on the mass spectrometer. This is probable confirmation of trichlorosilane due to the formation of the SiCl_2 fragment although not certain evidence because of the complexity of the product mixture.

(g) Ethyltrichlorosilane

This compound was shown to occur in the products after more than 10 half-lives by gas chromatographic analysis.

(h) Dimethylphenylchlorosilane

That ethylene and dimethylphenylchlorosilane comprised virtually all the products in the decomposition of $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ was indicated by gas chromatography. With the column at 110°C and a hydrogen flow rate of 60 ml./min. the retention times for ethylene and dimethylphenylchloro-

-silane were approximately 1.5 min. and 16 min. After fractionation to remove the ethylene the remaining liquid from 4 runs was analysed on an A 60 Varian N.M.R. spectrometer. This showed that the protons of the chloroethyl group had been effectively removed and the spectrum was consistent with ClSiMe_2Ph .

(viii) ANALYSIS USING THE MASS SPECTROMETER

To find out for certain whether the quantity of hydrogen chloride produced in the thermal decomposition of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ was in fact equal to that of vinyltrichlorosilane, analysis of the end products of a number of runs after more than 10 half-lives was carried out on an A.E.I. M.S. 10 mass spectrometer which was not available for earlier work. The spectrometer was only capable of analysis up to a molecular weight of 100 with a resolution of 1 in 50 so that analysis of higher molecular weight materials, especially trichlorosilane, was precluded.

The mass spectrometer had its own integral diffusion pump backed by a Genevac rotary pump to evacuate the ionization chamber. To the ionization chamber were attached two leads incorporating "metrosil" carborundum leaks. One of these leaks went to a 500 ml. cylindrical reaction vessel contained in a tubular furnace with the usual attachments for evacuation, pressure measurement and heating. The other leak was attached to a vacuum line containing a mercury manometer, a 2 l. bulb to take larger quantities of gases and a similar bulb containing pure Argon for calibration purposes. A small "carrot shaped" flask of 50 ml. capacity was included for small quantities of gases. All taps in this section were Springham greaseless taps with neoprene diaphragms.

In order to observe the molecular ions only of the various

reaction products it was necessary to reduce the ionization voltage to 15 volt. This voltage is below the ionization potential of Argon and hence, although useful when carrying out fragment analysis, Argon was inadequate at 15 volt. Use was made of the pure propene available in the laboratory for calibration purposes; this was not entirely satisfactory as some fragmentation did occur at 15 volt. The most satisfactory method of analysis was to introduce the propene via the reaction vessel and its associated leak and the product mixture via the other leak. During any one particular analysis the sensitivity of the instrument varied only slightly. No allowance was therefore made for this.

For all these analyses the run products were completely frozen down into a small "carrot shaped" flask with liquid nitrogen. The products volatile at -78°C were then transferred into another similar flask for connection to the mass spectrometer. In this way it was considered that all the ethylene, hydrogen chloride, vinyl chloride and, in one determination, the nitric oxide would be collected. Also some small quantity of silicon tetrachloride almost certainly was transferred and is reflected in the fact that the total pressure analysed exceeded the quantity which could be accounted for by analysis of the more volatile components although the discrepancy was not large.

Fractionation of the sample occurred on first carrying out the analysis but if left for a time varying from 20 - 50 min. the composition, as viewed on the chart, was constant and agreed with that of a mixture of known composition. The amount taken was less than the total pressure of the product mixture and only the relative percentages were calculated to enable comparison with chromatographic data.

(a) Results for 2-chloroethyltrichlorosilane

M.S.1 End products from pyrolysis overnight at 382.8°C

Compound	p mm.	m/e = 28	m/e = 36	m/e = 62
C ₂ H ₄	20.0	78.5	-	-
HCl	9.0	-	32.0	-
CH ₂ =CHCl	7.5	-	-	33.5
Mixture	22.0	56.7	15.8	8.9
Sensitivity	-	(250)	(100)	(100)

Hence pE = 14.45 mm., pHCl = 4.35 mm., pVC = 2.0 mm.

Total pressure accounted for = 20.8 mm.

%E = 69, %HCl = 21, %VC = 10

It may be noted that in this case the sensitivity to vinyl chloride is lower ~~in this case~~ than in subsequent analyses. The vinyl chloride used for calibration had probably not been properly purified.

M.S.2 Products from Run 115 at 385°C

Compound	p mm.	28	36	62
C ₂ H ₄	23.0	15.0	-	-
HCl	15.5	-	55.0	-
CH ₂ =CHCl	5.5	-	-	47.5
Mixture	73.0	33.7	51.2	18.5
Sensitivity	-	(1000)	(100)	(100)

pE = 51.7 mm., pHCl = 14.4 mm., pVC = 2.14 mm.

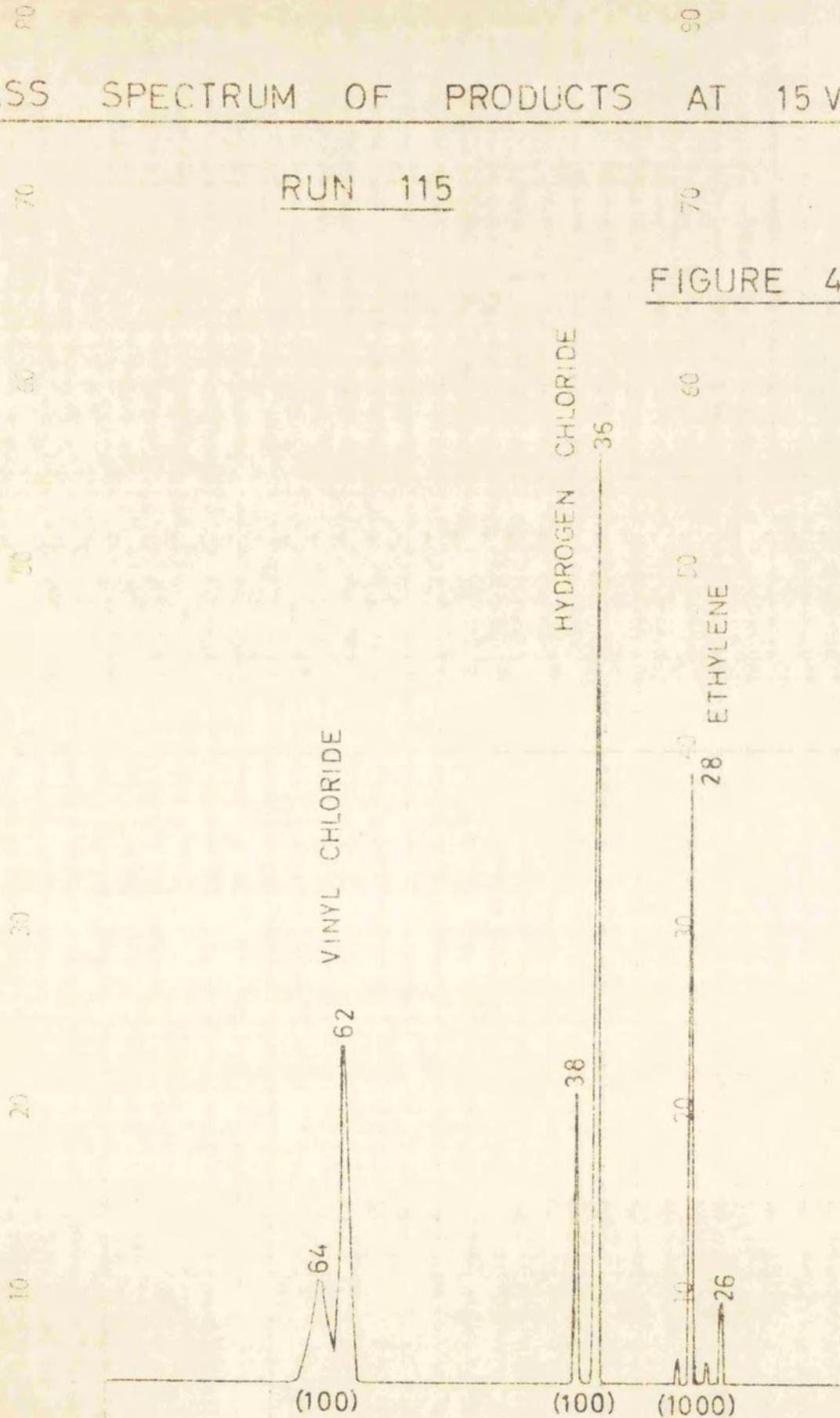
%E = 76, %HCl = 21, %VC = 3

The mass spectrum for this mixture is illustrated in Figure 40.

MASS SPECTRUM OF PRODUCTS AT 15 V.

RUN 115

FIGURE 40



M.S.3 Products of Run 116 at 385°C

Compound	p mm.	28	36	62
C ₂ H ₄	7.5	53.4	-	-
Sensitivity	-	(100)	-	-
HCl	7.0	-	69.8	-
CH ₂ =CHCl	2.5	-	-	76.5
Mixture	38.0	79.0	84.4	39.0
Sensitivity	-	(250)	(25)	(25)

pE = 27.7 mm., pHCl = 8.5 mm., pVC = 1.3 mm.

%E = 74 , %HCl = 23 , %VC = 3

M.S.4 Products of Run 117 in presence of nitric oxide at 383.3°C

Compound	p mm.	28	36	62
C ₂ H ₄	7.5	57.0	-	-
Sensitivity	-	(100)	-	-
HCl	16.0	-	61.0	-
CH ₂ =CHCl	6.0	-	-	66.3
Mixture	38.0	53.0	37.5	14.5
Sensitivity	-	(250)	(100)	(100)

pE = 17.4 mm., pHCl = 9.8 mm., pVC = 1.3 mm.

%E = 61 , %HCl = 34 , %VC = 5

Nitric oxide was shown to be the only other product with a mass of less than 100 but was not analysed for. It gave a peak height of 46.5 (100) for m/e = 30. This probably accounts for the majority of the 9.5 mm. not estimated. In any case results would be very inaccurate for nitric oxide

because some was undoubtedly lost on degassing the product mixture before analysis.

The above result is important in showing that excess hydrogen chloride above that obtained by dehydrochlorination of 2-chloroethyltrichlorosilane arises in the presence of nitric oxide.

(b) Results for 2-chloroethyldimethylphenylsilane

M.S.5 Products of Run 36 at 290°C

Compound	p mm.	28	36	62
C ₂ H ₄	12.0	32.0	-	-
Mixture	8.5	22.7	-	-
Sensitivity	-	(100)	-	-

pE = 8.5 mm., %E = 100

An extremely small movement of the chart recorder pen was observed at m/e = 62 when the ionization voltage was increased to 55 volt., 1.2 on sensitivity (100), and therefore a very minor amount of vinyl chloride may be produced in the decomposition. No hydrogen chloride was detected.

(C) CALCULATION OF KINETICS

(i) IN THE STUDY OF 2-CHLOROETHYLTRICHLOROSILANE

(a) The over-all rate constant

A first order reaction follows the equation:

$$dx/dt = k (a - x)$$

where k is the rate constant of the reaction, a is the initial concentration and x is the amount reacted after time t . Integration of this equation between the limits, $x = 0, t = 0; x = x, t = t$, gives:

$$\ln a/a - x = kt$$

For a gaseous reaction involving an increase in the total pressure then we can put: $a = p_0, x = \Delta p$. If p_0, p_t and p_{∞} are the pressures at zero time, time t and infinite time respectively and if Δp is the increase in pressure at time t then we have, if there is a two-fold increase of pressure,

$$a = p_0 = p_{\infty} - p_0$$

$$a - x = p_{\infty} - p_t = 2p_0 - p_t = p_0 - \Delta p$$

In this study p_{∞} was approximately $1.93p_0$ but because of the variation of p_{∞} , partly because of the removal of samples for analysis, and the good extrapolation to zero time to evaluate p_0 , the practise of using $p_0 - \Delta p$ was adopted for calculation of the amount of 2-chloroethyltrichlorosilane remaining at time t . Employment of the experimental p_{∞} had little effect on the over-all rate constant although it did improve the linearity of the rate plot at later times.

Hence we have:

$$\ln p_0 / (p_0 - \Delta p) = kt$$

$$\text{or} \quad kt = 2.303 \log p_0 - 2.303 \log (p_0 - \Delta p)$$

Therefore a plot of $\log (p_0 - \Delta p)$ against t gives a straight line of gradient = $-k / 2.303$ and intercept = $\log p_0$.

For all the runs on $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ the over-all reaction rate was obtained from the gradient of the graph of $\log (p_0 - \Delta p)$ against time and one run is shown completely worked out below, Table XXXXVI. The rate plot is shown in Figure 41. In the table of kinetic results following, Chapter Seven, Section (D), a selection of the experimental results of pressure measurements are given from the total number, usually more than 30, of readings taken. The accuracy of these rate data, in view of the reproducibility, is certainly within $\pm 10\%$.

It will be noticed in the run results outlined in the following table that the pressure fell slightly on removing a sample for analysis. Allowance was made for this in order to obtain a smooth curve.

TABLE XXXXVI

Run 64 on $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ alone at 383.3°C

Time (min.)	Scale	Scale -Zero	p	Δp	$(p_0 - \Delta p)$	log $(p_0 - \Delta p)$	pE	pS
Zero	1.70	-	-	-	-	-	-	-
0(ext)	20.50	18.80	29.90	0.0	29.90	1.475	-	-
0.5	20.65	18.95	30.15	0.25	29.65	1.472	-	-
1	20.90	19.20	30.50	0.60	29.30	1.467	-	-
1.5	21.10	19.40	30.85	0.95	28.95	1.462	-	-
2	21.20	19.50	31.00	1.10	28.80	1.459	-	-
3	21.40	19.70	31.30	1.40	28.50	1.455	-	-

TABLE XXXXVI (continued)

Time (min.)	Scale	Scale -Zero	p	Δp	$(p_0 - \Delta p)$	log $(p_0 - \Delta p)$	pE	pS
4	21.55	19.85	31.55	1.65	28.25	1.451	-	-
S5	21.80	20.10	31.85	1.95	27.95	1.446	0.75	1.50
	- 21.75							
6	21.90	20.25	32.20	2.30	27.60	1.441	-	-
7	22.10	20.45	32.50	2.60	27.30	1.436	-	-
8	22.25	20.60	32.75	2.85	27.05	1.432	-	-
S10	22.65	21.00	33.40	3.50	26.40	1.422	2.0	2.25
	- 22.60							
12	22.90	21.30	33.85	3.95	25.95	1.414	-	-
14	23.20	21.60	34.35	4.45	25.45	1.406	-	-
S16	23.55	21.95	34.85	4.95	24.95	1.396	3.0	3.2
	- 23.50							
18	23.75	22.20	35.30	5.40	24.50	1.389	-	-
20	24.10	22.55	35.80	5.90	24.00	1.380	-	-
S23	24.55	23.00	36.55	6.65	23.25	1.367	4.2	4.0
	- 24.50							
26	24.95	23.45	37.30	7.40	22.50	1.352	-	-
29	25.35	23.85	37.90	8.00	21.90	1.340	-	-
S32	25.75	24.25	38.55	8.65	21.25	1.327	6.5	6.0
	- 25.70							
35	26.10	24.65	39.20	9.30	20.60	1.314	-	-
40	26.70	25.25	40.10	10.20	19.70	1.294	-	-
S45	27.35	25.90	41.10	11.20	18.70	1.272	7.5	7.5
	- 27.30							

TABLE XXXXVI (continued)

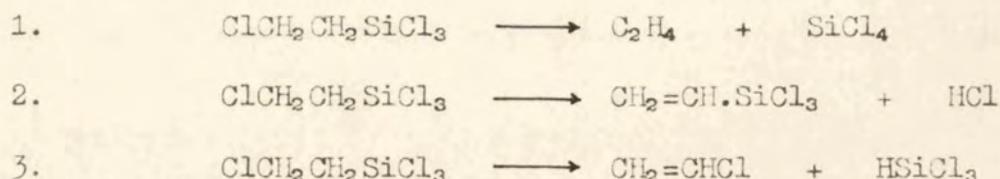
Time (min.)	Scale	Scale -Zero	p	Δp	$(p_0 - \Delta p)$	log $(p_0 - \Delta p)$	pE	pS
50	27.85	26.45	42.05	12.15	17.75	1.249	-	-
55	28.45	27.05	43.00	13.10	16.80	1.225	-	-
60	28.90	27.50	43.70	13.80	16.10	1.207	-	-
65	29.40	28.00	44.50	14.60	15.30	1.185	-	-
70	29.85	28.45	45.15	15.25	14.65	1.165	-	-
90	31.40	30.00	47.70	17.80	12.10	1.082	-	-
105	32.35	30.95	49.20	19.30	10.60	1.025	-	-
120	33.15	31.75	50.45	20.55	9.35	0.971	-	-
∞	38.05	36.65	58.30	28.40	-	-	20.0	20.0

Also $pV_0 = 7.0$

$$\%E = 67, \%S = 67, \%V = 23$$

(b) Calculation of the rates of formation of products

It was considered that the reactions 1, 2 and 3 below were in the initial stages simultaneous first order processes.



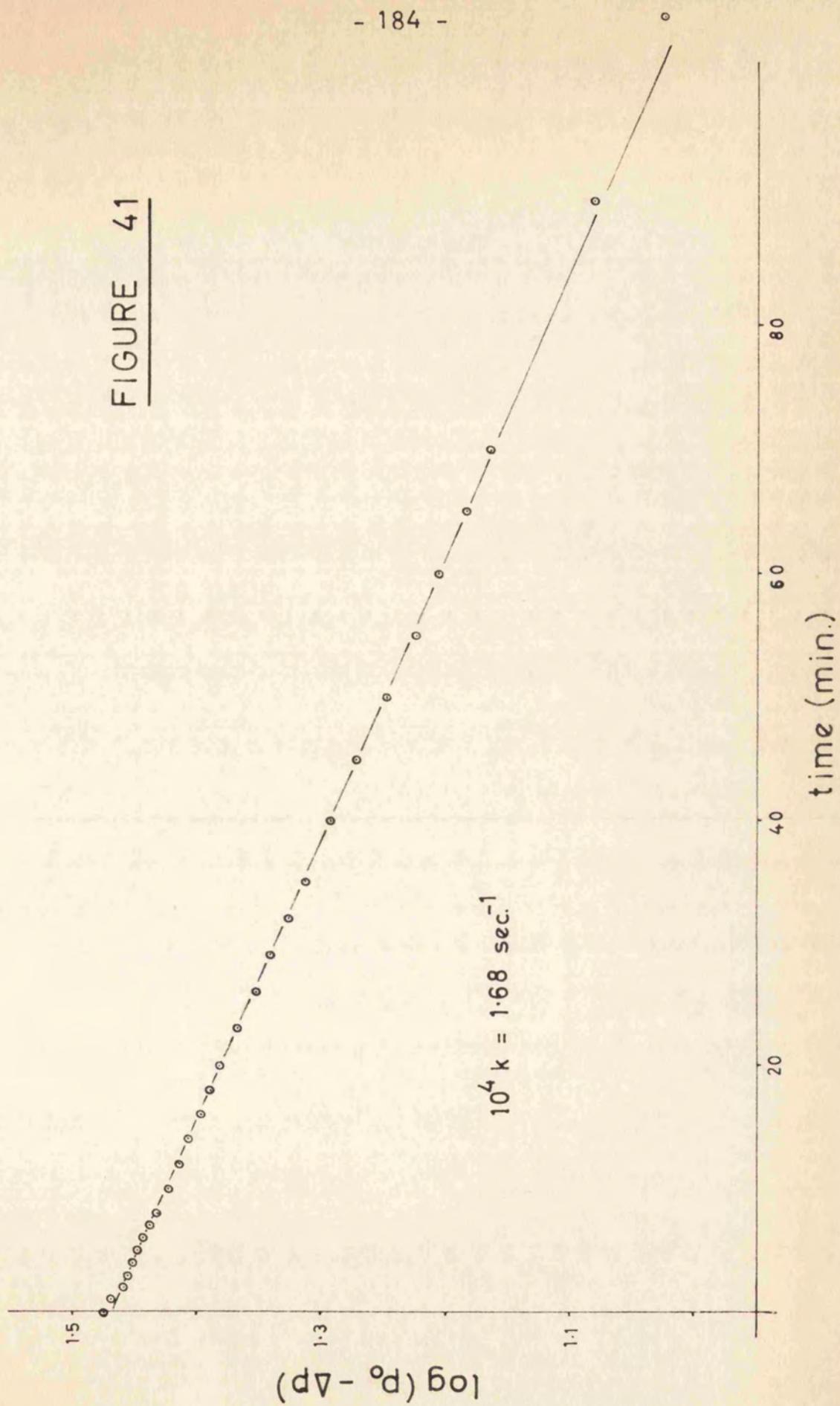
Since the over-all reaction is first order then:

$$k = k_1 + k_2 + k_3$$

If β_0 and β are the concentrations of 2-chloroethyltrichlorosilane at zero time and at time t then the concentration of β at time t can be expressed in the form:

RATE PLOT FOR RUN 64 ON ClCH₂CH₂SiCl₃

FIGURE 41



$$\beta = \beta_0 \cdot e^{-kt}$$

Similarly if kE , the rate of production of ethylene (E), is equal to k_1 then:

$$dE/dt = k_1 \beta = k_1 \beta_0 e^{-kt}$$

which on integration gives:

$$E = E_0 + kE \beta_0/k \cdot (1 - e^{-kt})$$

Substituting pE for E , p_0 for β_0 , and taking $E_0 = p_0E = 0$ at zero time, then:

$$pE = kE/k \cdot p_0 \cdot (1 - e^{-kt})$$

Hence a graph of pE against $(1 - e^{-kt})$ gives a straight line of gradient = $kE/k \cdot p_0$

Similarly the rates of formation of silicon tetrachloride, vinyl chloride and vinyltrichlorosilane can be evaluated.

Where reasonable data were available the above procedure was utilized for determination of the relative reaction rates. The value of the over-all rate constant was determined manometrically as described on the preceding pages and the initial pressure, p_0 , was obtained from extrapolation of the total pressure - time curve to zero time.

Taking the figures already given for Run 64 in Table XXXVI, the values of $(1 - e^{-kt})$ can be calculated as shown in Table XXXVII, and the rates of formation of ethylene and silicon tetrachloride obtained as illustrated in Figure 42.

TABLE XXXVII

Data used to calculate kE/k and kS/k for Run 64

$$p_0 = 29.90 \text{ mm.} \quad k = 1.68 \times 10^{-4} \text{ sec.}^{-1} = 1.00 \times 10^{-2} \text{ min.}^{-1}$$

Time (min.)	5	10	16	23	32	45
kt	0.050	0.100	0.160	0.230	0.320	0.450
e^{kt}	1.0513	1.105	1.174	1.126	1.377	1.569
e^{-kt}	0.950	0.905	0.851	0.795	0.727	0.638
$1 - e^{-kt}$	0.050	0.095	0.149	0.205	0.273	0.362
pE (mm.)	0.75	2.0	3.0	4.2	6.5	7.5
pS (mm.)	1.5	2.25	3.2	4.0	6.0	7.5

$$kE/k = 0.70, \quad kS/k = 0.71$$

As mentioned previously, page 167, the results obtained by this method are only accurate to within $\pm 10\%$ for ethylene and silicon tetrachloride and probably only to within $\pm 20\%$ for vinyl chloride and vinyltrichlorosilane because of the difficulties in chromatographic analysis.

(c) Rate of reaction between HSiCl_3 and $\text{CH}_2=\text{CHCl}$ or $\text{CH}_2=\text{CH}_2$

Second order rate constants were calculated at the time of analysis using the appropriate equation depending upon whether the initial pressures were equal or not.

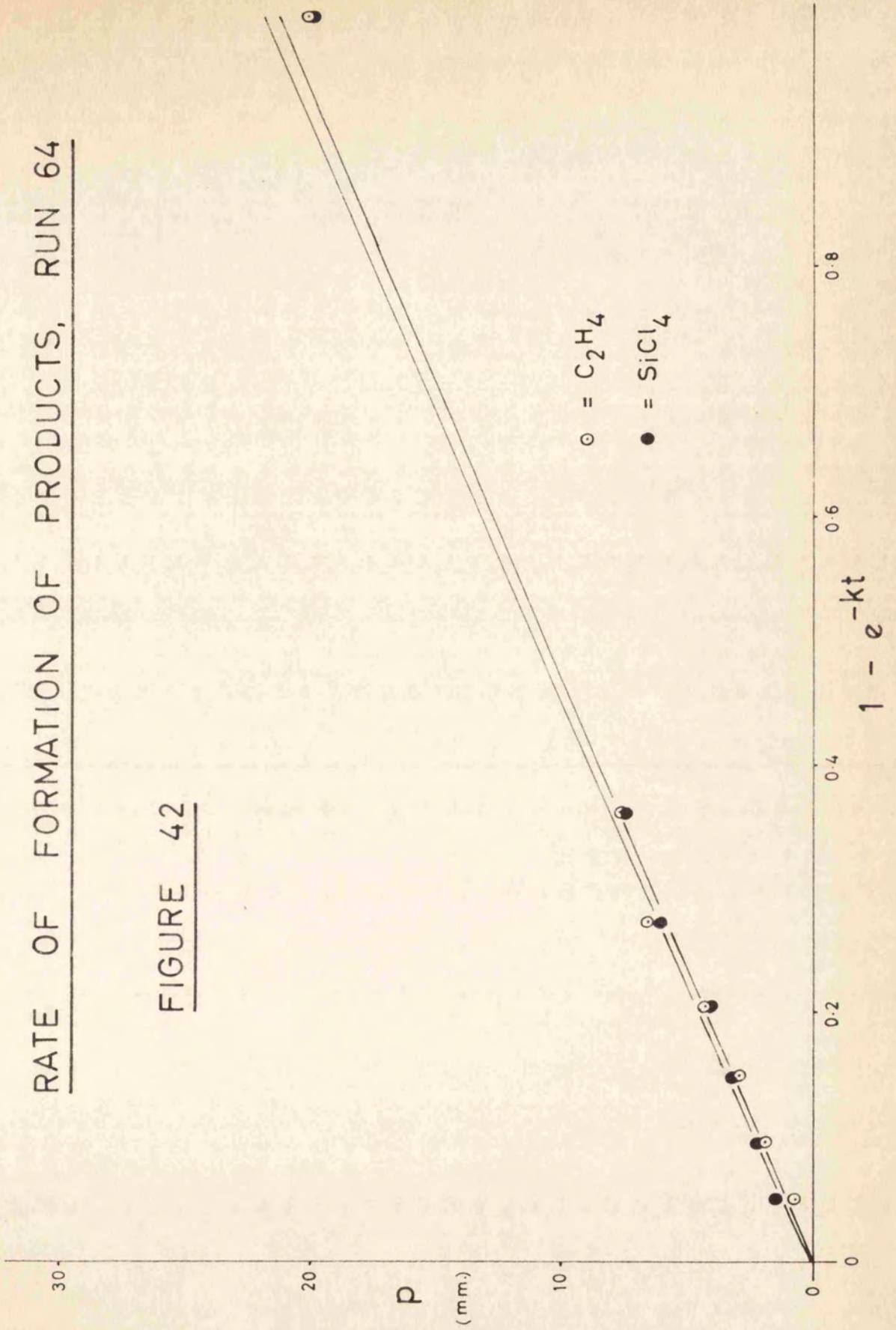
$$\text{For } A + B = \text{products} \quad : \quad k = 2.303/t(a - b) \cdot \log b(a - x)/a(b - x)$$

$$\text{For } 2A = \text{products} \quad : \quad k = 1/t \cdot x/a(a - x)$$

All the relevant data are given in the kinetic results for these reactions.

RATE OF FORMATION OF PRODUCTS, RUN 64

FIGURE 42



(ii) IN THE STUDY OF 2-CHLOROETHYLDIMETHYLPHENYLSILANE

Because of the speed of the thermal decomposition reaction and also because some decomposition often occurred on introduction of the substance into the reaction vessel, the determination of the reaction rate was by means which did not require the initial pressure, p_0 , nor the final pressure, p_{∞} , to be experimentally determined. For a few runs the Guggenheim method¹⁹³ was utilized but for the majority of calculations the Swinbourne method¹⁸⁴ was found to be simpler and more satisfactory because it did not depend so much upon accurate interpolation of small changes in pressure at times when the reaction had proceeded to a considerable extent. The Swinbourne method gave quite good agreement between experimental and calculated values of p_{∞} where experimental values were obtainable.

Both these methods originate from the first order rate law in the form:

$$(a - x) = a.e^{-kt}$$

which for a gaseous reaction involving an increase in pressure becomes:

$$(p_{\infty} - p) = (p_{\infty} - p_0). e^{-kt}$$

For both methods a set of pressure readings, $p_1, p_2 \dots p_n$ are taken at times, $t_1, t_2 \dots t_n$ and $p'_1, p'_2 \dots p'_n$ at $t_1 + T, t_2 + T \dots t_n + T$ where T is a constant time increment. For the Swinbourne method T is usually smaller than for the Guggenheim procedure because of the differences in graphical method. Hence we have the two basic equations:

$$(p_{\infty} - p_n) = (p_{\infty} - p_0). e^{-kt_n} \quad (1)$$

$$(p_{\infty} - p'_n) = (p_{\infty} - p_0). e^{-k(t_n + T)} \quad (2)$$

(a) Guggenheim method

Subtracting equation (2) from equation (1) and rearranging we obtain:

$$kt_n + \ln(p'_n - p_n) = \ln(p_{\infty} - p_0)(1 - e^{-kT})$$

In this work the values of the pressure increase, Δp , were obtained from the pressure - time curve to enable correlation with chromatography data. This makes no difference to the calculation as a constant quantity is removed from each pressure reading.

Therefore:

$$kt_n + \ln(\Delta p'_n - \Delta p_n) = \ln \Delta p_{\infty} (1 - e^{-kT})$$

The right hand side of this equation is a constant and so a graph of $\log(\Delta p'_n - \Delta p_n)$ against t_n gives a straight line with a gradient of $-k/2.303$.

The figures obtained for one run using this procedure are shown in Table XXXXVIII and illustrated graphically in Figure 43.

TABLE XXXXVIII

Run 26 on $\text{ClCH}_2\text{CH}_2\text{SiMe}_2\text{Ph}$ at 302°C

Time (min.)	Δp_1 t min.	Δp_2 (t + 60) min.	$\Delta p_2 - \Delta p_1$	log $\Delta p_2 - \Delta p_1$
0	0	17.25	17.25	1.237
2	1.80	17.45	15.65	1.194
4	3.10	17.65	14.55	1.163
6	4.25	17.90	13.65	1.135
8	5.30	18.10	12.80	1.107
10	6.30	18.30	12.00	1.079

GUGGENHEIM METHOD

RUN 26 ON CICH₂CH₂SiMe₂Ph

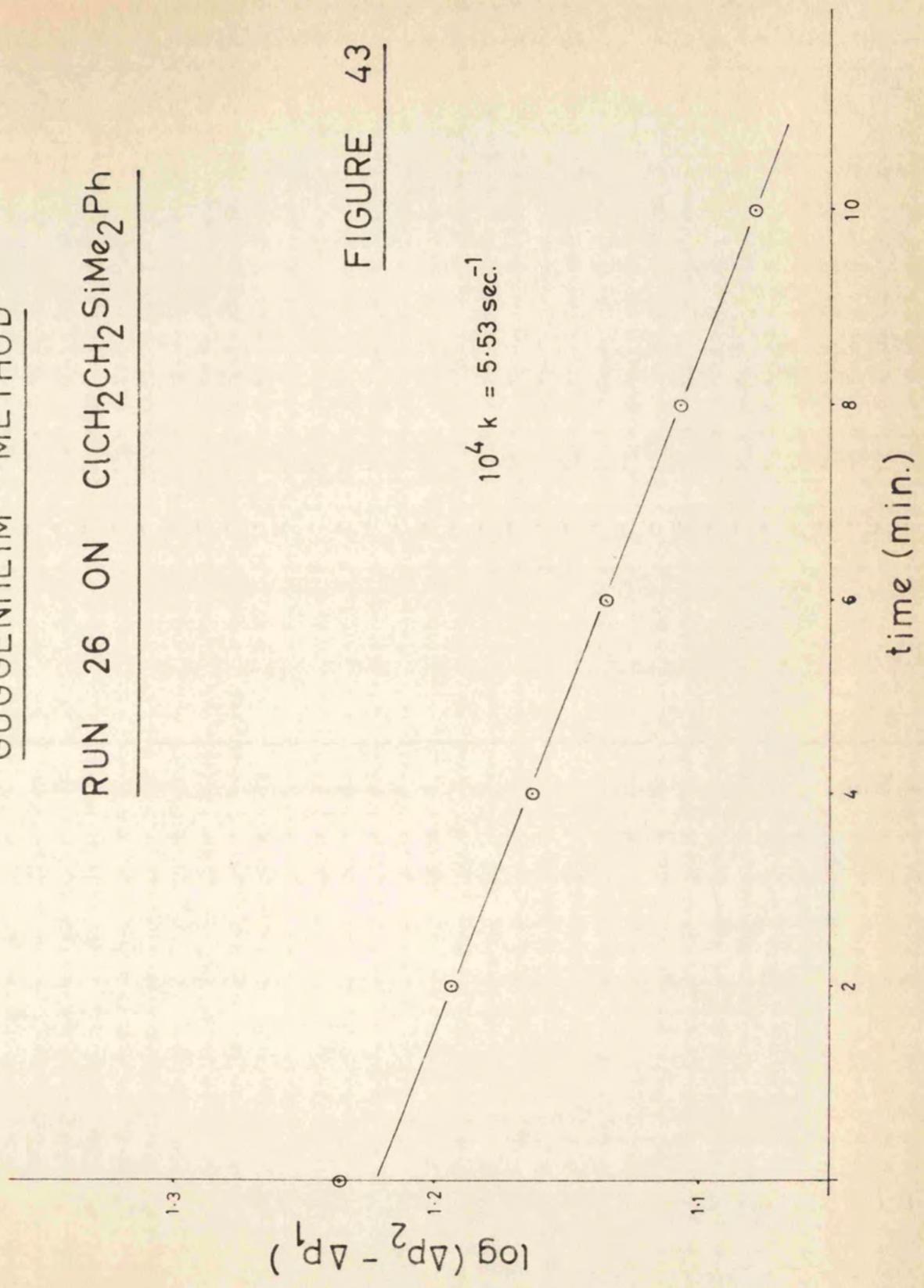


FIGURE 43

(b) Swinbourne method

Dividing equation (1) by equation (2), collecting terms and rearranging we obtain:

$$p_n - p'_n \cdot e^{kT} = p_{\infty} \cdot (1 - e^{kT})$$

The term on the right hand side is constant and hence a graph of p_n against p'_n , where p_n and p'_n are separated by the constant time interval T , should give a straight line for a first order reaction with $\log(\text{gradient}) = kT/2.303$.

Also the values of p_{∞} and p_0 can be calculated from the graph in the following way:-

When $t = \infty$; $p_n = p'_n = p_{\infty}$ Therefore p_{∞} is the point where the values of p_n and p'_n are identical.

The initial pressure, p_0 , can be obtained by extrapolating back to zero time from a pressure reading T min. from zero time.

The results obtained for one run are shown below in Table XXXIX and the graph is shown in Figure 45. Kinetic determinations were carried out in the presence of a small quantity, usually about 14 mm., of dry oxygen-free nitrogen. To try to establish that the pressure increased to double the initial pressure on pyrolysis this quantity of nitrogen, or of other added substance, was subtracted from the pressure readings in each case. Also for some runs the value of p_{∞} was obtained experimentally and compared with p_{∞} obtained by the Swinbourne method. The values were usually quite close but a graph of $\log(p_{\infty} - p)$ against time, illustrated in Figure 44, remained linear for a longer time using p_{∞} from the Swinbourne method.

TABLE XXXIX

Run 40 on ClCH₂CH₂SiMe₂Ph at 290°C

Time (min.)	Scale	Scale -Zero	p	(p _∞ - p)		log	
				experimental	Swinbourne	(p _∞ - p)	(p _∞ - p)
Zero + N ₂	9.2						
0 (extr.)	-	-	50.00	29.20	1.465	28.00	1.447
0.5	40.95	31.75	50.50	28.70	1.458	27.50	1.439
1	41.70	32.50	51.65	27.55	1.440	26.35	1.420
2	42.70	33.50	53.30	25.90	1.413	24.70	1.392
3	43.50	34.30	54.50	24.70	1.392	23.50	1.371
4	44.15	34.95	55.55	23.65	1.374	22.45	1.351
6	45.45	36.25	57.60	21.60	1.334	20.40	1.310
8	46.45	37.25	59.20	20.00	1.301	18.80	1.274
10	47.30	38.10	60.60	18.60	1.269	17.40	1.240
13	48.75	39.55	62.80	16.40	1.215	15.20	1.182
16	50.00	40.80	64.90	14.30	1.155	13.10	1.117
20	51.55	42.35	67.30	11.90	1.076	10.70	1.029
25	53.15	43.95	69.90	9.30	0.968	8.10	0.908
30	54.15	44.95	71.45	7.75	0.889	6.55	0.816
35	55.00	45.80	72.80	6.40	0.806	5.20	0.716
40	55.60	46.40	73.75	5.45	0.736	4.25	0.628
45	56.15	46.95	74.65	4.55	0.658	3.35	0.525
50	56.65	47.45	75.40	3.80	0.580	2.60	0.415
55	56.90	47.70	75.85	3.35	0.525	2.15	0.332
60	57.25	48.05	76.40	2.80	0.447	1.60	0.204
65	57.55	48.35	76.80	2.40	-	1.20	-
70	57.70	48.50	77.00	2.20	-	1.00	-
75	57.80	46.60	77.20	2.00	-	0.80	-
∞	59.00	49.80	79.20	-	-	p _∞ = 78.00	

From the pressure time curve the values of the pressure at 5 min. intervals were obtained and are shown in Table XXXXX. The rate plot is shown in Figure 45 with a constant time interval of 10 min.

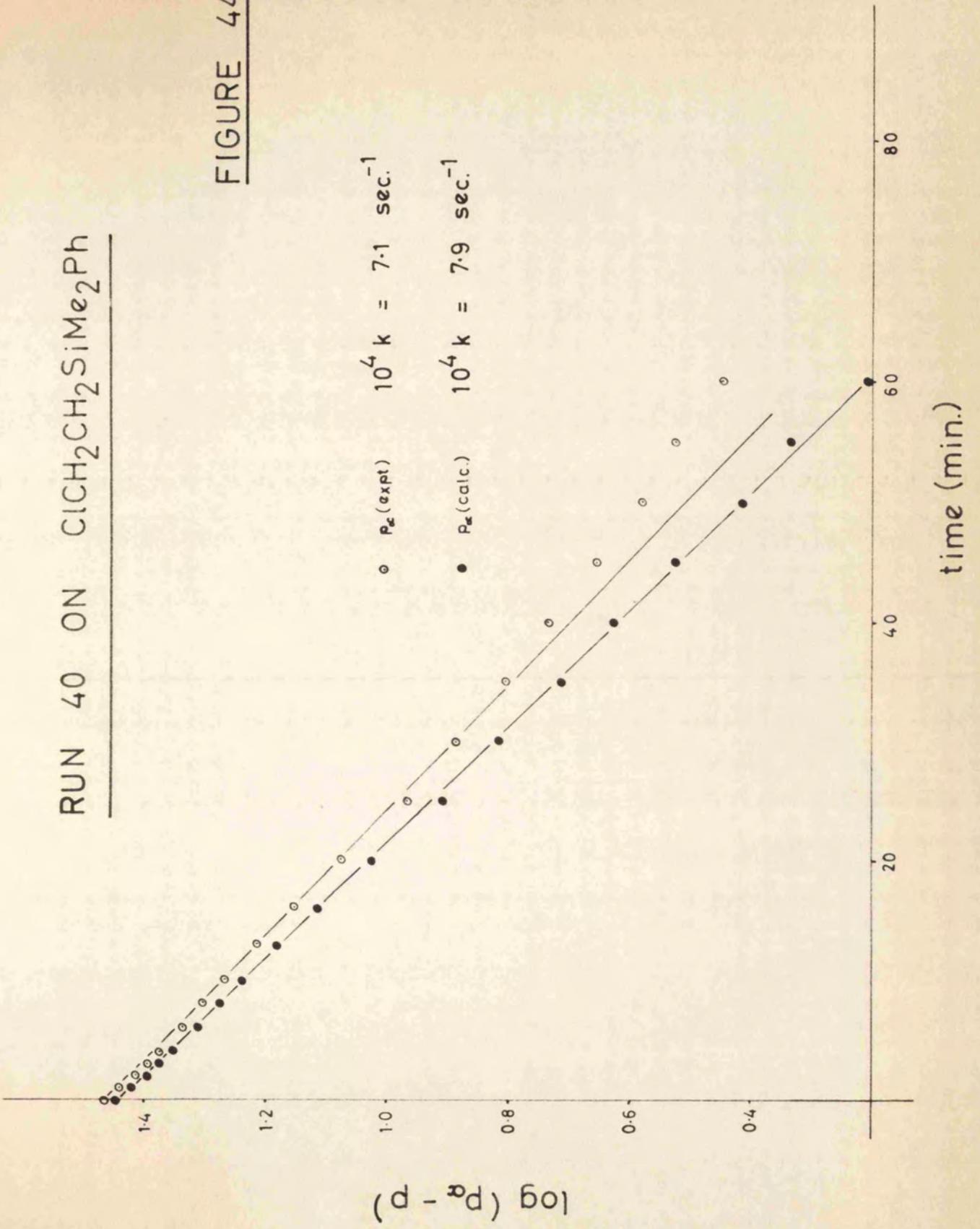
TABLE XXXXX

Data for Swinbourne plot on Run 40

Time (min.)	5	10	15	20	25	30	35
p (mm.)	56.5	60.6	64.3	67.2	69.9	71.4	72.8
Time (min.)	40	45	50	55	60	65	70
p (mm.)	73.8	74.3	75.3	75.8	76.3	76.8	77.0

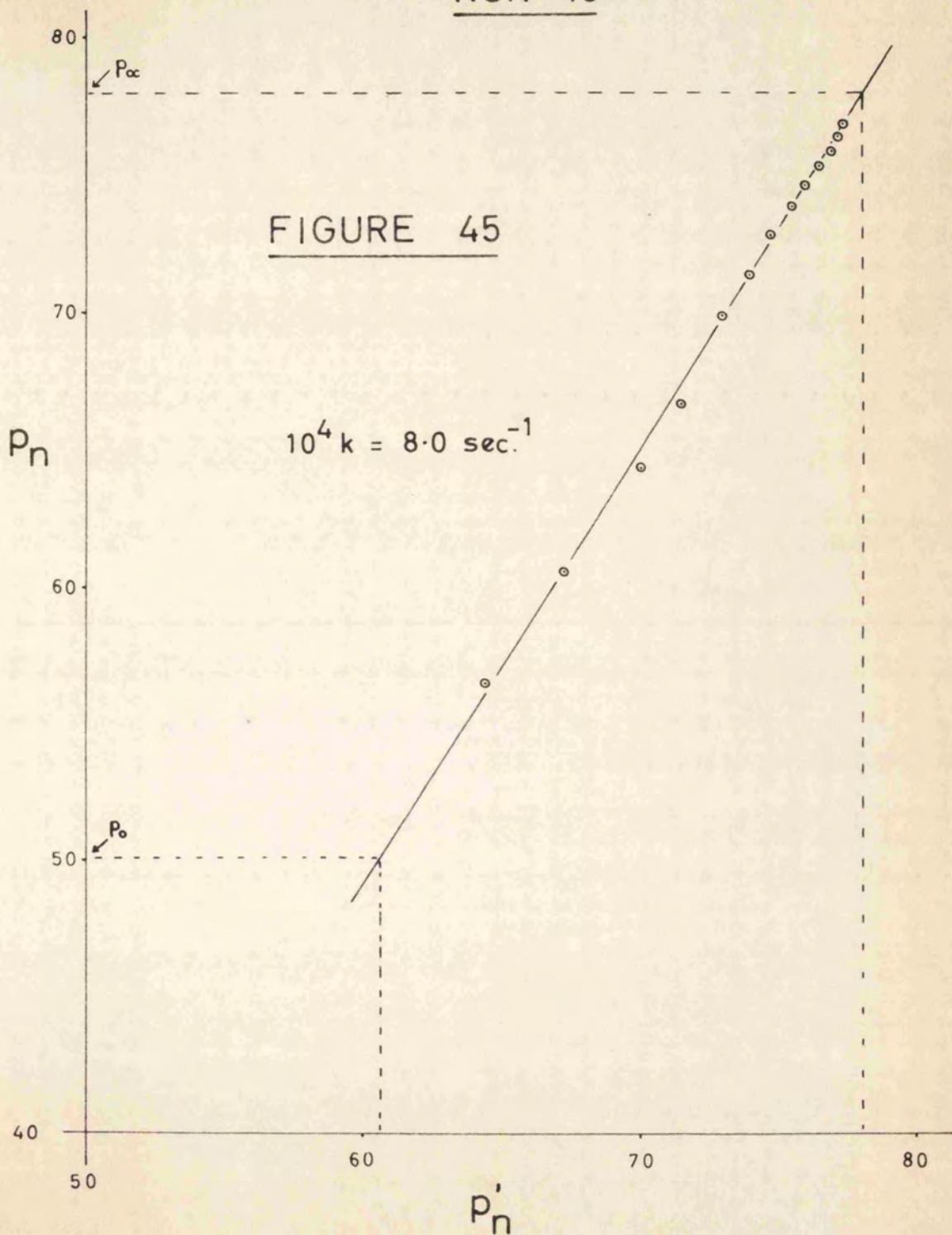
RUN 40 ON ClCH₂CH₂SiMe₂Ph

FIGURE 44



SWINBOURNE METHOD

RUN 40



(D) KINETIC RESULTS

(i) THERMAL DECOMPOSITION OF 2-CHLOROETHYLTRICHLOROSILANE

The following abbreviations are made in tabulating the results:

p_0 = Initial pressure of $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$, in mm., obtained by extrapolation

p_∞ = Final pressure of products, in mm., after more than 10 half-lives

Δp = Increase in pressure of reaction at time indicated, in mm.

$p_0 \text{In.}$, $p_0 \text{NO}$, $p_0 \text{C}_6\text{H}_6$ = Pressure of inhibitor, in mm., used

E = Ethylene

S = Silicon tetrachloride

V = Vinyltrichlorosilane

VC = Vinyl chloride

Et = Ethyltrichlorosilane

p_E , p_S , etc. = Pressure of component at time indicated

$p_{E\infty}$, $p_{S\infty}$, etc. = Pressure of component after more than 10 half-lives

$\%E$, $\%S$, etc. = Amount of component at p_∞ calculated as a % of p_0 so as to correlate with k_E/k , k_S/k , etc.

k = Over-all rate constant measured manometrically, in sec.^{-1}

k_E/k , k_S/k , etc. = Relative rate of formation of component

S/V = Surface area to Volume ratio

RUN 1 T = 381.6°C S/V = 0.28 cm.⁻¹
p₀ = 80.10 p_∞ = 157.9 p_∞/p₀ = 1.95 p₀ Inhib. = Nil
Time (min.) 6 11 20 30 40 70 95
Δp (mm.) 6.20 10.15 15.10 20.90 25.15 38.40 46.70

$$\underline{10^4 k = 1.50 \text{ sec.}^{-1}}$$

pS_∞ = 70, pV_∞ = 15 ; %S = 87, %V = 19

RUN 2 T = 399.3°C S/V = 0.28 cm.⁻¹
p₀ = 100.6 p_∞ = 190.4 p_∞/p₀ = 1.89 p₀ In. = Nil
Time (min.) 4 7 10 15 21 31 45
Δp (mm.) 9.25 15.40 21.00 30.10 38.05 50.55 62.10

$$\underline{10^4 k = 3.73 \text{ sec.}^{-1}}$$

pV_∞ = 31 ; %V = 29

RUN 3 T = 408.1°C S/V = 0.28 cm.⁻¹
p₀ = 35.85 p_∞ = 66.25 p_∞/p₀ = 1.85 p₀ In. = Nil
Time (min.) 3.5 6 9 12 20 28 37
Δp (mm.) 4.60 7.20 10.15 12.70 17.25 20.20 22.65

$$\underline{10^4 k = 5.98 \text{ sec.}^{-1}}$$

pS_∞ = 26, pV_∞ = 6.5 ; %S = 72, %V = 18

RUN 4 T = 406.4°C S/V = 0.28 cm.⁻¹
p₀ = 82.10 p_∞ = 163.4 p_∞/p₀ = 1.98 p₀ In. = Nil
Time (min.) 3.5 6.5 10 14 20 26 32
Δp (mm.) 8.00 16.70 23.80 30.15 38.20 45.45 47.15

$$\underline{10^4 k = 5.18 \text{ sec.}^{-1}}$$

pS_∞ = 55, pV_∞ = 11 ; %S = 67, %V = 13

RUN 17 T = 393.7°C S/V = 0.42 cm.⁻¹

 p₀ = 21.25 p_∞ = 40.85 p_∞/p₀ = 1.92 p₀In. = Nil

Time (min.) 4 10 16 23 32 45 60

Δ_p (mm.) 1.20 3.15 4.95 6.90 8.95 11.10 13.05

10⁴k = 2.94 sec.⁻¹

pE_∞ = 14.2, pS_∞ = 18.4, pV_∞ = 4.6 ; %E = 67, %S = 86, %V = 22

RUN 18. T = 393.7°C S/V = 0.42 cm.⁻¹

 p₀ = 29.80 p_∞ = 57.70 p_∞/p₀ = 1.93 p₀In. = Nil

Time (min.) 6 12 18 23 32 45 60

Δ_p (mm.) 3.10 5.70 7.95 9.75 12.25 15.20 17.90

10⁴k = 2.84 sec.⁻¹

pE_∞ = 24.2, pS_∞ = 26.4, pV_∞ = 5.5 ; %E = 82, %S = 89, %V = 18

RUN 19 T = 393.7°C S/V = 0.42 cm.⁻¹

 p₀ = 42.30 p_∞ = 85.50 p_∞/p₀ = 2.02 p₀In. = Nil

Time (min.) 4 10 16 23 32 45 60

Δ_p (mm.) 2.55 7.00 10.80 14.20 17.85 22.00 25.90

10⁴k = 2.94 sec.⁻¹

pE_∞ = 35.6, pS_∞ = 41.5, pV_∞ = 7.9 ; %E = 84, %S = 98, %V = 19

RUN 20 T = 393.7°C S/V = 0.42 cm.⁻¹

 p₀ = 38.20 p_∞ = 74.75 p_∞/p₀ = 1.96 p₀In. = Nil

Time (min.) 4 10 16 23 32 45 60

Δ_p (mm.) 2.25 5.55 8.65 11.85 15.15 19.00 22.40

10⁴k = 2.76 sec.⁻¹

pE_∞ = 32.1, pS_∞ = 35.6, pV_∞ = 6.3 ; %E = 84, %S = 93, %V = 17

RUN 21 T = 391.5°C S/V = 0.42 cm.⁻¹
p₀ = 52.40, p_∞ = 109.0 p_∞/p₀ = 2.08 p₀ In. = Nil
Time (min.) 4 6 8 10 16 23 29
Δp (mm.) 2.80 4.50 6.35 7.85 12.00 16.45 19.45
10⁴k = 2.64 sec.⁻¹
pE_∞ = 42.1, pV_∞ = 10.6 ; %E = 80, %V = 20

RUN 22 T = 391.5°C S/V = 0.42 cm.⁻¹
p₀ = 29.00 p₀ In. = Nil
Time (min.) 4 6 8 10 18 24 29
Δp (mm.) 1.65 2.40 3.25 4.10 6.90 8.75 10.15
10⁴k = 2.55 sec.⁻¹

RUN 23 T = 391.5°C S/V = 0.42 cm.⁻¹
p₀ = 50.00 p₀ In. = Nil
Time (min.) 4 6 12 16 20 23 29
Δp (mm.) 3.45 5.45 9.20 12.10 14.30 15.95 19.00
10⁴k = 2.62 sec.⁻¹
pE_∞ = 35.00, pS_∞ = 42.1, pV_∞ = 7.8 ; %E = 70, %S = 84, %V = 16

RUN 24 T = 398°C S/V = 0.42 cm.⁻¹
p₀ = 30.20 p_∞ = 60.00 p_∞/p₀ = 1.98 p₀ In. = Nil
Time (min.) 4 7 12 18 26 35 45
Δp (mm.) 2.40 4.00 6.55 9.55 12.45 15.20 17.40
10⁴k = 3.56 sec.⁻¹
pE_∞ = 21.3, pS_∞ = 24.0, pV_∞ = 3.5 ; %E = 70, %S = 79, %V = 12

RUN 25 T = 398°C S/V = 0.42 cm.⁻¹

 $p_0 = 43.00$ $p_{\infty} = 87.15$ $p_{\infty}/p_0 = 2.02$ $p_0 \text{ In.} = \text{Nil}$
Time (min.) 4 12 18 24 35 45 60
 Δp (mm.) 4.00 10.45 14.45 17.60 22.40 25.75 29.55
 $10^4 k = 3.65 \text{ sec.}^{-1}$

$pE_{\infty} = 28.1$, $pS_{\infty} = 39.0$, $pV_{\infty} = 3.4$; %E = 65, %S = 91, %V = 8

RUN 26 T = 398°C S/V = 0.42 cm.⁻¹

 $p_0 = 24.80$ $p_{\infty} = 48.00$ $p_{\infty}/p_0 = 1.94$ $p_0 \text{ In.} = \text{Nil}$
Time (min.) 4 8.5 14 20 26 35 45
 Δp (mm.) 1.85 3.65 5.85 7.70 9.55 11.60 13.65
 $10^4 k = 3.35 \text{ sec.}^{-1}$

$pE_{\infty} = 20.4$, $pV_{\infty} = 2.9$; %E = 82, %V = 12

RUN 27 T = 398°C S/V = 0.42 cm.⁻¹

 $p_0 = 31.25$ $p_{\infty} = 63.40$ $p_{\infty}/p_0 = 2.02$ $p_0 \text{ In.} = \text{Nil}$
Time (min.) 4 8.5 14 20 29 40 55
 Δp (mm.) 2.70 5.50 8.35 11.30 14.35 17.50 20.70
 $10^4 k = 3.71 \text{ sec.}^{-1}$

$pE_{\infty} = 23.7$, $pS_{\infty} = 26.6$, $pV_{\infty} = 4.9$; %E = 76, %S = 85, %V = 16

RUN 28 T = 398°C S/V = 0.42 cm.⁻¹

 $p_0 = 27.20$ $p_{\infty} = 51.60$ $p_{\infty}/p_0 = 1.92$ $p_0 \text{ In.} = \text{Nil}$
Time (min.) 4 8 12 18 23 40 60
 Δp (mm.) 2.80 4.80 6.80 9.20 11.05 15.30 18.40
 $10^4 k = 3.72 \text{ sec.}^{-1}$

RUN 48 (continued)

$10^4 k = 1.15 \text{ sec.}^{-1}$ $kE/k = 0.75$ $kVC/k = 0.11$

$pE_{\infty} = 22.4, pVC_{\infty} = 2.3$; $\%E = 69, \%VC = 7$

RUN 49

$T = 382.8^{\circ}\text{C}$ $S/V = 0.42 \text{ cm.}^{-1}$

$p_0 = 63.10$ $p_{\infty} = 122.5$ $p_{\infty}/p_0 = 1.94$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	6	10	15	21	28	35	45	60
Δp (mm.)	3.45	6.00	8.75	11.90	15.10	18.30	22.50	28.00

$10^4 k = 1.62 \text{ sec.}^{-1}$

$pE_{\infty} = 46.5, pV_{\infty} = 14.0, pVC_{\infty} = 3.0$; $\%E = 74, \%V = 22, \%VC = 5$

RUN 50

$T = 382.8^{\circ}\text{C}$ $S/V = 0.42 \text{ cm.}^{-1}$

$p_0 = 41.40$ $p_{\infty} = 81.50$ $p_{\infty}/p_0 = 1.97$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	5	10	16	22	31	40	50	80
Δp (mm.)	1.70	4.10	6.40	8.40	11.05	13.50	16.00	21.85
pE (mm.)	-	2.5	4.0	5.6	7.5	9.2	11.0	14.0
pVC (mm.)	-	0.65	0.95	1.3	1.5	1.6	1.5	-

$10^4 k = 1.63 \text{ sec.}^{-1}$ $kE/k = 0.68$ $kVC/k = 0.16$

$pE_{\infty} = 29.0, pV_{\infty} = 8.0, pVC_{\infty} = 3.2$; $\%E = 70, \%V = 19, \%VC = 8$

RUN 51

$T = 382.8^{\circ}\text{C}$ $S/V = 0.42 \text{ cm.}^{-1}$

$p_0 = 41.70$ $p_{\infty} = 85.00$ $p_{\infty}/p_0 = 2.04$ $p_0 \text{C}_6\text{H}_{10} = 31.20$

Time (min.)	12	20	35	60	91	120	160	240
Δp (mm.)	4.35	6.80	11.05	17.10	23.20	27.35	32.05	37.80
pE (mm.)	2.3	4.9	7.5	12.2	17.5	22.0	26.5	29.4
pVC (mm.)	0.6	1.0	1.5	2.0	-	-	-	-

$10^4 k = 1.46 \text{ sec.}^{-1}$ $kE/k = 0.75$ $kVC/k = 0.14$

$pVC_{\infty} = 5.5$; $\%VC = 13$

RUN 52 T = 382.8°C S/V = 0.42 cm.⁻¹

$p_0 = 43.80$ $p_{\infty} = 84.50$ $p_{\infty}/p_0 = 1.93$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	12	25	40	70	111	201	270
Δp (mm.)	1.50	4.75	9.15	13.90	21.00	28.00	35.10	37.90
pE (mm.)	1.8	3.5	6.3	9.8	14.7	19.0	23.5	25.0
pVC (mm.)	0.3	0.7	1.3	1.7	1.5	1.4	-	-

$10^4 k = 1.59 \text{ sec.}^{-1}$ $kE/k = 0.69$ $kVC/k = 0.14$

$pE_{\infty} = 28.4$, $pVC_{\infty} = 3.1$; $\%E = 65$, $\%VC = 7$

RUN 53 T = 380.6°C S/V = 0.42 cm.⁻¹

$p_0 = 34.80$ $p_{\infty} = 67.90$ $p_{\infty}/p_0 = 1.95$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	8	13	23	35	50	70	110	171
Δp (mm.)	1.80	3.45	6.05	8.60	11.80	15.40	20.80	25.70
pE (mm.)	-	2.5	4.2	6.3	7.5	10.8	14.2	17.2
pV (mm.)	-	-	-	-	2.3	3.2	4.0	-
pVC (mm.)	-	0.55	1.1	1.45	1.80	1.75	1.5	1.2

$10^4 k = 1.42 \text{ sec.}^{-1}$ $kE/k = 0.69$ $kVC/k = 0.18$

$pV_{\infty} = 6.3$, $pVC_{\infty} = 2.1$; $\%V = 20$, $\%VC = 6$

RUN 54 T = 380.6°C S/V = 0.42 cm.⁻¹

$p_0 = 36.50$ $p_{\infty} = 71.90$ $p_{\infty}/p_0 = 1.97$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	14	25	40	60	100	120
Δp (mm.)	1.50	2.60	3.90	6.80	10.30	14.40	20.20	22.80
pE (mm.)	-	-	2.3	4.2	7.0	9.5	13.6	15.5
pVC (mm.)	-	-	0.6	1.2	1.7	1.9	1.4	-

$10^4 k = 1.43 \text{ sec.}^{-1}$ $kE/k = 0.67$ $kVC/k = 0.16$

$pE_{\infty} = 24.7$, $pV_{\infty} = 9.3$, $pVC_{\infty} = 2.0$; $\%E = 68$, $\%V = 25$, $\%VC = 5$

RUN 55 T = 401.2°C S/V = 0.42 cm.⁻¹

$p_0 = 42.50$ $p_{\infty} = 82.90$ $p_{\infty}/p_0 = 1.95$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	3	7	14	19	24	40	65	95
Δp (mm.)	3.00	7.20	13.00	16.60	19.70	26.70	33.35	36.70
pE (mm.)	2.1	4.9	9.0	-	14.0	20.4	24.5	-
pVC (mm.)	0.35	0.8	1.5	-	1.95	1.75	1.4	-

$10^4 k = 4.23 \text{ sec.}^{-1}$ $kE/k = 0.72$ $kVC/k = 0.12$

$pE_{\infty} = 33.0$, $pV_{\infty} = 8.4$, $pVC_{\infty} = 2.3$; $\%E = 78$, $\%V = 20$, $\%VC = 5$

RUN 56 T = 380.6°C S/V = 2.39 cm.⁻¹

$p_0 = 29.50$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	8	13	20	27	50	80
Δp (mm.)	1.90	2.55	3.70	5.25	6.60	10.80	16.40

$10^4 k = 1.45 \text{ sec.}^{-1}$

RUN 57 T = 380.6°C S/V = 2.39 cm.⁻¹

$p_0 = 36.20$ $p_{\infty} = 70.00$ $p_{\infty}/p_0 = 1.93$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	12	22	30	36	55	80	130
Δp (mm.)	3.40	6.50	8.45	10.00	14.00	18.00	23.60
pE (mm.)	3.0	4.9	-	7.2	10.2	13.6	17.5
pVC (mm.)	0.6	1.1	-	1.6	1.9	1.6	1.55

$10^4 k = 1.49 \text{ sec.}^{-1}$ $kE/k = 0.73$ $kVC/k = 0.17$

$pE_{\infty} = 25.1$, $pV_{\infty} = 8.0$, $pVC_{\infty} = 2.0$; $\%E = 69$, $\%V = 22$, $\%VC = 6$

RUN 58 T = 380.6°C S/V = 2.39 cm.⁻¹
 $p_0 = 24.45$ $p_{\infty} = 46.00$ $p_{\infty}/p_0 = 1.88$ $p_0 VC = 7.25$
 Time (min.) 10 17 26 35 45 55 71
 Δp (mm.) 2.35 3.75 5.55 6.75 8.55 9.80 11.85

$$\underline{10^4 k = 1.42 \text{ sec.}^{-1}}$$

RUN 58A T = 380.6°C S/V = 2.39 cm.⁻¹
 $p_0 = 27.50$ $p_{\infty} = 43.20$ $p_{\infty}/p_0 = 1.57$ $p_0 \text{HSiCl}_3 = 27.60$
 Time (min.) 5 10 16 22 30 45 60 90
 Δp (mm.) 3.35 5.30 7.20 8.70 10.40 12.60 14.00 15.35

$10^4 k$ not determined

$pE_{\infty} = 10.9$, $pV_{\infty} = 6.2$, $pVC_{\infty} = 0$; %E = 40, %V = 23, %VC = 0, %Et = high

RUN 59 T = 385°C S/V = 0.38 cm.⁻¹
 $p_0 = 18.70$ $p_{\infty} = 37.30$ $p_{\infty}/p_0 = 1.99$ $p_0 \text{In.} = \text{Nil}$
 Time (min.) 5 10 20 30 40 50 70
 Δp (mm.) 1.10 2.30 4.50 6.35 7.95 9.25 11.65
 pE (mm.) - - 3.2 - 5.4 - 8.2

$$\underline{10^4 k = 2.31 \text{ sec.}^{-1}} \quad \underline{kE/k = 0.69}$$

$pE_{\infty} = 12.8$, ; %E = 69

RUN 60 T = 385°C S/V = 0.38 cm.⁻¹
 $p_0 = 51.65$ $p_{\infty} = 99.00$ $p_{\infty}/p_0 = 1.91$ $p_0 \text{In.} = \text{Nil}$
 Time (min.) 5 14 25 35 45 55 115
 Δp (mm.) 3.75 8.05 12.95 16.75 20.50 23.65 35.75
 pE (mm.) - 5.2 9.0 12.0 14.2 17.0 27.25
 pVC (mm.) - 0.9 1.6 2.1 2.5 2.7 3.3

RUN 60 (continued)

$$\underline{10^4 k = 1.76 \text{ sec.}^{-1}} \quad \underline{kE/k = 0.74} \quad \underline{kVC/k = 0.13}$$

$$pE_{\infty} = 40.0, pV_{\infty} = 10.0, pVC_{\infty} = 3.3 \quad ; \quad \%E = 77, \%V = 19, \%VC = 6$$

RUN 61

$$T = 385^{\circ}\text{C} \quad S/V = 0.38 \text{ cm.}^{-1}$$

$$p_0 = 56.40 \quad p_{\infty} = 106.0 \quad p_{\infty}/p_0 = 1.88 \quad p_0 \text{In.} = \text{Nil}$$

Time (min.)	5	10	16	26	40	60	80
Δp (mm.)	4.00	6.85	10.00	14.60	20.45	27.00	31.90
pE (mm.)	2.0	4.0	6.0	9.5	12.4	20.5	22.5
pVC (mm.)	0.4	0.8	1.4	2.0	2.6	3.5	4.0

$$\underline{10^4 k = 1.76 \text{ sec.}^{-1}} \quad \underline{kE/k = 0.71} \quad \underline{kVC/k = 0.15}$$

$$pE_{\infty} = 38.0, pV_{\infty} = 9.2, pVC_{\infty} = 3.8 \quad ; \quad \%E = 68, \%V = 16, \%VC = 7$$

RUN 62

$$T = 385^{\circ}\text{C} \quad S/V = 0.38 \text{ cm.}^{-1}$$

$$p_0 = 37.80 \quad p_{\infty} = 73.15 \quad p_{\infty}/p_0 = 1.93 \quad p_0 \text{In.} = \text{Nil}$$

Time (min.)	5	10	16	23	35	50	70
Δp (mm.)	2.30	4.30	6.55	8.75	12.65	16.50	20.70
pE (mm.)	-	2.8	4.5	6.1	8.2	11.8	-
pVC (mm.)	-	0.65	1.0	1.4	1.8	2.2	-

$$\underline{10^4 k = 1.88 \text{ sec.}^{-1}} \quad \underline{kE/k = 0.70} \quad \underline{kVC/k = 0.16}$$

$$pE_{\infty} = 28.3, pV_{\infty} = 6.0, pVC_{\infty} = 3.5 \quad ; \quad \%E = 75, \%V = 16, \%VC = 9$$

RUN 63

$$T = 383.3^{\circ}\text{C} \quad S/V = 0.38 \text{ cm.}^{-1}$$

$$p_0 = 49.10 \quad p_{\infty} = 93.70 \quad p_{\infty}/p_0 = 1.91 \quad p_0 \text{In.} = \text{Nil}$$

Time (min.)	5	11	18	26	35	55	85
Δp (mm.)	2.10	4.90	7.70	10.75	13.80	19.80	26.50
pE (mm.)	2.0	3.5	5.5	7.5	10.2	-	20.2
pS (mm.)	-	3.2	5.2	7.5	10.0	-	19.5

RUN 63 (continued)

$10^4 k = 1.57 \text{ sec.}^{-1}$

$kE/k = 0.75$

$kS/k = 0.725$

$pE_{\infty} = 34.0, pS_{\infty} = 39.5$

; %E = 69, %S = 80

RUN 64

$T = 383.3^{\circ}\text{C}$

$S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 29.90$

$p_{\infty} = 58.30$

$p_{\infty}/p_0 = 1.95$

$p_0 \text{ In.} = \text{Nil}$

Time (min.) 5 10 16 23 32 45 60

Δp (mm.) 1.95 3.50 4.95 6.65 8.65 11.20 13.80

pE (mm.) 0.75 2.0 3.0 4.2 6.5 7.5 -

pS (mm.) 1.5 2.25 3.2 4.0 6.0 7.5 -

$10^4 k = 1.68 \text{ sec.}^{-1}$

$kE/k = 0.70$

$kS/k = 0.71$

$pE_{\infty} = 20.0, pS_{\infty} = 20.0, pV_{\infty} = 7.0$; %E = 67, %S = 67, %V = 23

RUN 65

$T = 383.3^{\circ}\text{C}$

$S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 22.40$

$p_0 \text{ In.} = \text{Nil}$

Time (min.) 4 10 20 29 40 56 70

Δp (mm.) 1.50 2.85 4.55 6.05 7.65 9.80 11.40

$10^4 k = 1.62 \text{ sec.}^{-1}$

RUN 66

$T = 383.3^{\circ}\text{C}$

$S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 50.50$

$p_0 \text{ In.} = \text{Nil}$

Time (min.) 4 8 16 23 35 50 70

Δp (mm.) 3.45 5.40 8.90 11.70 16.05 20.90 26.10

$10^4 k = 1.68 \text{ sec.}^{-1}$

RUN 70 $T = 385^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 26.00$ $p_{\infty} = 51.20$ $p_{\infty}/p_0 = 1.97$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	23	32	45	65
Δp (mm.)	1.80	2.85	4.35	5.60	7.40	9.50	12.30
pE (mm.)	1.0	1.63	3.1	3.9	5.5	-	-
pS (mm.)	-	1.4	2.6	3.5	5.05	-	-
pVC (mm.)	0.15	0.35	0.5	0.6	0.75	-	-

$10^4 k = 1.63 \text{ sec.}^{-1}$ $kE/k = 0.74$ $kS/k = 0.72$ $kVC/k = 0.12$

$pE_{\infty} = 17.3$, $pS_{\infty} = 18.7$, $pV_{\infty} = 6.2$; $\%E = 67$, $\%S = 72$, $\%V = 24$

RUN 71 $T = 380.6^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 37.70$ $p_{\infty} = 72.40$ $p_{\infty}/p_0 = 1.92$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	23	32	45	65	97
Δp (mm.)	1.55	3.15	4.90	6.80	9.30	12.30	16.70	19.80
pE (mm.)	0.75	2.05	3.90	5.0	7.1	-	-	-
pVC (mm.)	0.2	0.45	0.7	1.0	1.15	-	-	-

$10^4 k = 1.49 \text{ sec.}^{-1}$ $kE/k = 0.71$ $kVC/k = 0.14$

$pE_{\infty} = 27.6$, $pV_{\infty} = 8.0$; $\%E = 73$, $\%V = 21$

RUN 72 $T = 382.8^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 32.40$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	23	32	45	65	85
Δp (mm.)	1.50	3.00	4.60	6.40	8.55	11.10	14.70	17.45
pE (mm.)	1.0	2.0	3.14	5.1	6.5	-	-	-
pVC (mm.)	0.35	0.65	1.0	1.2	1.0	-	-	-

$10^4 k = 1.60 \text{ sec.}^{-1}$ $kE/k = 0.70$ $kVC/k = 0.20$

RUN 73 $T = 382.8^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 28.10$ $p_{\infty} = 54.50$ $p_{\infty}/p_0 = 1.94$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	6	10	16	23	32	45	65	105
Δp (mm.)	1.50	2.45	3.85	5.25	7.10	9.30	12.40	16.90
pE (mm.)	1.0	1.45	2.8	3.9	5.7	-	-	-
pVC (mm.)	0.2	0.45	0.55	0.55	0.50	-	-	-

$10^4 k = 1.49 \text{ sec.}^{-1}$ $kE/k = 0.72$ $kVC/k = 0.16$

$pE_{\infty} = 20.3$, $pS_{\infty} = 22.1$, $pV_{\infty} = 6.2$; $\%E = 72$, $\%S = 76$, $\%V = 22$

RUN 74 $T = 382.8^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 21.45$ $p_{\infty} = 42.60$ $p_{\infty}/p_0 = 1.99$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	6	10	16	22	32	48	65	85
Δp (mm.)	1.75	2.55	3.60	4.55	6.10	8.30	10.20	12.05

$10^4 k = 1.57 \text{ sec.}^{-1}$

$pE_{\infty} = 16.1$, $pS_{\infty} = 16.1$, $pV_{\infty} = 5.0$; $\%E = 75$, $\%S = 75$, $\%V = 23$

RUN 75 $T = 382.8^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 26.20$ $p_{\infty} = 51.60$ $p_{\infty}/p_0 = 1.97$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	23	32	45	65	95
Δp (mm.)	1.20	2.45	3.70	5.15	6.90	9.20	12.15	15.50
pE (mm.)	0.45	1.63	2.45	3.9	5.6	-	-	-
pVC (mm.)	0.2	0.6	0.77	-	-	-	-	-

$10^4 k = 1.60 \text{ sec.}^{-1}$ $kE/k = 0.70$ $kVC/k = 0.21$

$pS_{\infty} = 20.0$, $pV_{\infty} = 6.8$; $\%S = 76$, $\%V = 26$

RUN 76 T = 382.8°C S/V = 0.38 cm.⁻¹

 p₀ = 41.20 p_∞ = 79.90 p_∞/p₀ = 1.94 p₀In. = Nil

Time (min.)	5	10	17	23	32	45	65	105
Δp (mm.)	1.90	3.75	6.10	8.00	10.60	14.20	18.50	24.90
pE (mm.)	1.0	1.78	3.88	5.2	7.7	-	-	-
pVC (mm.)	0.2	0.7	1.0	1.0	0.95	-	-	-

10⁴k = 1.56 sec.⁻¹ kE/k = 0.65 kVC/k = 0.16

pV_∞ = 10.5 ; %V = 25

RUN 77 T = 382.8°C S/V = 0.38 cm.⁻¹

 p₀ = 41.10 p₀In. = Nil

Time (min.)	5	10	16	23	32	45	65	85
Δp (mm.)	1.80	3.70	5.70	8.00	10.60	14.10	18.50	21.00
pE (mm.)	1.4	2.8	4.6	5.95	8.25	-	-	-
pVC (mm.)	0.25	0.65	0.9	0.9	0.85	-	-	-

10⁴k = 1.58 sec.⁻¹ kE/k = 0.74 kVC/k = 0.16

RUN 78 T = 402.6°C S/V = 0.38 cm.⁻¹

 p₀ = 16.40 p_∞ = 32.25 p_∞/p₀ = 1.96 p₀In. = Nil

Time (min.)	5	10	16	23	32	45	60	80
Δp (mm.)	2.20	4.00	5.80	7.50	9.40	11.20	12.70	13.80
pE (mm.)	0.95	2.8	3.8	5.5	7.0	-	-	-
pS (mm.)	1.0	2.25	4.0	6.0	7.0	-	-	-

10⁴k = 4.38 sec.⁻¹ kE/k = 0.74 kS/k = 0.73

pE_∞ = 12.5, pS_∞ = 12.0, pV_∞ = 4.1 ; %E = 76, %S = 72, %V = 25

RUN 79 T = 402.6°C S/V = 0.38 cm.⁻¹
p₀ = 34.30 p_∞ = 66.50 p_∞/p₀ = 1.94 p₀ In. = Nil
Time (min.) 5 10 16 23 34 45 65
Δp (mm.) 4.15 7.95 11.90 15.70 20.10 23.20 26.80
pS (mm.) 3.0 5.5 7.0 10.0 13.5 - -
10⁴k = 4.36 sec.⁻¹ kS/k = 0.67
pS_∞ = 23.8, pV_∞ = 6.1 ; %S = 70, %V = 18

RUN 80 T = 402.6°C S/V = 0.38 cm.⁻¹
p₀ = 26.00 p₀ In. = Nil
Time (min.) 5 10 16 23 35 50 70
Δp (mm.) 3.30 6.30 9.25 12.10 16.00 19.05 21.60
pS (mm.) - 4.3 6.0 8.0 11.0 - -
10⁴k = 4.52 sec.⁻¹ kS/k = 0.69

RUN 81 T = 402.6°C S/V = 0.38 cm.⁻¹
p₀ = 28.20 p₀ In. = Nil
Time (min.) 5 10 16 23 35 45 55
Δp (mm.) 3.40 6.60 9.70 12.80 16.90 19.40 21.15
pE (mm.) 2.15 5.0 6.75 9.0 12.5 - -
pS (mm.) 2.5 - 7.0 10.0 12.0 - -
10⁴k = 4.40 sec.⁻¹ kE/k = 0.73 kS/k = 0.71

RUN 82 T = 402.6°C S/V = 0.38 cm.⁻¹

$p_0 = 28.25$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	28	40	50	70
Δp (mm.)	2.80	6.05	9.30	14.45	17.95	20.15	23.05
pE (mm.)	-	-	6.7	9.7	13.1	16.1	-
pS (mm.)	-	-	-	10.0	12.5	14.5	-
pV (mm.)	-	-	1.1	1.7	2.0	2.5	-

$10^4 k = 4.20 \text{ sec.}^{-1}$ $kE/k = 0.725$ $kS/k = 0.71$ $kV/k = 0.12$

RUN 83 T = 402.6°C S/V = 0.38 cm.⁻¹

$p_0 = 33.20$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	27	38	49	75
Δp (mm.)	5.15	8.60	12.20	17.30	21.20	23.80	27.30
pE (mm.)	-	-	7.6	14.3	16.0	18.5	22.0
pV (mm.)	-	-	1.42	2.15	2.45	3.05	3.7

$10^4 k = 4.45 \text{ sec.}^{-1}$ $kE/k = 0.77$ $kV/k = 0.12$

RUN 84 T = 402.6°C S/V = 0.38 cm.⁻¹

$p_0 = 17.50$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	27	38	49	70
Δp (mm.)	2.80	4.60	6.50	9.30	11.45	12.95	14.50
pE (mm.)	-	-	4.25	6.8	8.35	9.4	-
pS (mm.)	-	-	4.0	6.4	7.4	9.0	-
pV (mm.)	-	-	-	0.95	1.15	1.43	-

$10^4 k = 4.45 \text{ sec.}^{-1}$ $kE/k = 0.76$ $kS/k = 0.72$ $kV/k = 0.11$

RUN 85 $T = 399.3^{\circ}\text{C}$ $S/v = 0.38 \text{ cm}^{-1}$

$p_0 = 45.00$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	16	27	38	49	65	100
Δp (mm.)	4.70	9.60	14.70	21.80	27.00	30.60	34.00	37.90
p_E (mm.)	-	-	9.6	14.3	18.0	20.5	-	-
p_S (mm.)	-	-	9.0	14.7	17.5	21.0	-	-
p_V (mm.)	-	-	1.3	2.0	2.5	3.6	-	-

$10^4 k = 3.84 \text{ sec}^{-1}$ $kE/k = 0.70$ $kS/k = 0.69$ $kV/k = 0.10$

RUN 86 $T = 402.6^{\circ}\text{C}$ $S/V = 0.38 \text{ cm}^{-1}$

$p_0 = 25.00$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	10	16	27	38	49	65	90
Δp (mm.)	5.55	7.90	11.85	14.60	16.50	18.50	20.15
p_E (mm.)	-	6.0	8.5	11.0	12.0	-	-
p_S (mm.)	-	5.0	8.5	10.0	11.5	-	-
p_V (mm.)	-	1.1	1.6	2.1	2.7	-	-

$10^4 k = 4.36 \text{ sec}^{-1}$ $kE/k = 0.75$ $kS/k = 0.70$ $kV/k = 0.14$

RUN 94 $T = 402.6^{\circ}\text{C}$ $S/V = 0.38 \text{ cm}^{-1}$

$p_0 = 29.95$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	3	9	16	23	32	45	60	80
Δp (mm.)	2.15	6.55	10.50	13.70	17.05	20.35	22.95	25.05
p_E (mm.)	0.7	4.1	6.7	9.5	12.3	-	-	17.5

$10^4 k = 4.36 \text{ sec}^{-1}$ $kE/k = 0.72$

RUN 98 $T = 407.3^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 20.40$ $p_{\infty} = 40.05$ $p_{\infty}/p_0 = 1.96$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	6	10	17	29	40	50	60
Δp (mm.)	3.65	5.95	9.10	12.80	14.90	16.10	17.00
pE (mm.)	2.0	-	8.0	11.6	13.35	-	-
pV (mm.)	-	-	0.9	1.7	2.1	-	-

$10^4 k = 5.65 \text{ sec.}^{-1}$ $kE/k = 0.83$ $kV/k = 0.13$

RUN 99 $T = 407.3^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 52.00$ $p_{\infty} = 99.40$ $p_{\infty}/p_0 = 1.91$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	3	6	10	17	29	40	50	60
Δp (mm.)	4.20	9.00	14.60	22.40	31.10	36.10	38.70	40.60
pE (mm.)	-	5.75	-	14.4	22.05	26.4	-	-
pV (mm.)	-	-	-	2.0	2.65	3.2	-	-

$10^4 k = 5.24 \text{ sec.}^{-1}$ $kE/k = 0.70$ $kV/k = 0.09$

RUN 100 $T = 407.3^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 36.20$ $p_0 \text{ In.} = \text{Nil}$

Time (min.)	5	10	14	20	26	36	45	60
Δp (mm.)	6.10	11.20	14.70	18.70	21.80	25.50	27.70	30.00
pE (mm.)	-	-	10.6	-	16.0	19.5	-	-
pV (mm.)	-	-	1.55	-	2.2	3.0	-	-

$10^4 k = 6.03 \text{ sec.}^{-1}$ $kE/k = 0.74$ $kV/k = 0.11$

RUN 101 T = 407.3°C S/V = 0.38 cm.⁻¹

$p_0 = 27.15$ $p_{\infty} = 52.90$ $p_{\infty}/p_0 = 1.95$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	3	6	10	16	26	36	50	65
Δp (mm.)	2.80	5.35	8.45	12.10	16.50	19.35	21.55	23.15
pE (mm.)	1.7	-	-	9.7	14.5	17.6	-	-
pV (mm.)	-	-	-	1.6	2.2	2.6		

$\underline{10^4 k = 5.80 \text{ sec.}^{-1}}$ $\underline{kE/k = 0.88}$ $\underline{kV/k = 0.14}$

RUN 102 T = 407.3°C S/V = 0.38 cm.⁻¹

$p_0 = 20.90$ $p_0 \text{C}_6\text{H}_6\text{O} = 9.70$

Time (min.)	6	10	16	23	32	44	60
Δp (mm.)	4.15	6.45	9.10	11.55	13.85	15.75	17.25
pE (mm.)	-	-	6.6	-	10.8	13.6	-

$\underline{10^4 k = 6.00 \text{ sec.}^{-1}}$ $\underline{kE/k = 0.74}$

RUN 103 T = 407.3°C S/V = 0.38 cm.⁻¹

$p_0 = 23.40$ $p_0 \text{C}_6\text{H}_6\text{O} = 21.20$

Time (min.)	3	10	16	20	29	42	55
Δp (mm.)	2.90	7.60	10.60	12.30	15.20	17.80	19.40
pE (mm.)	1.45	-	7.45	-	10.4	14.0	17.3

$\underline{10^4 k = 6.30 \text{ sec.}^{-1}}$ $\underline{kE/k = 0.72}$

RUN 104 T = 407.3°C S/V = 0.38 cm.⁻¹

$p_0 = 40.70$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	3	5	7	10	14	18
Δp (mm.)	4.30	6.80	9.00	11.95	15.60	18.60

$\underline{10^4 k = 5.65 \text{ sec.}^{-1}}$

RUN 105 T = 407.3°C S/V = 0.38 cm.⁻¹
p₀ = 40.00 p₀In. = Nil

Time (min.)	3	5	7	10	14	19
Δp (mm.)	4.60	7.20	9.50	12.60	16.30	20.10

10⁴k = 6.08 sec.⁻¹

RUN 106 T = 407.3°C S/V = 0.38 cm.⁻¹
p₀ = 11.50 p₀In. = Nil

Time (min.)	3	5	8	10	14	18
Δp (mm.)	1.45	2.10	3.00	3.65	4.70	5.60

10⁴k = 6.10 sec.⁻¹

RUN 107 T = 379.3°C S/V = 0.38 cm.⁻¹
p₀ = 40.85 p₀In. = Nil

Time (min.)	4	10	15	21	30	45	60
Δp (mm.)	1.65	3.50	5.05	6.65	9.05	12.80	16.00

10⁴k = 1.37 sec.⁻¹

RUN 108 T = 379.3°C S/V = 0.38 cm.⁻¹
p₀ = 29.25 p₀In. = Nil

Time (min.)	4	8	14	20	32	45	60
Δp (mm.)	1.35	2.25	3.50	4.75	7.00	9.25	11.35

10⁴k = 1.31 sec.⁻¹

RUN 109 $T = 379.3^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 30.45$ $p_{\infty} = 59.70$ $p_{\infty}/p_0 = 1.96$ $p_0 \text{C}_2\text{H}_4 = 11.60$

Time (min.)	3	8	14	20	28	55	80
Δp (mm.)	1.25	2.45	3.75	5.10	6.65	11.35	14.70
pE (mm.)	0.15	-	2.60	3.60	5.0	8.4	10.9
pVC (mm.)	-	0.3	0.65	0.85	0.9	0.8	-

$10^4 k = 1.35 \text{ sec.}^{-1}$ $kE/k = 0.74$ $kVC/k = 0.18$

RUN 110 $T = 377.6^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 37.50$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	10	14	23	35	47	60	100
Δp (mm.)	2.40	3.40	5.50	8.30	10.55	13.05	18.80
pE (mm.)	2.6	-	4.9	6.6	8.1	10.0	13.4
pV (mm.)	0.5	-	1.15	1.85	2.2	-	-

$10^4 k = 1.22 \text{ sec.}^{-1}$ $kE/k = 0.75$ $kV/k = 0.20$

RUN 111 $T = 377.6^{\circ}\text{C}$ $S/V = 0.38 \text{ cm.}^{-1}$

$p_0 = 47.40$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	5	10	15	27	40	60	80
Δp (mm.)	1.80	3.40	5.00	8.10	11.60	16.10	19.85
pE (mm.)	1.2	-	3.2	5.8	8.0	-	14.0

$10^4 k = 1.14 \text{ sec.}^{-1}$ $kE/k = 0.70$

RUN 112 T = 382.9°C S/V = 0.38 cm.⁻¹
p₀ = 33.10 p₀In. = Nil
Time (min.) 5 10 18 28 37 45 57
Δp (mm.) 1.45 3.05 5.00 7.50 9.40 11.20 13.40
10⁴k = 1.52 sec.⁻¹

RUN 113 T = 382.8°C S/V = 0.78 cm.⁻¹
p₀ = 99.0 p_∞ = 185.6 p_∞/p₀ = 1.88 p₀In. = Nil
Time (min.) 4 12 17 23 35 50
Δp (mm.) 3.0 11.40 14.80 19.50 28.40 37.60
pE (mm.) 2.5 7.5 - 13.5 20.0 26.5
10⁴k = 1.595 sec.⁻¹ kE/k = 0.70

RUN 114 T = 385°C S/V = 0.78 cm.⁻¹
p₀ = 31.00 p_∞ = 59.00 p_∞/p₀ = 1.90 p₀In. = Nil
Time (min.) 3 5 7 11 15 18
Δp (mm.) 1.60 2.30 2.85 4.00 5.15 5.85
10⁴k = 1.75 sec.⁻¹

RUN 115 T = 385°C S/V = 0.78 cm.⁻¹
p₀ = 29.55 p_∞ = 58.20 p_∞/p₀ = 1.97 p₀In. = Nil
Time (min.) 3 4 5 6 7 8 9
Δp (mm.) 0.95 1.35 1.65 2.05 2.30 2.60 2.95
10⁴k = 1.88 sec.⁻¹

RUN 120 T = 417°C S/V = 0.78 cm.⁻¹

$p_0 = 49.40$ $p_{\infty} = 95.00$ $p_{\infty}/p_0 = 1.92$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	3	6	10	14	20	26	38	60
Δp (mm.)	9.10	15.40	22.00	26.75	32.10	35.60	39.60	41.60
pE (mm.)	5.8	-	-	19.0	-	25.2	29.0	-

$10^4 k = 9.22 \text{ sec.}^{-1}$ $kE/k = 0.69$

$pE_{\infty} = 31.0$, $pV_{\infty} = 13.0$, $pVC_{\infty} = 1.5$, $pEt_{\infty} = 0.5$

%E = 69 , %V = 26 , %VC = 3 , %Et = 1

RUN 121 T = 356°C S/V = 0.78 cm.⁻¹

$p_0 = 45.70$ $p_{\infty} = 92.00$ $p_{\infty}/p_0 = 1.93$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	10	20	30	40	60	90	120	160
Δp (mm.)	0.70	2.05	2.90	4.10	6.00	8.80	10.90	14.00

$10^4 k = 0.384 \text{ sec.}^{-1}$

RUN 122 T = 356°C S/V = 0.78 cm.⁻¹

$p_0 = 43.00$ $p_{\infty} = 81.70$ $p_{\infty}/p_0 = 1.90$ $p_0 \text{NO} = 20.40$

Time (min.)	20	30	40	50	70	90	120
Δp (mm.)	2.00	3.20	4.10	5.00	7.00	8.90	11.60
pE (mm.)	2.0	-	3.0	-	-	6.6	8.0
pV (mm.)	0.4	-	0.6	-	-	1.3	1.75
pVC (mm.)	0.2	-	0.5	-	-	1.0	1.3

$10^4 k = 0.416 \text{ sec.}^{-1}$ $kE/k = 0.75$ $kV/k = 0.15$ $kVC/k = 0.12$

$pE_{\infty} = 30.9$, $pV_{\infty} = 6.0$, $pVC_{\infty} = 5.0$, $pEt_{\infty} = 0$

%E = 72 , %V = 14 , %VC = 12 , %Et = 0

RUN 123 $T = 356^{\circ}\text{C}$ $S/V = 0.78 \text{ cm.}^{-1}$

$p_0 = 39.20$ $p_{\infty} = 75.50$ $p_{\infty}/p_0 = 1.93$ $p_0 \text{NO} = 18.80$

Time (min.)	20	30	40	60	80	100	120
Δp (mm.)	2.00	3.00	3.80	5.20	6.60	7.95	9.00
pE (mm.)	1.3	-	2.3	-	5.0	-	7.8

$10^4 k = 0.397 \text{ sec.}^{-1}$ $kE/k = 0.73$

$pE_{\infty} = 27.6$, $pV_{\infty} = 6.4$, $pVC_{\infty} = 6.0$, $pEt_{\infty} = 0$

%E = 71 , %V = 16 , %VC = 15 , %Et = 0

RUN 124 $T = 356^{\circ}\text{C}$ $S/V = 0.78 \text{ cm.}^{-1}$

$p_0 = 36.20$ $p_{\infty} = 71.00$ $p_{\infty}/p_0 = 1.96$ $p_0 \text{NO} = 4.40$

Time (min.)	8	16	20	30	40	60	80
Δp (mm.)	0.80	1.60	1.95	2.65	3.35	4.70	6.05
pE (mm.)	0.5	-	1.3	-	2.3	-	4.5
pVC (mm.)	-	-	0.3	-	0.5	-	0.8

$10^4 k = 0.371 \text{ sec.}^{-1}$ $kE/k = 0.72$ $kVC/k = 0.16$

$pE_{\infty} = 25.9$, $pV_{\infty} = 7.2$, $pVC_{\infty} = 4.0$, $pEt_{\infty} = 0$

%E = 72 , %V = 20 , %VC = 11 , %Et = 0

RUN 125 $T = 356^{\circ}\text{C}$ $S/V = 0.78 \text{ cm.}^{-1}$

$p_0 = 37.50$ $p_{\infty} = 72.70$ $p_{\infty}/p_0 = 1.94$ $p_0 \text{In.} = \text{Nil}$

Time (min.)	8	16	20	30	40	60	80	110
Δp (mm.)	0.80	1.50	1.80	2.50	3.20	4.70	5.75	6.90
pE (mm.)	-	-	1.0	-	2.0	-	4.0	-
pVC (mm.)	-	-	0.3	-	0.5	-	0.7	-

$10^4 k = 0.371 \text{ sec.}^{-1}$ $kE/k = 0.67$ $kVC/k = 0.15$

$pE_{\infty} = 26.7$, $pV_{\infty} = 9.7$, $pVC_{\infty} = 1.2$, $pEt_{\infty} = 0.7$

%E = 71 , %V = 26 , %VC = 3 , %Et = 2

(ii) REACTION BETWEEN VINYL CHLORIDE AND TRICHLOROSILANE

<u>RUN 87</u>	T = 402.6°C		S/V = 0.38 cm. ⁻¹			
	p ₀ VC = 11.30		p ₀ HSiCl ₃ = 5.10			
Time (min.)	0	10	20	30	45	60
pVC (mm.)	11.3	10.9	10.4	9.9	9.35	8.75
pHSiCl ₃ (mm.)	5.10	4.70	4.20	3.70	3.15	2.55
10 ⁵ k mm. ⁻¹ sec. ⁻¹	-	1.67	1.46	1.69	1.74	1.95

<u>RUN 88</u>	T = 402.6°C		S/V = 0.38 cm. ⁻¹		
	p ₀ VC = 6.90		p ₀ HSiCl ₃ = 3.30		
Time (min.)	0	5	15	30	75
pVC (mm.)	6.90	6.85	6.70	6.55	6.00
pHSiCl ₃ (mm.)	3.30	3.25	3.10	2.95	2.40
10 ⁵ k mm. ⁻¹ sec. ⁻¹	-	0.85	1.00	0.89	1.08

<u>RUN 89</u>	T = 402.6°C		S/V = 0.38 cm. ⁻¹			
	p ₀ VC = 7.00		p ₀ HSiCl ₃ = 4.05			
Time (min.)	0	10	21	32	44	55
pVC (mm.)	7.00	6.81	6.62	6.30	6.02	5.81
pHSiCl ₃ (mm.)	4.05	3.86	3.67	3.35	3.07	2.86
10 ⁵ k mm. ⁻¹ sec. ⁻¹	-	2.73	1.12	1.47	1.63	1.68

The values given in the columns for the amounts of vinyl chloride and trichlorosilane remaining are the average values obtained from chromatographic analysis of vinyl chloride and vinyltrichlorosilane.

(iii) REACTION BETWEEN ETHYLENE AND TRICHLOROSILANE

<u>RUN 90</u>	$T = 402.6^{\circ}\text{C}$	$S/V = 0.38 \text{ cm.}^{-1}$		
	$p_0\text{E} = 8.60$	$p_0\text{HSiCl}_3 = 8.60$		
Time (min.)	0	50	105	150
pE (mm.)	8.60	8.40	8.20	8.10
pHSiCl ₃ (mm.)	8.60	8.40	8.20	8.10
$10^5 k \text{ mm.}^{-1} \text{ sec.}^{-1}$	-	0.092	0.09	0.08

(iv) THERMAL DECOMPOSITION OF 2-CHLOROETHYLDIMETHYLPHENYLSILANE

The results given for Runs 24 - 37 inclusive were obtained using the injection valve and the rate constants evaluated using the Guggenheim procedure. The reaction vessel had a surface area to volume ratio of 0.78 cm.^{-1} . No additional gas was present in these pyrolyses.

Runs 39 - 101 were, unless otherwise stated, carried out in the presence of ca. 14 mm. of dry, oxygen-free nitrogen. The sample was injected through a serum cap using a hypodermic syringe. Except for the few runs specifically noted the reaction vessel had a surface area to volume ratio of 0.78 cm.^{-1} . The rate constants were evaluated using the Swinbourne procedure and the values of p_0 and p_{∞} are those estimated by this method.

RUN 24	T = 302°C		Line temp. = 170°C			
<u> </u>	$p_0 = 36.70$					
Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	0.80	1.45	2.00	2.55	3.20
$\Delta p(t + 60)$ (mm.)	11.10	11.30	11.40	11.50	11.65	11.80
	<u>$10^4 k = 4.07 \text{ sec.}^{-1}$</u>					

RUN 25	T = 302°C		Line temp. = 170°C			
<u> </u>	$p_0 = 26.60$					
Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	1.15	1.80	2.35	2.95	3.65
$\Delta p(t + 60)$ (mm.)	13.20	13.40	13.60	13.80	14.10	14.30
	<u>$10^4 k = 3.65 \text{ sec.}^{-1}$</u>					

RUN 26 T = 302°C Line temp. = 170°C
 p₀ = 33.60 p_∞ = 67.20 p_∞/p₀ = 2.00
Time (min.) 0 2 4 6 8 10
Δ_p (t) (mm.) 0 1.80 3.10 4.25 5.30 6.30
Δ_p (t + 60) (mm.) 17.25 17.45 17.65 17.90 18.10 18.30
10⁴k = 5.53 sec.⁻¹
pE_∞ = 33.0 ; %E = 98

RUN 27 T = 302°C Line temp. = 170°C
 p₀ = 28.10
Time (min.) 0 2 4 6 8 10
Δ_p (t) (mm.) 0 1.65 2.70 3.55 4.35 5.10
Δ_p (t + 60) (mm.) 14.70 14.85 14.95 15.10 15.25 15.40
10⁴k = 5.07 sec.⁻¹

RUN 28 T = 321°C Line temp. = 170°C
 p₀ = 31.00 p_∞ = 61.70 p_∞/p₀ = 1.99
Time (min.) 0 2 4 6 8 10
Δ_p (t) (mm.) 0 1.75 3.20 4.45 5.65 6.65
Δ_p (t + 60) (mm.) 17.90 18.00 18.15 18.30 18.45 18.60
10⁴k = 6.69 sec.⁻¹
pE_∞ = 31.5 ; %E = 102

RUN 29 T = 321°C Line temp. = 170°C

$p_0 = 32.80$

Time (min.)	0	2	4	6	8	10
$\Delta_p(t)$ (mm.)	0	0.75	1.40	1.85	2.35	2.80
$\Delta_p(t + 60)$ (mm.)	11.00	11.25	11.45	11.65	11.85	12.05

$$\underline{10^4 k = 3.07 \text{ sec.}^{-1}}$$

RUN 30 T = 321°C Line temp. = 170°C

$p_0 = 31.00$

Time (min.)	0	2	4	6	8	10
$\Delta_p(t)$ (mm.)	0	1.10	1.90	2.60	3.25	3.80
$\Delta_p(t + 60)$ (mm.)	13.65	13.80	13.95	14.10	14.25	14.35

$$\underline{10^4 k = 3.84 \text{ sec.}^{-1}}$$

RUN 31 T = 321°C Line temp. = 170°C

$p_0 = 11.20$ $p_{\infty} = 21.90$ $p_{\infty}/p_0 = 1.96$

Time (min.)	0	2	4	6	8	10
$\Delta_p(t)$ (mm.)	0	0.50	0.80	1.05	1.30	1.50
$\Delta_p(t + 60)$ (mm.)	5.00	5.10	5.20	5.30	5.40	5.50

$$\underline{10^4 k = 3.07 \text{ sec.}^{-1}}$$

$$pE_{\infty} = 10.9 \quad ; \quad \%E = 97$$

RUN 32 T = 321°C Line temp. = 170°C

$p_0 = 35.50$

Time (min.)	0	2	4	6	8	10
$\Delta_p(t)$ (mm.)	0	8.0	10.20	13.05	14.30	15.15
$\Delta_p(t + 60)$ (mm.)	18.20	18.20	18.20	18.20	18.20	18.20

$$\underline{10^4 k = 27.3 \text{ sec.}^{-1}}$$

RUN 33 T = 321°C Line temp. = 170°C

$p_0 = 32.60$

Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	6.0	10.65	13.65	15.55	16.90
$\Delta p(t + 60)$ (mm.)	21.00	21.00	21.00	21.00	21.00	21.00

$$\underline{10^4 k = 27.3 \text{ sec.}^{-1}}$$

RUN 34 T = 290°C Line temp. = 170°C

$p_0 = 25.50$

Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	1.35	2.50	3.50	4.70	5.65
$\Delta p(t + 60)$ (mm.)	14.30	14.40	14.50	14.55	14.60	14.75

$$\underline{10^4 k = 7.50 \text{ sec.}^{-1}}$$

RUN 35 T = 290°C Line temp. = 170°C

$p_0 = 18.30$

Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	0.55	1.00	1.50	1.85	2.20
$\Delta p(t + 60)$ (mm.)	6.70	6.85	7.00	7.15	7.25	7.40

$$\underline{10^4 k = 4.26 \text{ sec.}^{-1}}$$

RUN 36 T = 290°C Line temp. = 170°C

$p_0 = 24.50$

$p_{\infty} = 50.50$

$p_{\infty} / p_0 = 2.06$

Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	2.10	3.95	5.15	6.15	7.00
$\Delta p(t + 60)$ (mm.)	12.00	12.05	12.10	12.15	12.20	12.25

$$\underline{10^4 k = 12.05 \text{ sec.}^{-1}}$$

$pE_{\infty} = 24.50$; %E = 100

← This result must be in error since p_{∞} and the analysis are correct.

RUN 37

T = 290°C

Line temp. = 170°C

$p_0 = 53.50$

Time (min.)	0	2	4	6	8	10
$\Delta p(t)$ (mm.)	0	3.50	7.10	10.00	12.20	14.00
$\Delta p(t + 60)$ (mm.)	25.00	25.15	25.30	25.40	25.50	25.60

$$\underline{10^4 k = 12.80 \text{ sec.}^{-1}}$$

RUN 39

T = 290°C

Line temp. = 190°C

$p_0 = 49.6$

$p_{\infty} = 100.5$

Time (min.)	10	20	30	40	50	60	70	80
p (mm.)	63.9	78.8	86.0	90.1	93.0	95.0	96.9	98.1

$$\underline{10^4 k = 5.55 \text{ sec.}^{-1}}$$

RUN 40

T = 290°C

Line temp. = 190°C

$p_0 = 50.0$

$p_{\infty} = 78.0$

Time (min.)	10	20	30	40	50	60	70
p (mm.)	60.6	67.2	71.4	73.8	75.3	76.3	77.0

$$\underline{10^4 k = 8.0 \text{ sec.}^{-1}}$$

RUN 41

T = 290°C

Line temp. = 190°C

$p_0 = 33.5$

$p_{\infty} = 67.0$

Time (min.)	10	20	30	40	50	60	70	80
p (mm.)	48.5	56.7	61.1	63.3	64.8	65.6	66.2	66.6

$$\underline{10^4 k = 10.2 \text{ sec.}^{-1}}$$

RUN 42 T = 290°C Line temp. = 190°C
 $p_0 = 31.0$ $p_{\infty} = 62.4$
Time (min.) 10 20 30 40 50 60 70 80
p (mm.) 44.1 52.0 56.3 58.7 60.2 61.2 61.7 62.1
 $10^4 k = 9.15 \text{ sec.}^{-1}$

RUN 43 T = 290°C Line temp. = 190°C
 $p_0 = 24.4$ $p_{\infty} = 51.5$
Time (min.) 10 20 30 40 50 60 70 80
p (mm.) 34.3 41.0 44.9 47.3 48.8 49.8 50.5 50.85
 $10^4 k = 7.6 \text{ sec.}^{-1}$

RUN 44 T = 290°C Line temp. = 190°C
 $p_0 = 23.2$ $p_{\infty} = 48.2$
Time (min.) 10 20 30 40 50 60 70 80
p (mm.) 31.3 38.2 41.5 43.9 45.1 46.0 46.7 47.2
 $10^4 k = 6.65 \text{ sec.}^{-1}$

RUN 45 T = 270°C Line temp. = 190°C
 $p_0 = 40.7$ $p_{\infty} = 78.0$
Time (min.) 10 20 30 40 50 60
p (mm.) 62.8 71.9 75.4 76.7 77.6 78.0
 $10^4 k = 15.0 \text{ sec.}^{-1}$

RUN 46 T = 270°C Line temp. = 190°C

 p₀ = 30.5 p_∞ = 63.3

Time (min.) 10 20 30 40 50 60 70

 p (mm.) 44.0 51.8 56.6 59.4 60.9 61.85 62.4

$$\underline{10^4 k = 8.35 \text{ sec.}^{-1}}$$

RUN 47 T = 270°C Line temp. = 175°C

 p₀ = 41.5 p_∞ = 84.0

Time (min.) 10 20 30 40 50 60 70

 p (mm.) 60.6 71.0 76.9 80.0 81.7 82.65 83.3

$$\underline{10^4 k = 10.0 \text{ sec.}^{-1}}$$

RUN 48 T = 270°C Line temp. = 175°C

 p₀ = 33.4 p_∞ = 67.0

Time (min.) 10 20 30 40 50

 p (mm.) 45.7 53.5 58.4 61.65 63.8

$$\underline{10^4 k = 7.6 \text{ sec.}^{-1}}$$

RUN 49 T = 270°C Line temp. = 165°C

 p₀ = 27.8 p_∞ = 55.0

Time (min.) 10 20 30 40 50 60

 p (mm.) 36.2 42.0 45.7 48.5 50.5 52.0

$$\underline{10^4 k = 6.2 \text{ sec.}^{-1}}$$

RUN 50 T = 270°C Line temp. = 205°C

 p₀ = 42.5 p_∞ = 80.0

Time (min.)	10	20	30	40	50
p (mm.)	59.0	67.5	73.0	76.0	77.8

$$\underline{10^4 k = 9.8 \text{ sec.}^{-1}}$$

RUN 51 T = 253.6°C Line temp. = 205°C

 p₀ = 41.0 p_∞ = 79.0

Time (min.)	10	20	30	40	50	60
p (mm.)	57.8	66.7	72.2	75.1	77.0	78.0

$$\underline{10^4 k = 9.7 \text{ sec.}^{-1}}$$

RUN 52 T = 289.5°C Line temp. = 190°C

 p₀ = 58.8 p_∞ = 81.0

Time (min.)	10	20	30	40	50	60
p (mm.)	65.6	71.6	74.7	76.7	78.35	79.35

$$\underline{10^4 k = 6.08 \text{ sec.}^{-1}}$$

RUN 53 T = 289.5°C Line temp. = 190°C

 p₀ = 33.5 p_∞ = 67.0

Time (min.)	10	20	30	40	50	60
p (mm.)	49.2	57.8	61.9	64.2	65.45	66.1

$$\underline{10^4 k = 10.6 \text{ sec.}^{-1}}$$

RUN 54 T = 289.5°C Line temp. = 190°C

$p_0 = 27.4$ $p_{\infty} = 58.6$

Time (min.) 10 20 30 40 50 60

p (mm.) 42.8 50.5 54.5 56.5 57.5 58.0

$$\underline{10^4 k = 11.3 \text{ sec.}^{-1}}$$

RUN 55 T = 289.5°C Line temp. = 190°C

$p_0 = 31.5$ $p_{\infty} = 65.7$

Time (min.) 10 20 30 40 50 60

p (mm.) 45.8 54.2 58.95 62.0 63.5 64.2

$$\underline{10^4 k = 9.05 \text{ sec.}^{-1}}$$

RUN 56 T = 266.5°C Line temp. = 205°C

$p_0 = 40.0$ $p_{\infty} = 79.4$

Time (min.) 10 20 30 40 50 60

p (mm.) 57.6 66.9 72.5 75.8 77.5 78.3

$$\underline{10^4 k = 9.75 \text{ sec.}^{-1}}$$

RUN 58 T = 266.5°C Line temp. = 205°C

$p_0 = 38.7$ $p_{\infty} = 67.0$

Time (min.) 10 20 30 40 50 60

p (mm.) 50.9 57.7 61.5 63.7 64.9 65.9

$$\underline{10^4 k = 9.45 \text{ sec.}^{-1}}$$

RUN 59 T = 266.5°C Line temp. = 205°C

$p_0 = 40.8$ $p_{00} = 70.4$

Time (min.) 10 20 30 40 50 60

p (mm.) 51.6 58.4 63.1 65.85 67.5 68.5

$$\underline{10^4 k = 7.65 \text{ sec.}^{-1}}$$

RUN 60 T = 250°C Line temp. = 205°C

$p_0 = 28.0$ $p_{00} = 45.0$

Time (min.) 5 10 15 20 25 30 35 40

p (mm.) 32.6 36.6 39.3 41.2 42.3 43.0 43.6 44.0

$$\underline{10^4 k = 11.7 \text{ sec.}^{-1}}$$

RUN 61 T = 250°C Line temp. = 205°C

$p_0 = 31.0$ $p_{00} = 53.4$

Time (min.) 5 10 15 20 25 30

p (mm.) 43.1 49.5 51.6 52.65 53.0 53.2

$$\underline{10^4 k = 29.2 \text{ sec.}^{-1}}$$

RUN 62 T = 250°C Line temp. = 205°C

$p_0 = 26.0$ $p_{00} = 49.75$

Time (min.) 5 10 15 20 25 30 35 40

p (mm.) 37.1 42.7 46.1 47.6 48.5 49.0 49.3 49.45

$$\underline{10^4 k = 20.5 \text{ sec.}^{-1}}$$

RUN 63 T = 320°C Line temp. = 205°C

$p_0 = 33.25$ $p_{\infty} = 56.0$

Time (min.)	2	4	6	8	10	12	14
p (mm.)	41.85	48.15	50.9	53.0	54.1	54.85	55.35

$$\underline{10^4 k = 40.0 \text{ sec.}^{-1}}$$

RUN 64 T = 320°C Line temp. = 205°C

$p_0 = 28.25$ $p_{\infty} = 44.2$

Time (min.)	2	4	6	8	10	12	14
p (mm.)	32.9	36.35	38.6	40.1	41.2	42.1	42.7

$$\underline{10^4 k = 29.4 \text{ sec.}^{-1}}$$

RUN 65 T = 320°C Line temp. = 205°C

$p_0 = 45.70$ $p_{\infty} = 65.7$ $p_0 \text{C}_6\text{H}_{10} = 16.0$

Time (min.)	2	4	6	8	10	12	14	16
p (mm.)	50.25	53.75	56.5	58.5	60.0	61.2	62.15	62.9

$$\underline{10^4 k = 22.3 \text{ sec.}^{-1}}$$

RUN 66 T = 320°C Line temp. = 205°C

$p_0 = 38.7$ $p_{\infty} = 63.0$

Time (min.)	2	4	6	8	10	12	14	16
p (mm.)	45.5	51.0	54.5	56.9	58.6	59.8	60.55	61.25

$$\underline{10^4 k = 27.7 \text{ sec.}^{-1}}$$

RUN 67 T = 330°C Line temp. = 205°C
 p₀ = 38.65 p_∞ = 57.3
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 43.9 48.35 50.9 52.6 53.9 54.7 55.4 55.9
10⁴k = 28.0 sec.⁻¹

RUN 68 T = 330°C Line temp. = 205°C
 p₀ = 42.5 p_∞ = 65.5
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 47.7 52.1 55.1 57.4 59.1 60.4 61.5 62.45
10⁴k = 21.4 sec.⁻¹

RUN 69 T = 330°C Line temp. = 175°C
 p₀ = 31.45 p_∞ = 51.5
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 35.3 38.4 40.9 42.85 44.4 45.65 46.9 47.85
10⁴k = 18.1 sec.⁻¹

RUN 70 T = 370°C Line temp. = 205°C
 p₀ = 36.9 p_∞ = 56.5
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 45.5 50.4 53.1 54.7 55.35 55.8 56.05 56.3
10⁴k = 48.0 sec.⁻¹

RUN 71 T = 370°C Line temp. = 205°C
p₀ = 34.35 p_∞ = 48.70
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 38.6 41.85 43.8 45.25 46.3 47.0 47.5 48.0
10⁴k = 29.0 sec.⁻¹

RUN 72 T = 370°C Line temp. = 205°C
p₀ = 31.20 p_∞ = 46.75
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 35.7 39.1 41.35 42.85 44.0 44.75 45.3 45.85
10⁴k = 25.2 sec.⁻¹

RUN 73 T = 350°C Line temp. = 205°C
p₀ = 42.5 p_∞ = 70.5
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 45.9 48.75 51.1 53.35 55.45 57.25 58.75 60.25
10⁴k = 11.5 sec.⁻¹

RUN 74 T = 350°C Line temp. = 205°C
p₀ = 32.0 p_∞ = 48.5
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 34.8 37.5 39.4 40.8 41.9 42.9 43.7 44.4
10⁴k = 15.6 sec.⁻¹

RUN 75 T = 350°C Line temp. = 205°C
 $p_0 = 30.0$ $p_{\infty} = 49.0$
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 33.55 36.55 39.0 41.0 42.5 43.65 44.6 45.4

 $10^4 k = 16.9 \text{ sec.}^{-1}$

RUN 76 T = 330°C Line temp. = 205°C
 $p_0 = 39.8$ $p_{\infty} = 64.0$
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 41.8 44.45 46.2 47.8 49.1 50.25 51.4 52.4

 $10^4 k = 7.9 \text{ sec.}^{-1}$

RUN 77 T = 330°C Line temp. = 205°C
 $p_0 = 38.0$ $p_{\infty} = 59.0$
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 40.85 43.8 45.95 47.6 49.15 50.4 51.6 52.55

 $10^4 k = 12.5 \text{ sec.}^{-1}$

RUN 78 T = 330°C Line temp. = 205°C
 $p_0 = 38.0$ $p_{\infty} = 61.2$
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 41.55 45.15 47.9 49.85 51.45 52.9 54.0 54.95

 $10^4 k = 14.0 \text{ sec.}^{-1}$

RUN 80 T = 310°C Line temp. = 205°C
p₀ = ? p_∞ = 48.5
Time (min.) 4 10 16 22 28 34 40 46
p (mm.) 35.4 38.25 40.0 41.45 42.7 43.85 44.6 45.4
10⁴k = 5.5 sec.⁻¹

RUN 81 T = 310°C Line temp. = 205°C
p₀ = 41.25 p_∞ = 63.0
Time (min.) 6 12 18 24 30 36 42 48
p (mm.) 45.95 49.7 52.55 54.8 56.6 58.0 59.15 60.0
10⁴k = 6.8 sec.⁻¹

RUN 82 T = 390°C Line temp. = 205°C
p₀ = 36.7 p_∞ = 62.0
Time (min.) 2 4 6 8 10 12 14
p (mm.) 49.1 55.45 58.7 60.35 61.15 61.5 61.8
10⁴k = 57.0 sec.⁻¹

RUN 83 T = 390°C Line temp. = 205°C
p₀ = 35.5 p_∞ = 60.5
Time (min.) 2 4 6 8 10 12
p (mm.) 49.0 55.35 58.15 59.5 59.9 60.15
10⁴k = 64.5 sec.⁻¹

RUN 84 T = 360°C Line temp. = 205°C
p₀ = 35.5 p_∞ = 56.8
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 40.7 45.35 48.4 50.5 52.0 53.2 54.05 54.85
10⁴k = 24.0 sec.⁻¹

RUN 85 T = 360°C Line temp. = 205°C
p₀ = 36.8 p_∞ = 59.0
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 41.75 46.0 48.9 51.1 52.9 54.3 55.4 56.1
10⁴k = 21.3 sec.⁻¹

RUN 86 T = 236.5°C Line temp. = 205°C
p₀ = 30.5 p_∞ = 50.0
Time (min.) 10 20 30 40 50 60 130 140
p (mm.) 33.3 35.55 37.6 39.6 41.2 42.65 46.9 47.3
10⁴k = 2.58 sec.⁻¹

RUN 87 T = 236.5°C Line temp. = 205°C
p₀ = 32.8 p_∞ = 52.0
Time (min.) 10 20 30 40 50 60 126 136
p (mm.) 35.85 37.95 40.15 42.1 43.85 45.25 49.6 49.9
10⁴k = 2.92 sec.⁻¹

RUN 88 T = 228.5°C Line temp. = 205°C

$p_0 = 30.25$ $p_{\infty} = 51.3$

Time (min.)	10	20	30	40	50
p (mm.)	33.85	36.8	39.4	41.6	43.25

$$\underline{10^4 k = 3.19 \text{ sec.}^{-1}}$$

RUN 89 T = 266.5°C Line temp. = 205°C

$p_0 = 33.3$ $p_{\infty} = 53.8$

Time (min.)	6	12	18	24	30	36
p (mm.)	38.9	43.4	46.35	48.45	50.0	51.1

$$\underline{10^4 k = 9.0 \text{ sec.}^{-1}}$$

RUN 91 T = 267°C Line temp. = 205°C

$p_0 = 11.6$ $p_{\infty} = 18.7$ $p_{O_2} = 500$

Time (min.)	3	6	9	12	15	18	21
p (mm.)	12.8	14.65	15.8	16.4	16.95	17.35	17.75

$$\underline{10^4 k = 16.0 \text{ sec.}^{-1}}$$

RUN 92 T = 267°C Line temp. = 205°C

$p_0 = 22.9$ $p_{\infty} = 41.8$ $p_{O_2} = 160$

Time (min.)	4	8	12	16	20	24	28
p (mm.)	27.6	30.85	33.55	35.65	37.3	38.35	39.1

$$\underline{10^4 k = 6.25 \text{ sec.}^{-1}}$$

RUN 93 T = 267°C Line temp. = 205°C
 $p_0 = 17.25$ $p_{\infty} = 27.5$ $p_0 N_2 = 190$
Time (min.) 4 8 12 16 20 24
p (mm.) 19.80 21.85 23.4 24.4 25.15 25.75
 $10^4 k = 11.9 \text{ sec.}^{-1}$

RUN 94 T = 267°C Line temp. = 205°C
 $p_0 = 32.0$ $p_{\infty} = 44.0$ $p_0 \text{ Air} = 135$
Time (min.) 4 8 12 16 20 24
p (mm.) 35.4 37.8 39.6 40.9 41.8 42.4
 $10^4 k = 14.0 \text{ sec.}^{-1}$

RUN 95 T = 268°C Line temp. = 205°C
 $p_0 = 18.2$ $p_{\infty} = 25.5$ S/V = 2.74 cm.⁻¹
Time (min.) 4 8 12 16 20
p (mm.) 19.9 21.6 22.5 23.3 23.8
 $10^4 k = 11.3 \text{ sec.}^{-1}$

RUN 96 T = 268.5°C Line temp. = 205°C
 $p_0 = 21.85$ $p_{\infty} = 31.20$ S/V = 2.74 cm.⁻¹
Time (min.) 4 6 8 10 12 14 16 18
p (mm.) 25.1 26.65 27.65 28.45 28.95 29.35 29.65 30.0
 $10^4 k = 17.8 \text{ sec.}^{-1}$

RUN 97 T = 268.5°C Line temp. = 205°C
 $p_0 = 28.0$ $p_{\infty} = 41.3$ $p_0 C_6H_{10} = 32.0$ S/V = 2.74 cm.⁻¹
Time (min.) 4 8 12 16 20
p (mm.) 33.0 36.6 38.6 39.6 40.25
 $10^4 k = 19.4 \text{ sec.}^{-1}$

RUN 98 T = 268.5°C Line temp. = 205°C
 $p_0 = 43.0$ $p_{\infty} = 57.2$ $p_0 C_6H_{10} = 39.0$ S/V = 2.74 cm.⁻¹
Time (min.) 4 8 12 16 20 24
p (mm.) 48.5 52.0 54.1 55.2 56.0 56.6
 $10^4 k = 19.6 \text{ sec.}^{-1}$

RUN 99 In the lines only at 190 - 205°C
 $p_0 = 17.0$ $p_{\infty} = 25.7$
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 19.3 21.95 23.2 23.95 24.55 24.9 25.15 25.3
 $10^4 k = 25.2 \text{ sec.}^{-1}$

RUN 100 In the lines only at 190 - 205°C
 $p_0 = 25.5$ $p_{\infty} = 48.5$
Time (min.) 2 4 6 8 10 12 14 16
p (mm.) 31.85 37.5 41.5 44.2 45.7 46.5 47.1 47.5
 $10^4 k = 27.3 \text{ sec.}^{-1}$

RUN 101

In the lines only at 165 - 176°C

$$p_0 = 59.5$$

$$p_{\infty} = 107.0$$

Time (min.)	2	4	6	8	10	12	14	16
p (mm.)	66.05	71.6	76.45	80.75	84.35	87.5	90.25	92.6

$$\underline{10^4 k = 12.5 \text{ sec}^{-1}}$$

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