KINETIC AND ELECTRON IMPACT STUDIES ON SOME

TRIMETHYLSILYL COMPOUNDS

A thesis presented by

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for the degree of

DOCTOR OF PHILOSOPHY

in the

UNIVERSITY OF LEICESTER

Department of Chemistry   December 1968
University of Leicester

UMI Number: U309014

Dissertation Publishing

To

Shirley and Sarah

Statement.

The experimental work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester between September 1965 and September 1968.

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

Signed ....

December 1968

Acknowledgements

Sincere thanks to my supervisor, Dr. I. M. T. Davidson,
for his unselfish help and encouragement throughout
the course of this work.

My thanks are also due to Mr. M. Jones of this depart-
ment who carried out the mass spectral analysis of my
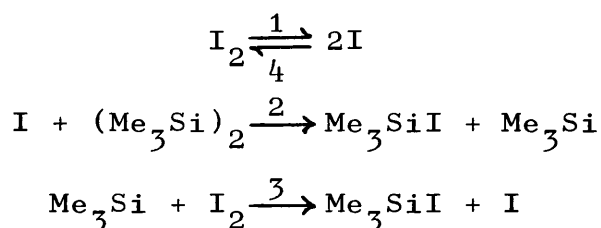compounds, and to my wife, Shirley, who typed this thesis.

Abstract

Bond dissociation energies, $D(Me_3Si-X)$, and molecular heats of formation, $\Delta H_f^o(Me_3SiX)_g$, are derived from electron impact measurements on the trimethylsilyl halides (X = Cl, Br and I). In particular $D(Me_3Si-Cl)$ = 88 $\pm$ 2 kcal mole^{-1}, $D(Me_3Si-Br)$ = 78.5 $\pm$ 2 kcal mole^{-1} and $D(Me_3Si-I)$ = 69 $\pm$ 2 kcal mole^{-1}. The method used for the measurement of appearance potentials is simple and rapid, utilising the high sensitivity of the MS9 mass spectrometer. The possibility of $(p-d)\pi$ bonding in the trimethylsilyl halides is discussed.

A brief description of exploratory work on the gas phase reactions between organosilanes and halogens is given and the system hexamethyldisilane, $(Me_3Si)_2$, + iodine discussed in detail. This system has been studied kinetically between 188 and 250°C at initial reactant pressures of 1.5 - 11.0 mm Hg. The simple stoiceiometry $(Me_3Si)_2 + I_2 = 2Me_3SiI$ exists under the conditions used and the reaction is 3/2 order overall, being first order in hexamethyldisilane and half order in iodine.

The simple chain mechanism:

$$I_2 \underset{4}{\overset{1}{\rightleftharpoons}} 2I$$

$$I + (Me_3Si)_2 \overset{2}{\longrightarrow} Me_3SiI + Me_3Si$$

$$Me_3Si + I_2 \overset{3}{\longrightarrow} Me_3SiI + I$$

is suggested, leading to the overall rate equation:

$$-d\left[\frac{(Me_3Si)_2}{dt}\right] = k_2 K_{I_2}^{\frac{1}{2}} [I_2]^{\frac{1}{2}} \left[(Me_3Si)_2\right]$$

where K_{I_2} is the constant for the iodine equilibrium.

The complex rate constants, $k_2 K_{I_2}^{\frac{1}{2}}$, are found to obey the Arrhenius equation:

$$k_2 K_{I_2}^{\frac{1}{2}} = 1.16 \times 10^{13} \exp(-26,100 \pm 1,100)/RT$$

where $k_2 K_{I_2}^{\frac{1}{2}}$ is in $cc^{\frac{1}{2}}$ $mole^{-\frac{1}{2}}$ sec^{-1} and energies are in cal $mole^{-1}$. Calculation of $K_{I_2}^{\frac{1}{2}}$ at one temperature in the range studied allows the evaluation of k_2, the rate constant for attack of iodine atoms on hexamethyl-disilane, at that temperature. In this way k_2 is shown to be governed by the relationship:

$$k_2 = 1.70 \times 10^{11} \exp(-8,100 \pm 1,100)/RT$$

with k_2 in cc $mole^{-1}$ sec^{-1} and energies in cal $mole^{-1}$

CONTENTS

INTRODUCTION.

Bond dissociation energies (B.D.E's), heats of formation and energies of activation, together with a wealth of mechanistic information, are available from kinetic and electron impact measurements. Such studies have helped to place the qualitative estimates of chemical reactivity within carbon containing systems on a more quantitative basis, thus providing a much clearer insight into the energy barriers involved in chemical processes generally.

It is of interest to observe the trends produced by moving from carbon to the other elements of group 4, particularly silicon, its closest neighbour. The differences in chemical behaviour between carbon and silicon can plainly be attributed to the changes involved in passing from the first to the second short period. Two such changes are immediately apparent, the larger size of the silicon atom (R_{Si} = I.I7$\overset{o}{A}$ whereas R_C = 0.77$\overset{o}{A}$) and the availability of empty d orbitals in silicon. One would then expect the ionisation potential of the silicon atom to be lower than that for carbon and in fact I_{Si} = 8.15ev and I_C = 11.1ev. It is also generally held that silicon is less electronegative than carbon, being assigned a value of 1.8 on the Pauling scale compared to 2.5 for carbon.

As yet there is very little information available for
silicon containing systems. Thermochemical data contain many
significant discrepancies[1,2] (reflecting the difficulties
involved in the use of conventional combustion bomb calorimetric
techniques for silicon compounds[3]), B.D.E. values are not well
established and few activation energies for free radical re-
actions have been recorded. The work described here seeks to
contribute towards the accumulation of such data. Preliminary
kinetic studies between silanes and halogens have been carried
out and the system hexamethyldisilane (HMDS), $(Me_3Si)_2$, + Iodine
considered in detail. B.D.E's and heats of formation for the
trimethylsilyl halides, $Me_3Si - X$, have been derived from
electron impact studies to support this kinetic work. Incident-
ally such compounds are currently of interest due to the possibility
of the formation of the much discussed $(p-d)\pi$ bonds between
silicon and the halogens.

At this point a short survey of the methods used for the
measurement of B.D.E's in polyatomic molecules (full accounts
of the uses and measurement of B.D.E's can be found in the
recent literature[4-7]) is given with particular emphasis on the
work pertinent to this research; and this is followed by a
brief account of the factors which would be expected to affect
the reactions between silanes and halogens.

Bond Dissociation Energies.

The B.D.E. of R_1R_2, $D(R_1-R_2)$, is defined as the enthalpy change at absolute zero for the process:

$$R_1R_2 \longrightarrow R_1 + R_2 \qquad (1).$$

in the ideal gas state, the products being in their ground states. ΔH measured at normal temperatures does not differ greatly from the true value of D and many of the techniques used are not sufficiently accurate to warrant the correction (for which the heat capacity data is often lacking anyway). B.D.E. values vary greatly from a mere 13 kcal mole^{-1} for $D(O_2N - NO_2)$ to $D(C - O)$ and $D(N-N)$ which are probably greater than 200 kcal mole^{-1}.

$D(R_1 - R_2)$ is not to be confused with the bond energy, $E(R_1 - R_2)$, which is only equivalent to $D(R_1 - R_2)$ for diatomic molecules. Bond energies are quantities which summed over all the bonds of a molecule are equal to the heat of atomisation of that molecule. The assumption is made that the energy of a bond is constant from molecule to molecule and this is clearly not always true.

Thus

$$E(M - X) \text{ in } MX_n = 1/n\left[\Delta H_f^o (M) + n\Delta H_f^o (X) - \Delta H_f^o (MX_n)\right]$$

whereas

$$D(M - X) = \Delta H_f^O (X) + \Delta H_f^O (MX_{n-1}) - \Delta H_f^O (MX_n)$$

Methods of measuring B.D.E's in polyatomic molecules.

In general the heat of the dissociation process (1) can-
not be determined directly for polyatomic molecules and only
in a few cases have B.D.E's been derived by measuring the
exothermic recombination of radicals. Spectroscopic techniques
are extremely accurate but applicable only to diatomic mole-
cules, the spectra of polyatomics being too complex to yield
B.D.E's. The thermal equilibrium methods in which D values
are derived thermodynamically from measurement of equilibrium
concentrations, are also largely confined to use with diatomic
molecules.

By direct calculation.

It ought to be possible to calculate B.D.E's directly from
the fundamental physical properties of the atoms. The necessary
data are available but unfortunately its application leads to
very complex equations which have only been solved for the
H_2^+ case[8,9]. For less simple molecules the number of necessary
approximations introduce gross errors into the final result.

Several simpler equations of a semi-empirical nature have been
derived and these have been applied with some measure of success
to the carbon series. Insufficient data are presently available,
however, for this approach to be of use in the corresponding
silicon compounds.

Use of known B.D.E's.

For the dissociation process (1) it follows that

$$D(R_1 - R_2) = \Delta H_f^o \ (R_1) + \Delta H_f^o \ (R_2) - \Delta H_f^o \ (R_1 R_2)$$

Therefore if $D(R_1 - R_2)$ can be determined and $\Delta H_f^o \ (R_1)$ is known

from the case where $R_1 = R_2$, $\Delta H_f^o \ (R_2)$ can often be derived because

$\Delta H_f^o \ (R_1 R_2)$ is generally available from thermochemical experiments.

From this we can use $\Delta H_f^o \ (R_2)$ in similar equations to calculate

B.D.E's for a whole series of compounds $R_2 - X$, provided the

heat of formation of the fragment X is known; once some thermo-

chemical data is available this method will be of use in silicon

systems.

Kinetic methods.

This method is particularly suitable for polyatomic molecules.
The most general approach is to assume that the activation energy
for radical recombination is zero[10,11] and therefore the activation
energy of the dissociation reaction can be identified with the
dissociation energy.

Thus for $R_1R_2 \underset{r}{\overset{f}{\rightleftharpoons}} R_1 + R_2$, $\Delta H = E_f - E_r = E_f = D(R_1-R_2)$.
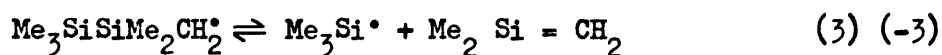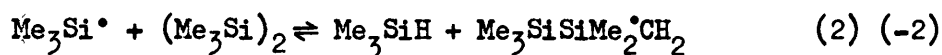This is only true if the initial dissociation is rate determining and the subsequent reactions of R_1 and R_2 are simple and non chain. A chain process would tend to lower the overall activation energy. Such chain processes can be prevented by use of the toluene carrier technique introduced by Szwarc[12] in which a very efficient radical scavenger is introduced to the reaction mixture and takes up the radicals as they are formed.

Several kinetic studies on the Si - Si bond have been undertaken. Early work on the pyrolysis of disilane by Eméleus et al[13,14,] led to an overall activation energy of 51.3 kcal mole^{-1} which they equated to $D(H_3Si -SiH_3)$. This was a doubtful assumption as the mechanism of the process was, and still is, uncertain. Stokland[15] later obtained an activation energy of 48.9 kcal mole^{-1} for this pyrolysis but did not relate this to the B.D.E. Later electron impact work placed much higher values on $D(Si-Si)$. Steele,Nichols and Stone[16,17] recorded $D(H_3Si-Si H_3) = 81.3$ kcal mole^{-1} and $D(Cl_3Si-SiCl_3) = 85$ kcal mole^{-1} whilst Hess, Lampe and Sommer[18] obtained $D(Me_3Si-SiMe_3) = 86$ kcal mole^{-1}.

Recent workers have attempted to determine $D(Si-Si)$ in HMDS unambiguously by direct pyrolysis of the compound. Haszeldine et al have measured $D(Me_3Si-SiMe_3)$ in two separate experiments[20,21]. Both pyrolyses were carried out in flow

systems using a version of the toluene carrier technique in order

to take up the trimethylsilyl radicals formed in the initial

dissociation $(Me_3Si)_2 \underset{r}{\overset{f}{\rightleftharpoons}} 2Me_3Si$. Their first determination

was carried out at $650\text{-}710^\circ C$ using $0.1 - 1.0mm$ Hg HMDS. In the

second pyrolysis the reaction was studied by continuous use of

a mass spectrometer, temperatures were slightly higher $(660\text{-}770^\circ C)$

and pressures lower $(10^{-3}$ to $10^{-5}mm$ Hg of HMDS). They followed

the decay of HMDS and obtained figures of 58 ± 4 and 49 ± 6 kcal

mole^{-1} respectively for $D(Me_3Si\text{-}Si\ Me_3)$ in good agreement with the

values of Eméleus et al[13,14]. They felt that the lower value was

the nearest to the truth.

Davidson and Stephenson[19] working in this laboratory,

pyrolysed HMDS at lower temperatures ($523\text{-}555^\circ C$) in a static

system. Initial pressures of $0.2 - 0.8mm$ Hg were used and the

rate of formation of one product $(Me_3Si.Si\ Me_2CH_2SiMe_3)$ was

monitored continuously on a mass spectrometer up to about 5%

decomposition of HMDS. Under the conditions used the decomposition

proceeded via a non-chain, homogeneous, unimolecular, radical process.

By strict analogy with hydrocarbons one may expect the break

down to follow a Rice-Hertzfeld type mechanism of the form:

$$(Me_3Si)_2 \rightleftharpoons 2Me_3Si \bullet \qquad\qquad (1)\ (-1)$$

$$Me_3Si \bullet + (Me_3Si)_2 \rightleftharpoons Me_3SiH + Me_3SiSiMe_2^\bullet CH_2 \qquad (2)\ (-2)$$

$$Me_3SiSiMe_2CH_2^\bullet \rightleftharpoons Me_3Si \bullet + Me_2\ Si = CH_2 \qquad (3)\ (-3)$$

ΔH for reaction (2) is the difference in B.D.E's for the bonds formed and the bonds broken i.e $\Delta H = -D(Si-H) + D(C-H)$. The carbon-hydrogen bond is some 20-30 kcal mole^{-1} stronger than silicon-hydrogen and therefore (2) would be strongly endothermic. As silicon does not form olefinic compounds, step (3) would have to produce the highly unstable biradical Me$_2$Si$^\bullet$CH$_2^\bullet$, necessitating a high activation energy. In fact the reaction preferred to proceed via,

$$Me_3Si\bullet + (Me_3Si)_2 \rightarrow Me_3SiMe + Me_3SiSi\bullet Me_2 \qquad (4)$$
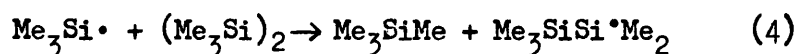
followed by combination processes. The overall activation energy of 67 ± 2 kcal mole^{-1} was therefore identified with $D(Me_3Si-SiMe_3)$

This last figure seems the more likely to be correct for several reasons:

1. An activation energy of 49 kcal mole^{-1} seems unusually low to be attributed to a homogeneous, unimolecular dissociation around 700°C.

2. If the reaction is complicated by unexpected interference e.g. chain reactions, heterogeneous behaviour, competing reactions, reaction with absorbed impurities etc., they will tend to lower the activation energy. Thus the higher of the values obtained is most likely to relate to the unimolecular dissociation.

3. Reaction temperatures used by Haszeldine et al were higher than those of Davidson and Stephenson and,therefore,the mechanism

was likely to be more complex. This would have been overcome

if the flow system had been used to observe very small percentage

decompositions but, in fact, the reaction was studied at quite high

degrees of decomposition.

4. The toluene carrier seems to have been ineffective in

simplifying the mechanism, since the activation energy was found

to be the same whether or not it was present (The possibility

of the trapping reaction $Me_3Si\cdot$ + $PhCH_3 \rightarrow Me_3SiH$ + $PhCH_2\cdot$

being considerably endothermic has been suggested[22]. If this

is so the use of this process seems hardly feasible)

5. Haszeldine et al[20] have derived a value for $I(Me_3Si\cdot)$

the ionisation potential of the trimethylsilyl radical, by

combining their values for $D(Me_3Si-SiMe_3)$ with the appearance

potential of m/e 73, $A(Me_3Si^+)$, from HMDS derived by electron

impact (see later). Their figure for $I(Me_3Si\cdot)$ was higher than

that for the carbon analogue whereas values for $I(SiH_3\cdot)$ and

$I(Cl_3Si\cdot)$ were found to be lower than those for their carbon

analogues[16,17]. Davidson and Stephenson's figure for $I(Me_3Si\cdot)$

derived in the same way[19] fitted in with this latter trend.

6. Use of $I(Me_3Si\cdot)$ to derive other B.D.E's from electron

impact figures led Haszeldine et al to a figure of 64 - 74 kcal

$mole^{-1}$ for $D(Me_3Si-H)$. Kerr et al[22] combined this with their

kinetic data (obtained from abstraction reactions of methyl
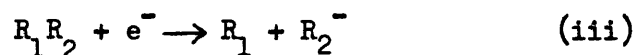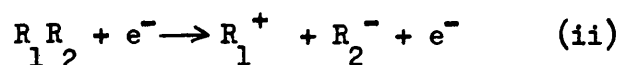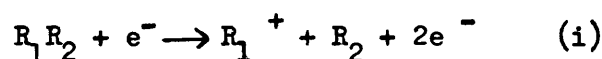
radicals with organosilanes) and showed that the reaction:

$$Me_3Si\cdot + MeH \longrightarrow Me_3SiH + Me\cdot$$

would need an activation energy of 37 - 47 kcal mole^{-1}. This

seems excessively high and probably indicates that D(H - SiMe$_3$)

has been considerably underestimated. Kerr et al suggested a

figure of 81 $\pm$ 5 kcal mole $^{-1}$ for this B.D.E and fortuitously

this is the figure obtained by combining Davidson and Stephenson's

I (Me$_3$Si$\cdot$) value with Haszeldine's electron impact data.

Electron Impact Methods.

Molecules are subjected to bombardment by a beam of electrons

of known energy in order to produce ionisation and dissociation.

Fission of the molecule may occur in several ways:

$$R_1R_2 + e^- \longrightarrow R_1^{\ +} + R_2 + 2e^- \qquad (i)$$

$$R_1R_2 + e^- \longrightarrow R_1^{\ +} + R_2^{\ -} + e^- \qquad (ii)$$

$$R_1R_2 + e^- \longrightarrow R_1 + R_2^{\ -} \qquad (iii)$$

Dissociation by process (iii) is unimportant in normal positive

ion mass spectrometry. The negative ions are actually formed via:

$$R_1R_2 + e^- \rightarrow R_1R_2^{\ -} \longrightarrow R_1 + R_2^{\ -}$$
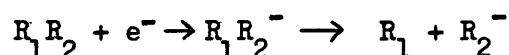
There are no product electrons to carry away excess energy in

the electron capture step and, therefore, this is a resonance process

which will only occur over a narrow range of electron beam energies.

Processes (i) and (ii) generally occur at considerably higher

energies than (iii) and become more favourable as the energy

increases. Fission by (ii) only takes place when the two types

of ion are formed coincidently. Ionisation in this way has

been postulated by Dibeler and Mohler[23] for electron impact
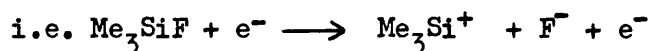
on SiF_4 and by Hess,Lampe and Sommer[18] for fission of trimethylsilyl

fluoride

i.e. $Me_3SiF + e^- \longrightarrow Me_3Si^+ + F^- + e^-$

Process (i) is by far the more important in electron impact

studies and all the dissociations referred to in this work occur

in this way.

Appearance Potentials

We define the appearance potential of an ion as the potential

necessary to accelerate the ionising electrons in a mass spectrometer

so that they have just sufficient energy to cause the ion to appear.

Thus for process (i) it follows that

$$A(R_1^+) = D(R_1 - R_2) + I(R_1) \qquad (2)$$

where $A(R_1^+)$ is the appearance potential of R_1^+ and $I(R_1)$ is the

ionisation potential of R_1. This relationship assumes that

the ions are formed with no excess energy. This assumption is

reasonable from Stevenson's rule[24] ie. that the radicals and

radical ions are produced in their ground states if for process

(i) $I(R_1) < I(R_2)$. If $I(R_1) > I(R_2)$ then $A(R_1^+)$ will be greater than

the sum of $I(R_1)$ and $D(R_1-R_2)$ and the neutral fragment R_2 will

either be in an excited state or will dissociate into smaller

fragments. This rule has since been extended to include all compounds

studied by electron impact. Even so, it is still extremely difficult

to prove that excitation energy is not involved in the ionisation

process. For this reason the lower of two values for the same

appearance potential is the more likely to be correct.

From the general equation (2) above it follows that, given the

means to measure $A(R_1^+)$, one could determine B.D.E's in three

possible ways.

(i) By direct measurement of $I(R_1)$,

(ii) By estimating or eliminating $I(R_1)$ from thermochemical

data, and

(iii) By measuring $D(R_1-R_2)$ in some way, calculating $I(R_1)$,

and using this to find $D(R_1-X)$ values for a series

R_1-X.

Workers on trimethylsilyl compounds[18,19,20,25] have used

all these approaches to obtain $D(Me_3Si-X)$. The results obtained

are summarised in Tables I and II. Method (i) was used by

Lappert et al[25] who have attempted to measure $I(Me_3Si.)$ and

Table I

Electron Impact Data for the Trimethylsilyl Halides and Related

Compounds.

Compound.	Ion.	Appearance Potentials (ev)			
		ref. 49	ref. 18	ref. 25	ref. 20
Me_6Si_2	Me_3Si^+		10.69 ± 0.04		10.0 ± 0.1
Me_4Si	Me_4Si^+	9.8 ± 0.15	9.9 ± 0.03		
	Me_3Si^+	11.3 ± 0.15	10.4 ± 0.1		10.5 ± 0.1
Me_3SiH	Me_3SiH^+	9.8 ± 0.3			
	Me_3Si^+	10.9 ± 0.2	10.78 ± 0.07		10.7 ± 0.1
	Me_2SiH^+	11.9 ± 0.3	11.70 ± 0.06		
Me_3SiCl	Me_3SiCl^+		10.58 ± 0.04	10.2 ± 0.10	
	Me_3Si^+		12.4 ± 0.06	12.16 ± 0.10	11.5 ± 0.2
	Me_2SiCl^+		11.0 ± 0.16		
Me_3SiBr	Me_3SiBr^+		10.24 ± 0.02	10.04 ± 0.10	
	Me_3Si^+		10.69 ± 0.06		
	Me_2SiBr^+		10.97 ± 0.02		

Table II

Bond Dissociation Energies for Trimethylsilyl Compounds, Me_3Si-X.

Me_3Si-X.	Bond Dissociation Energies (kcal mole^{-1})		
	ref. 18	ref. 20	ref. 19
Me_6Si_2	86 ± 10	$49\pm6,58\pm4$	67 ± 2
Me_4Si	85 ± 10	$59\pm5,69\pm5$	
Me_3SiH	88 ± 10	$64\pm5,74\pm5$	
Me_3SiCl	126 ± 10	$82\pm5,92\pm5$	
Me_3SiBr	86 ± 10		

A (Me_3Si^+) directly. As yet appearance potentials only are given as their results have not been reported fully. Even so their figures differ considerably from those of Hess, Lampe and Sommer[18] who used method (ii) to estimate a figure for $I(Me_3Si.)$. This was achieved by calculating a value for ΔH_f^O $(Me_3Si)_2$ using Franklin's[26] group parameter method and determining ΔH_f^O (Me_3Si^+) by combining Tannenbaum's[27] heat of formation data for tri- and tetramethylsilane with the appropriate radical heats of formation. Then using:
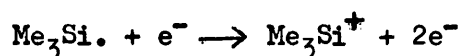
$$(Me_3Si)_2 + e^- \longrightarrow Me_3Si^+ + Me_3Si. + 2e^-$$
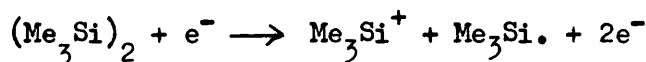
from which $\Delta H = A(Me_3Si^+)$ $= \Delta H_f^O$ $(Me_3Si^+) + \Delta H_f^O$ $(Me_3Si.)$
$$- \Delta H_f^O \ (Me_3Si)_2$$

they found a value for ΔH_f^O $(Me_3Si.)$.

The enthalpy change in the ionisation

$$Me_3Si. + e^- \longrightarrow Me_3Si^+ + 2e^-$$

is equivalent to $I(Me_3Si.)$

therefore

$$\Delta H = I(Me_3Si.) = \Delta H_f^O \ (Me_3Si^+) - \Delta H_f^O \ (Me_3Si.)$$

giving $I(Me_3Si.)$

The group equivalent method is not known to apply to organo-silicon systems and so these authors estimated their B.D.E's to be true only to $\pm$ 10 kcal mole^{-1}. It is now fairly certain that their m/e 73 appearance potential for HMDS was 0.7 e.v too high.[19,20]

If we use the lower value, their figure for $D(Me_3Si - SiMe_3)$ is 60 ± 10

kcal mole^{-1}, which brings it in line with the kinetic estimates.

Steele, Nichols and Stone[16,17] estimated $D(H_3Si - X)$ values by

measuring appearance potentials for the series $H_3Si - X$. Their

results agreed with those of Hess, Lampe and Sommer in that both

groups found that B.D.E's to silicon were higher than previous

kinetic data predicted. It has, however, been shown[22] that some

heats of formation of organosilicon compounds, derived indirectly

from the results of these two groups, are in serious disagreement

with more conventional thermochemical determinations[28].

Method (iii) has been used by Haszeldine et al[20,21] and

by Davidson and Stephenson[29]. They both measured $A(Me_3Si^+)$ from

HMDS and obtained the value of $10.0 \pm 0.1ev$. Thus their

differences in $I(Me_3Si.)$ lie in the kinetic determination of

$D(Me_3Si - SiMe_3)$.

If the value of $I(Me_3Si.)$ obtained by Davidson and Stephenson

is accepted it follows that $D(Me_3Si - X)$ can be determined for a

whole series of compounds, Me_3SiX, by measurement of $A(Me_3Si^+)$.

Such measurements have been carried out by this author for the

series $X = Cl$, Br and I.

Factors Influencing The Halogenation of Silanes.

Studies of radical reactions of organosilicon compounds are few in number. Gilman et al[30] reported the first kinetic investigation in 1957 and subsequent work has been pulished only recently. The indication to date is that silicon compounds will undergo radical initiated reactions in much the same way as their carbon analogues.

Hydrocarbon studies indicate that iodination is mechanistically the simplest type of halogenation. Thus the systems RH + I_2 and RI + HI have been shown to proceed in a kinetically straightforward manner and to yield fruitful results. Several reactions of iodine with alkanes have recently been studied by Benson's group[31 - 33], as part of a general survey of iodine containing systems[34-41], and by others[42-44]. All these iodinations proceeded to equilibrium via an atomic mechanism and the important steps were:

$$I_2 + M = 2I + M \qquad (1) \quad (-1)$$

$$I + RH = HI + R \qquad (2) \quad (-2)$$

$$R + I_2 = RI + I \qquad (3) \quad (-3)$$
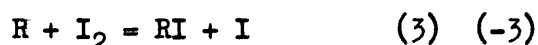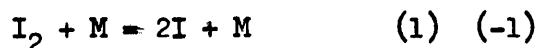
This mechanism proved satisfactory for the analysis of the initial stages of the reactions where R = Me and Et, but as the molecular weight of R increased the alkyl iodides formed were

found to decompose at appreciable rates at quite low temperatures
($> 250^{\circ}$). This necessitated the inclusion of:

$$RI = A + HI \; (A = olefin) \qquad (4) \; (-4)$$
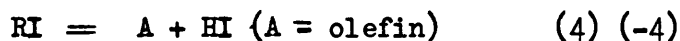
to account for olefin formation.

Because silicon does not form double bonds there is a
possibility that the Si- I bond, if formed in the $HMDS/I_2$
reaction, will be stabilised leading to a kinetically simple
system. There is a considerable amount of evidence in favour
of the suggestion that Si - Hal bonds are more stable than C- Hal.
The B.D.E's and bond energies derived so far all show this trend[16,17,18].
Thus a value of $D(Me_3Si-Cl) = 103$ kcal mole^{-1} (compared to
$D(Me_3C-Cl) = 79$ kcal mole^{-1}) is obtained by combining Haszeldines[20]
m/e 73 appearance potential from Me_3SiCl with Davidson and Stephenson's
value for $I(Me_3Si.)$[19].

Gowenlock and Thomas's[45] sodium flame work also indicated
this trend. They measured the rates of reaction of the methyl-
chlorosilanes and compared them to the analogous carbon reactions.
The carbon compounds reacted about one hundred times faster than
their silicon analogues (See Table III.)

TABLE III

Bimolecular Velocity Constants ($cc\ mole^{-1}sec^{-1}$)

Halide	PhBr	Me_3CCl	Me_2CCl_2	$MeCCl_3$	CCl_4
$10^{-11}k$	11.5	2.76	42.3	393	2260

Halide	Me_3SiCl	Me_2SiCl_2	$MeSiCl_3$	$SiCl_4$
$10^{-11}k$	0.0249	0.0204	0.0587	6.95

They also noticed that the reaction rate increased regularly with the successive replacement of methyl groups by chlorine in the carbon series, whereas no significant increase in rate was found for the chlorosilanes until the last methyl was displaced. They suggested that this effect could be due to $(p - d)\pi$ bonding in the Cl - Si bonds, the π contribution reaching a maximum when three donating groups were attached resulting in a weakening of the bonds for addition of a fourth.

This stabilisation is further reflected in the work of Haszeldine and Young[46] who noted that silyl radicals, produced by photolysis of a silane, tended to abstract a halogen from alkyl halides rather than a hydrogen atom as in the carbon reactions. The chain carrying steps appeared to be:

$$RX + Me_3Si\cdot \longrightarrow R\cdot + Me_3SiX$$
$$R\cdot + Me_3SiH \longrightarrow RH + Me_3Si\cdot$$
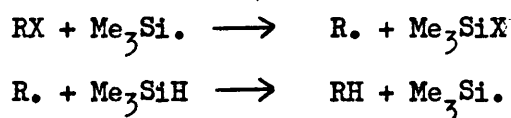
They suggested that this was due to the fact that the Si - Cl bond was stronger than Si - H, the reverse of the carbon situation.

Other workers[47] examined this system gas kinetically and found this observation to be correct, the trichlorosilyl radical abstracting a halogen atom from alkyl halides, RX, where X was chlorine or bromine. A similar effect was noted by Gilman et al[30] who found that the triphenylsilyl radical, $Ph_3Si.$, abstracted chlorine (from chlorobenzene) rather than a hydrogen atom.

This evidence, together with the fact that the reaction HMDS + I_2 has been shown to proceed quantitatively to trimethylsilyl iodide, Me_3SiI, in the liquid phase[48], suggests that this system could well lead to kinetically simple meaningful results. Therefore, this reaction has been studied in the gas phase and an account of the results obtained is given in the following pages.

EXPERIMENTAL SECTION

Part I. Preparation and Purification of Compounds.

1) Trimethylsilane, Me₃SiH.

A one litre flask was fitted with a stirrer, dropping funnel
and cold finger condenser filled with crushed ice. The top of the
condenser was connected to a trap, which was surrounded by liquid
nitrogen. The whole apparatus was swept through with a steady
stream of dry, oxygen-free nitrogen both before and during the
preparation. Drechsel bottles containing the reaction solvent
were used to indicate the rate of flow of nitrogen. The flask was
kept at about $40^{\circ}C$ by heating on an electric mantle.

The reaction:

$$LiAlH_4 + 4Me_3SiCl = 4Me_3SiH + LiCl + AlCl_3.$$

was employed on a quarter molar scale. 4.25g lithium aluminium
hydride (approx. 1/8th mole) were weighed into a previously tared
beaker containing a few mls of di-n-butyl ether. The slurry was
washed into the flask with about 250ml of solvent. 25.7g (1/4 mole)
of freshly distilled trimethylchlorosilane, Me_3SiCl, in 250ml

of solvent were added dropwise over a period of about ninety

minutes. When addition was complete the mixture was heated with

stirring for a further half hour.

A white solid was seen to collect in the cold trap. The trap

was transfered to the vacuum system for purification of the product.

A crude yield of 1/6th mole was obtained.

Purification.

Analysis of the product gas chromatographically showed that

less than 1% impurity was present. Mass spectral analysis indicated

the presence of hexamethyldisiloxane, $Me_3SiOSiMe_3$, and dimethyl-

silane (present as dimethyldichlorosilane in the starting material).

The mixture was fractionally distilled under vacuum from a methanol

slush bath (-97.8°C; vap. pres. Me_3SiH = 1mm) into a liquid nitrogen

trap. This removed the less volatile impurities. The dimethyl-

silane was removed by pumping the product from an allyl chloride

slush bath (-136°C; vap. pres. Me_3SiH = 10^{-2}mm). The resulting

product gave only one peak on the gas chromatograph, whilst mass

spectral analysis indicated the presence of negligible amounts of

siloxane and dimethylsilane.

2) Hexamethyldisilane, $(Me_3Si)_2$.

This compound was prepared by the method of Wilson and Smith[50]

using the reaction:

$$2Me_3SiCl + Na/K = (Me_3Si)_2 + 2KCl ,$$
$$\qquad\qquad (alloy) \qquad\qquad (Na)$$
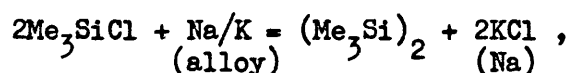
which was carried out under dry, oxygen-free nitrogen.

9.1g sodium (0.4 g atom) and 63g potassium (1.6 g atom) were
cut into thin slices and placed in a three litre flask together
with 400 ml sodium-dried ethyl benzene. The reaction would be
more efficient if sodium and potassium wire were used, but the
sheer bulk of metal present makes this impracticable. 260ml
(224g, 2.0 moles) of trimethylchlorosilane were added dropwise to
the stirred mixture. After a while the solution turned purple and
began to reflux gently. The solution was refluxed overnight,
diluted with ethyl benzene and distilled over until the vapour
temperature reached 130°C. The remaining slurry was filtered into
the distillate through glass wool and washed well with ethyl benzene.

Purification

Products were separated on a Vigreaux column. The refractive
indices of the fractions were measured periodically and samples
were only collected when this property reached the desired value.
A 60% yield (approx. 1/2 mole) of hexamethyl disilane was obtained,
together with small fractions of Me_3SiCl and $(Me_3Si)_2O$.

Physical Data.

Me_3SiCl : B pt = $57^{o}C$

$Me_3SiSiMe_3$: B pt = $112.5^{o}C$, M pt = $12.5 - 14^{o}C$

M.W. = 146, n_D^{25} = 1.4198, n_D^{20} = 1.4229.

$Me_3SiOSiMe_3$: B pt = $100.4^{o}C$, n_D^{20} = 1.3772.

n_D^{20} of the sample taken from purest fraction = 1.4223.

Even after this procedure about 3% impurity remained, being mainly Me_3SiCl and EtPh. Because HMDS is stable in air it was possible to purify it further by preparative gas chromatography.

Use of Auto-Prep A.700.

The chromatograph used was the Auto-Prep A.700. 1/2 ml samples of HMDS were injected onto the column by use of a hypodermic syringe. The column used was 30% silicone oil on embacel and this separated all the peaks admirably. The apparatus is so arranged that a sample can be collected as it is being eluted from the column. A Honeywell-Brown recorder is coupled to the chromatograph and by collecting sample whilst the top half of the peak is being displayed one can obtain extremely pure specimens.

HMDS purified in this way gave one peak by g.l.c. and only trace amounts of impurities were found by mass spectrometry.

3) Trimethylchlorosilane,Me$_3$SiCl.

Technical grade trimethylchlorosilane was obtained free from Midland Silicones Ltd. In this form it contained small quantities of hexamethyldisiloxane and dimethyldichlorosilane. These were removed by fractionation on a Vigreaux column. The sample used for electron impact contained less than 1/2% impurity.

4) Trimethylbromosilane, Me$_3$SiBr.

(a) From HMDS.

The method of Kumada et al[51] was employed using the reaction:

$$(Me_3Si)_2 + Br_2 = 2Me_3SiBr.$$
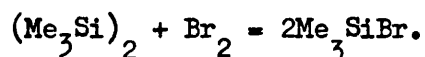
3.4 cc Br$_2$ were added dropwise to 10 g of ice-cooled HMDS in a nitrogen dry box. The addition occupied about three hours as reaction was extremely vigorous. The resulting liquid was distilled and trimethylbromosilane collected at 79.5-80°C. A quantitive yield was obtained. The product was stored over AlBr$_3$ and mass spectral analysis showed that only small amounts of siloxane, $(Me_3Si)_2O$. were present. There were no other impurities.

### (b) From Hexamethyldisiloxane.

The method used for preparation of the iodosilane was also used here. An excess of aluminium tribromide was refluxed with

the siloxane under nitrogen and a quantitative yield of tri-

methylbromosilane obtained.

5) Trimethyliodosilane, Me$_3$SiI.

This compound was prepared by the method of Voronkov et al[52]

The reaction employed was:

$$(Me_3Si)_2O + AlI_3 = Me_3SiI + Me_3SiO \ AlI_2 \xrightarrow{heat} Me_3SiI + AlOI......(1)$$
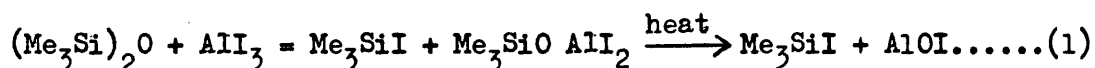
This preparation is convenient because the siloxane, $(Me_3Si)_2 O$,

occurs as a waste product in several of our preparations.

Due to the instability of the product it is necessary to carry

out this preparation under dry nitrogen.

To 6 g powdered aluminium in dry benzene was added 76.2g

I$_2$. The solvent was distilled off and the residue refluxed for

half an hour with 32.4 g (1/5th g mole) hexamethyldisiloxane.

Purification.

The resulting mixture was separated on a Vigreaux column.

The conversion was virtually quantitive but a great deal of

the iodosilane (b_{760} = 107°C, d_4^{20} = 1.470) was left on the

column. This could have been avoided by adding a high boiling

solvent to the mixture so that the remaining iodosilane could be

forced out of the column. In the event, a 40% yield (approx.

1/6 g mole) of the pure product was obtained. This product

discoloured very quickly as it was easily hydrolysed back to the

siloxane when only traces of moisture were present:

$$2Me_3SiI + 'O' = (Me_3Si)_2O + I_2$$

Addition of copper to the discoloured mixture removed the

iodine colouration by reacting to form cuprous iodide.

Unfortunately this left the siloxane impurity unaltered. Thus for

the electron impact studies the iodosilane was stored over

aluminium tri-iodide and the mixture heated from time to time

to promote reaction 1. Introduction of this product to the

mass spectrometer, through the all glass inlet, gave strongm/e

185 and 200 peaks corresponding to the parent minus methyl and

parent ions of the iodosilane. Siloxane interference was very

small if the temperature of the source was low and the sample

was allowed to flow through the source for some time prior

to the recording of a mass spectrum.

6) Electron Impact Standards.

The method developed for the measurement of appearance

potentials involved the use of several standards of known

ionisation potential. If the Analar compounds were available

these were used as received. Other-wise, the samples were

purified by fractional distillation.

7) Purification of Halogens.

B.D.H. A.R. Iodine was purified by 'dynamic sublimation' as described by Knox and Musgrave[44].

The sample of iodine was placed in the inlet of a heated tube 130cm X 1cm diam, packed with 1mm diam.glass beads. The inlet end of the tube was held at about $200^\circ C$ and the outlet at $100^\circ C$. A steady flow of dry nitrogen carried the halogen vapour along the tube and it was collected on a water cooled finger at the tube outlet. Volatile impurities did not collect on the finger, whilst involatile compounds remained behind in the sample boat.

A.R Bromine was purified by a series of bulb to bulb distillations. Both halogens were then seen to be mass spectrometrically and chromatographically pure.

Part II. Apparatus and Technique - Electron Impact Studies.

The appearance potential measurements were carried out on
an A.E.I MS9 mass spectrometer fitted with a device similar in
principle to that devised by Gallegos and Klaver[53], which allowed
the automatic recording of appearance potentials.

The Mass Spectrometer.

The M.S.9 is built to a Nier - Johnson[54] design and utilises
a double focusing analyser system, so called because the ion
beam is velocity (or energy)focused by passage through a radial
electrostatic field prior to the usual mass separation in the
magnetic analyser. A standard electron bombardment source was
used in the electron impact studies, the ionising electron beam
being generated from a heated tungsten filament (fig.2). A schematic
diagram of the M.S.9 vacuum system is shown in fig.1.

The M.S.9 is fitted with dual detectors (see fig.3); a
standard collector plate/amplifier system which amplifies and
records the intensity of the ion beam falling on it and an electron
multiplier which provides increased sensitivity. In the multiplier
the energetic ions impinge upon the metal surface of a cathode and
cause the emission of a number of secondary electrons. These
are accelerated and allowed to strike another electrode causing
additional electron emission. This is repeated several times
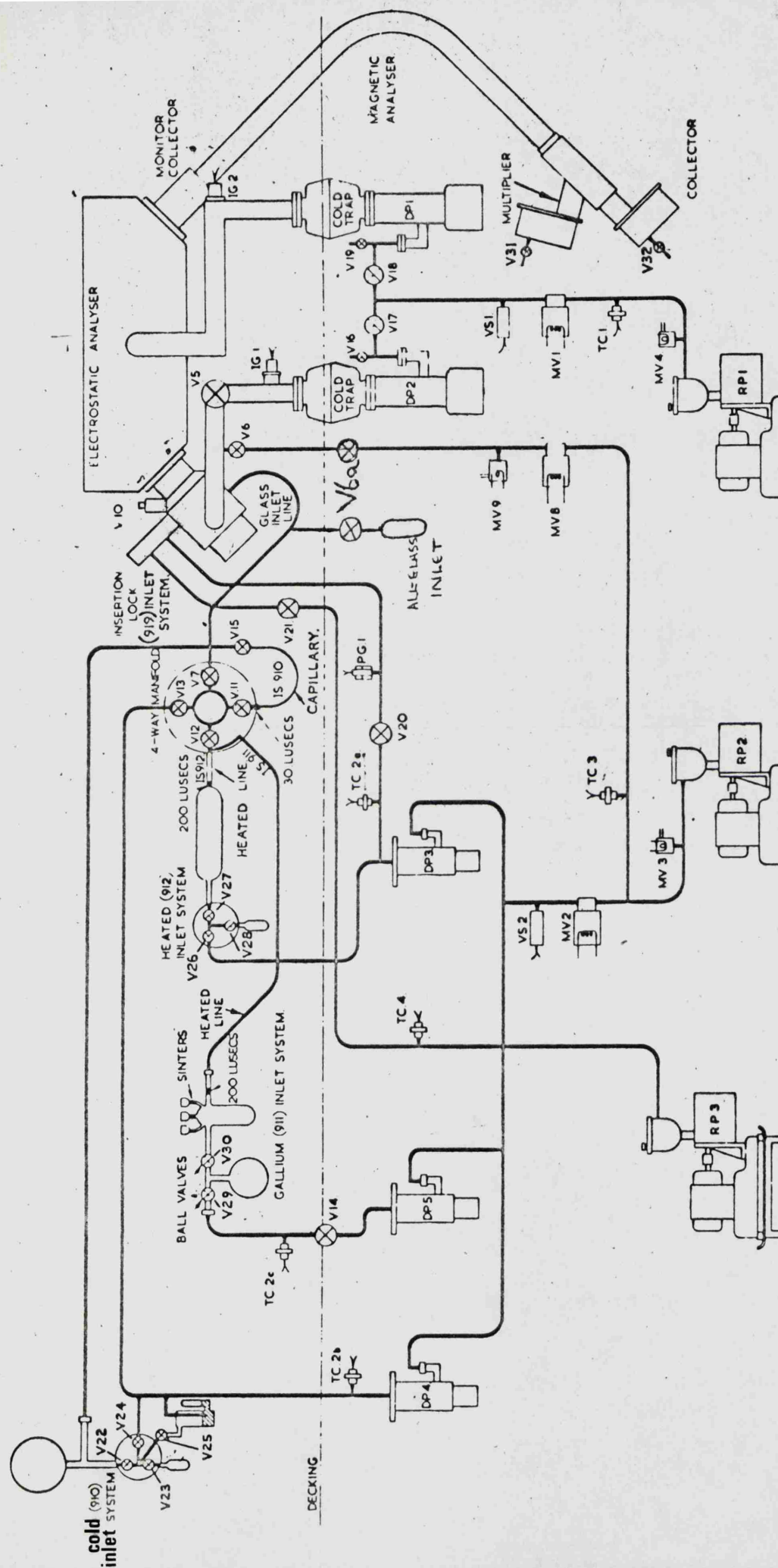with the result that a large electron current is built up from

FIGURE 1. MS 9 Vacuum System (schematic).

29

each ion collected. The strength of the electron current, and hence the sensitivity of the instrument, can be varied by changing the potential between the electrode plates. This detector has high sensitivity and rapid response but suffers from the drawback that the number of electrons formed are not always directly proportional to the number of ions collected. However, it was found that this factor did not decrease the efficiency of the instrument in electron impact studies.

The mass spectrometer was fitted with several sample inlet systems through which components of varying volatility could be introduced to the source. Unfortunately all these inlets contained metal parts and it was found that the unstable trimethyl-silylhalides tended to decompose on their way to the source. An all-glass inlet was, therefore, constructed (see fig 1) and this provided a metal-free path to the source. Samples were introduced through this inlet from a reservoir (fig 4) which was adapted to fit onto both the mass spectrometer and the vacuum equipment used in the kinetic studies.

Appearance Potential Measurements.

The M.S.9 is fitted with a peak switching unit which allows two ions of different m/e to be displayed alternately on an oscilloscope by automatic switching of the ion accelerating voltage at constant magnetic field. Thus the ion to be studied could be displayed along with some reference ion, the appearance
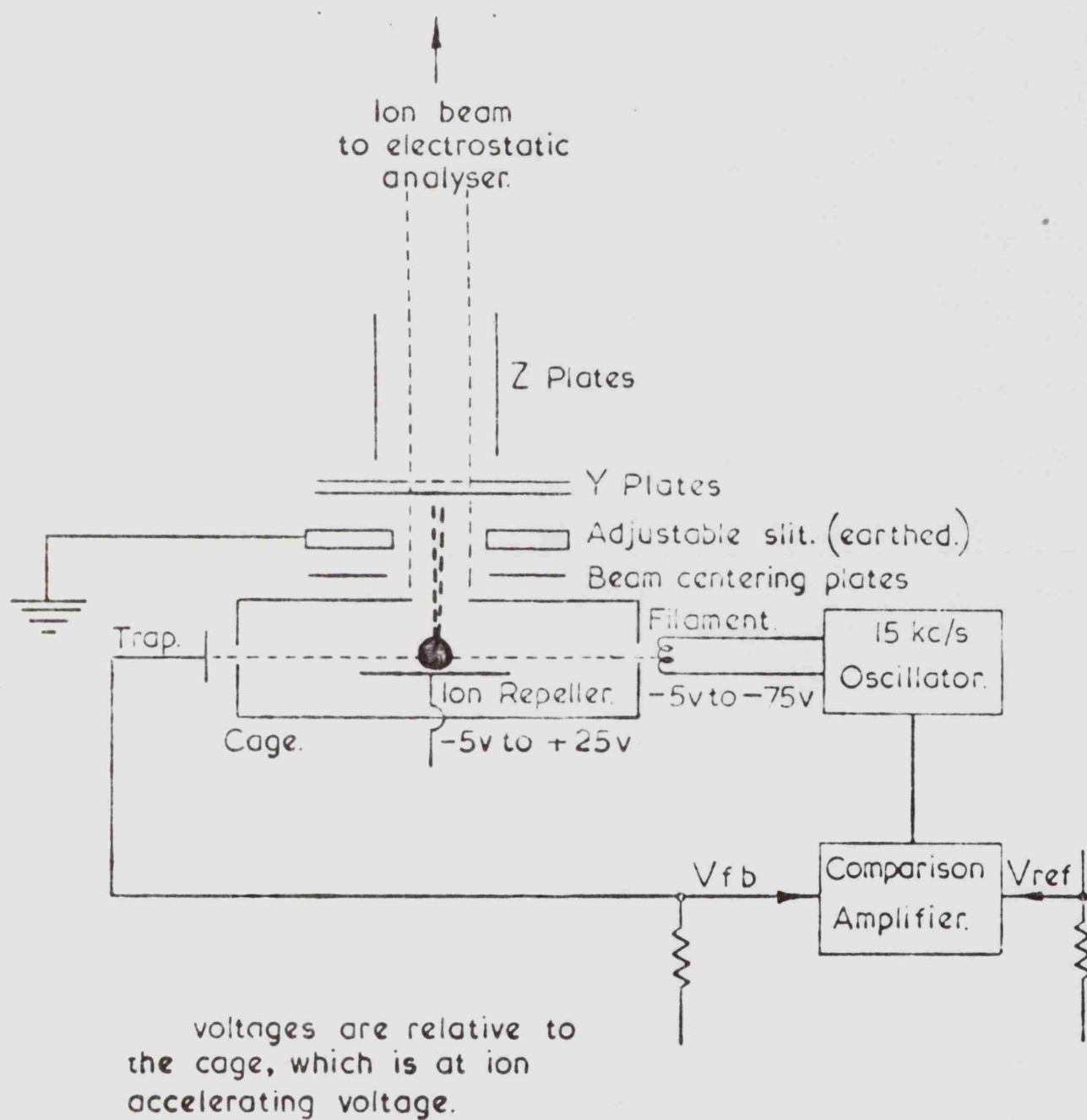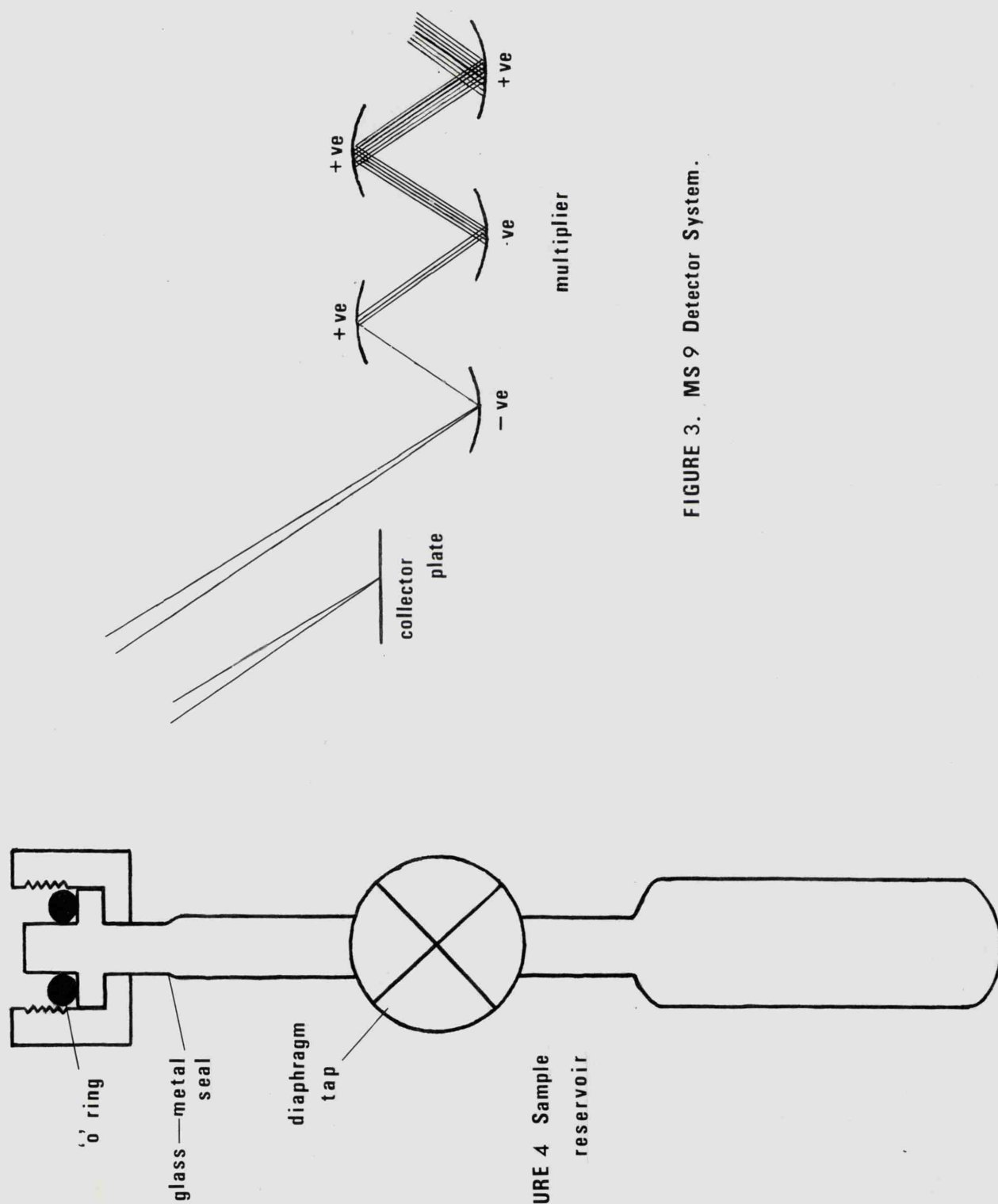
FIG. 2   ION SOURCE & ELECTRODE SUPPLIES.

FIGURE 3. MS 9 Detector System.

+ve

+ve

-ve

+ve

-ve

multiplier

collector plate

'o ring

glass—metal seal

diaphragm tap

FIGURE 4 Sample reservoir

potential of which was accurately known. The circuit relays were made to actuate a stepping motor which automatically decreased the electron beam energy by 0.05 V after each complete display cycle. a cycle occupied only 4 secs and, therefore, ionisation efficiency curves were obtained very rapidly.

Procedure.

Measurements were only made when the mass spectrometer background in the region of the two ions was clean. 70 e.v. mass spectra were also obtained to ascertain that the ions sought after were in fact present in reasonable abundance.

The sample and reference compounds were introduced to the source through different inlets, the peaks of the two ions displayed on the oscilloscope and their heights 'normalised' by adjustment of the sample pressures. The stepping motor and recorder were started and ionisation efficiency curves obtained simultaneously for the two ions by allowing the electron beam energy to gradually decrease below the threshold of the two curves.

Some of the more established methods of extrapolating ionisation efficiency curves (their relative merits are described elsewhere[58]) were applied, viz. semi-log plot[56], critical slope[55] and extrapolated voltage difference[57]. Whilst these all yielded

results which agreed to $\pm$ 0.1 ev, at least as good appearance

potentials were obtained by the following, simpler procedure:

The instrument was adjusted for maximum sensitivity by

setting the multiplier to the highest safe value. Reference and

sample peaks were displayed as above but equalised very close

to the threshold (about 2V above) and the tail regions only of

the ionisation efficiency curves obtained. Appearance potentials

were then determined by simply counting the number of motor steps

between the disappearing points of the two ions.

Exploratory Experiments.

The step counting procedure is analogous to the 'initial

upward break' method in which the ionisation efficiency curve is

extrapolated back to the energy axis and the point of 'initial

break' taken as the appearance potential. The method has been

criticised partly because of the difficulty in determining this

point[58] but more especially because the results obtained were

found to be dependent on sample pressure[59]. In the approach

used here, however, no such problem was encounted and results agreed

to 1 step (i.e. 0.05 v) over a considerable range of pressures.

Results obtained in early studies were found to vary

markedly with the m/e and appearance potential of the reference

ion. This latter effect is well known and common to all

Table IV

Effect of Variation in Mass Ratio and Appearance
Potentials of Reference and Sample Ions.

(a) Variation in Mass Ratio.

Standards (X, Y)	$X^+ : Y^+$	Δ (volts) *
$MeBr/C_6H_5CH_3$	1.01	0.10
$n-C_6H_{14}/c-C_6H_{12}$	1.02	0.00
$C_4H_9OH/i-C_5H_{12}$	1.03	0.10
$C_3H_7Cl/i-C_5H_{12}$	1.08	0.10
$Xe/c-C_6H_{12}$	1.57	0.50

* see
text

The same trend can be seen in the measurement of $A(Me_3Si^+)$ from
Me_3SiCl against reference ions of increasing mass number. Thus with
$i-C_5H_{12}$ $(X^+ : Y^+ = 1.01)$ and $n-C_3H_7Cl$ $(X^+ : Y^+ = 1.07)$ as reference
ions $A(Me_3Si^+) = 10.9$ e.v., whereas $c-C_6H_{12}$ $(X^+ : Y^+ = 1.15)$ and
Xe $(X^+ : Y^+ = 1.81)$ yield 11.15 e.v. and 11.6 e.v. respectively.

b) Variation in Appearance Potentials.

Standards (X, Y)	$\left[\dfrac{A.P._{X^+} - A.P._{Y^+}}{(volts)} \right]_{lit}$	Δ(volts)
$n-C_6H_{14}/c-C_6H_{12}$	0.20	0.00
$C_4H_9OH/i-C_5H_{12}$	0.30	0.10
$C_3H_7Cl/i-C_5H_{12}$	0.40	0.10
$MeBr/C_6H_5CH_3$	1.30	0.10
C_4H_9Br/Xe	2.00	0.25
$Xe/C_6H_5CH_3$	2.90	0.80
$Kr/i-C_5H_{12}$	4.20	2.10

methods of measuring appearance potentials[58]. The dependence

on the m/e of the reference ion was also expected and was due to

the presence of electric fields in the ionisation chamber.

These fields can normally be minimised by keeping the ion

repeller plate and the electron trap close to cage potential.

The peak switching unit, however, focuses the reference and

sample ions by alternating the ion accelerating voltage, thus

producing fluctuating electrostatic fields in the source

region.

It was essential to estimate the importance of these effects

quantitatively and, therefore, molecular and atomic ions with well

established ionisation potentials and widely differing m/e were

cross checked against each other and the appearance potentials

derived by the step counting method. At least six determinations

at various initial pressures were carried out on each pair of

ions and the results obtained were independent of pressure, agreeing

to one motor step.

The resulting trends are summarised in table **IV.** Δ in the

last column is the error in measurement.

i.e. $\Delta = \left[A(X^+) - A(Y^+) \right]_{lit} - \left[A(X^+) - A(Y^+) \right]_{expt}$

Plots of Δ v.s. mass ratio $X^+ : Y^+$ and Δ v.s. $\left[A(X^+) - A(Y^+) \right]_{lit}$

(see fig.5) indicate as expected that the errors increase with the

difference in m/e and appearance potential of the sample and

FIGURE 5. Plots to test appearance potential apparatus.
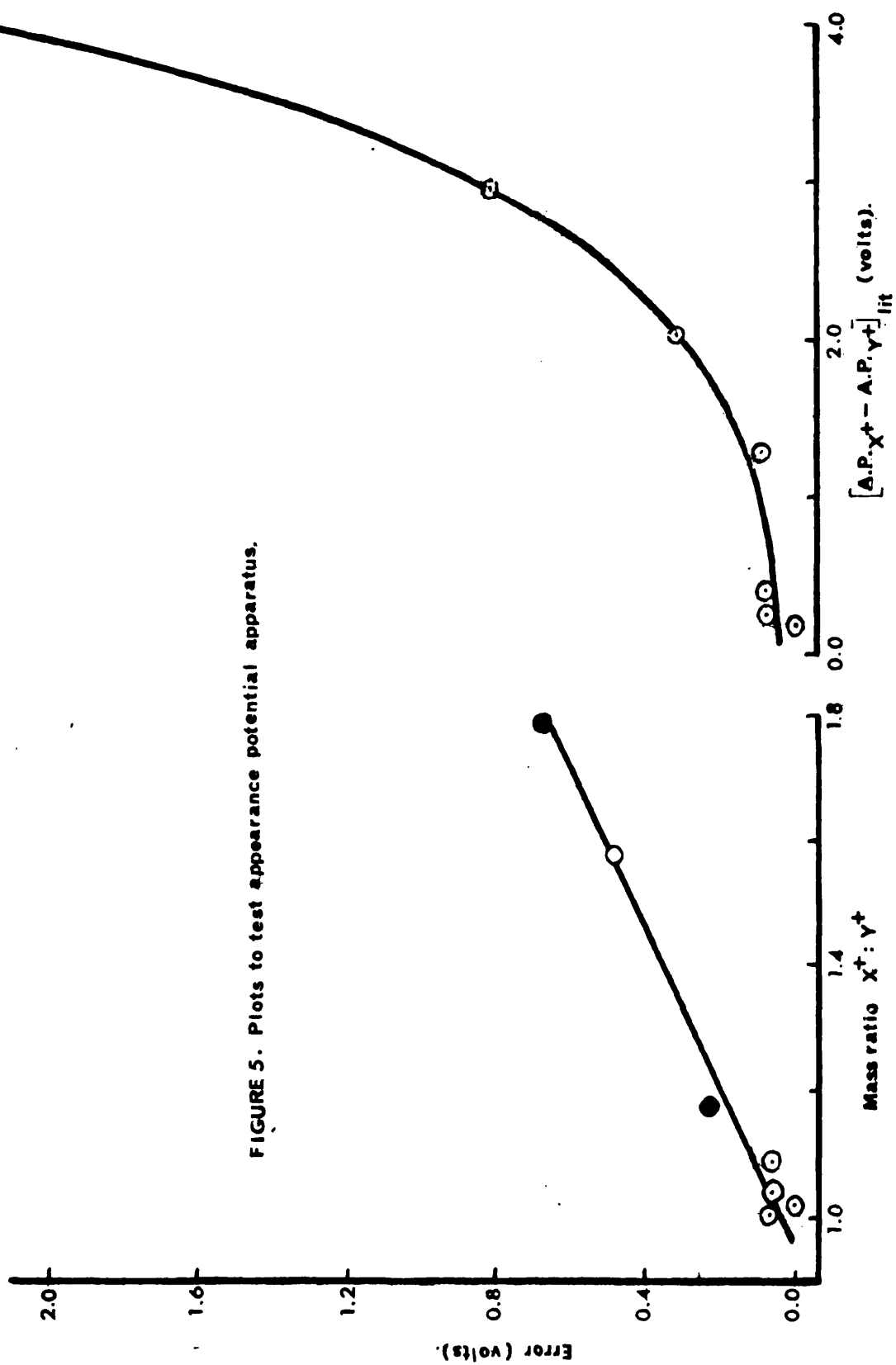
reference ions. The plots in fig. 5 indicate also that the step

counting method yields results accurate to ± 0.1ev:

(a) if the sample and reference ions have a mass ratio less

than 1.07 and

(b) if the difference in appearance potential between the

two ions is less than 1.3ev. Therefore the method was used,

within these limits, in the studies on the trimethylsilyl halides.

Part III. Apparatus and Technique-Kinetic Studies.

All the gas kinetic experiments were carried out in a static system. The reactions were studied in a pyrex vessel and the products analysed by passage through a gas chromatograph joined directly to the vacuum system.

Furnace.

The furnace consisted of a hollow aluminium cylinder closed at one end. It was 35cm long with I.D = 6.5cm and O.D = 17cm. The cylinder's curved surface was wrapped with $\frac{1}{8}$" asbestos board wound with nichrome heating wire. The whole was further insulated by 2" thick firebrick, which was sealed at the joins with asbestos packing. Free spaces were packed with asbestos to assist uniform heating and reduce heat loss.

The furnace was mounted horizontally and the reaction vessel held in place by a solid aluminium plug which fitted exactly into the open end of the furnace. Two holes were bored through this plug; one for the reaction vessel inlet and the other held the hot junction of a thermocouple. A heavy duty Variac transformer controlled the heating to the furnace, whilst sensitive temperature control was provided by a Sunvic R.T.2 proportional controller incorporating a platinum resistance thermometer.

Temperature Measurement.

The temperature of the furnace was measured by a chromel/alumel thermocouple, which was calibrated against a N.P.L - certified platinum/ 13% rhodium - platinum thermocouple. Measurement was accurate to $\pm$ 1°C.

Reaction Vessel.

The reaction vessel was a sphere with an approximate volume of 120cc. The surface to volume ratio of the vessel could be altered by packing with thin walled pyrex tubes, 2.5cm long with O.D = 3mm and I.D = 2mm. We can calculate approximate figures for the surface to volume ratio (S/V) of the two vessels.

	Surface area	Volume	S/V Ratio
Empty Vessel	144cm^2	120cc	1.2
Packed Vessel	849cm^2	103cc	8.2

The Vacuum System.

(a) Pumping.

The system was evacuated by a single stage, Genevac rotary pump (GRS.2) coupled to an all-glass mercury diffusion pump.

This section was fitted with greased vacuum taps where necessary

and condensable materials were removed by a trap at liquid

nitrogen temperatures. A further trap protected the filament of

a Pirani gauge head (Edwards High Vacuum Limited)

(b) Pressure Measurement.

The Pirani gauge was used continuously and kinetic runs

were only undertaken at pressures less than 5×10^{-4}mm Hg.

This gauge was useful for daily leak testing. Regular vacuum

checks were carried out with a McLeod gauge.

(c) Heating of the System.

Because of the low volatility of iodine it was necessary

to heat all the sections through which it passed. The reaction

system was kept completely grease free because of the tendency

of silicon compounds to attack tap grease. Fischer - Porter

teflon vacuum taps were, therefore, used (fig.6) in place of the

standard greased tap. The heating of these taps had to be

carefully controlled as they soften and distort very easily.

A temperature of about 75°C was felt to be the highest per-

missable and this was obtained by heating the glassware through

nichrome wire windings.

(d) Pre-mixing.

It was found necessary to premix the reactants at relatively low temperatures before introduction to the reaction vessel. This mixing took place in a 250 ml cylindrical vessel which was drawn out into a freezing pip. The 'mixer' was enclosed by a steel tube, which was insulated by asbestos board and wrapped with nichrome wire. This furnace was held at $85^{\circ}C$ by manual adjustment of a Variac transformer. There was less than 1% reaction in three hours between iodine and HMDS at this temperature.

(e) Leak Testing.

Large leaks were found by use of a high frequency Tesla coil in the usual way. Smaller ones were detected by an Edwards (L.T.2.B type) leak detector coupled to the Pirani gauge head. A sensitive galvanometer across the leak detector completed a Wheatstone bridge circuit. Small changes in pressure at the gauge head then caused an out-of-balance signal leading to a deflection on the galvanometer. The signal could be magnified by playing a jet of hydrogen on the suspected area. An A.E.I M.S.10 mass spectrometer was indirectly joined to the vacuum system and it was, therefore, possible to use this as a very sensitive leak detector. The machine was focused on the background hydrogen (or methane) peak and then that gas was sprayed around

the suspected area. A sudden increase in the strength of the background peak was indicative of a leak.

The Fischer-Porter vacuum taps were tested extensively in this way and showed no inclination to leak either over the seat or through the 'o' ring. Heating the taps to the temperatures used did not decrease their leak tightness to any significant extent.

(f) Reactants.

Reactants were rigo rously purified and de-gassed daily before use. Gas chromatography and mass spectrometry were used as criteria of purity. Samples were transferred to the mass spectrometer (A.E.I. MS9) in the reservoir (fig.4), 70 e.v. mass spectra obtained, and the cracking patterns compared to those of known samples. Gaseous materials were stored on the vacuum system in 2 litre bulbs, whilst liquid and solid reactants were kept in 50cc pear shaped vessels.

Injection Procedure.

Introduction of the reactants on a straight forward pressure basis using a glass spiral gauge proved to be too

FIGURE 7. Vacuum system.

FIGURE 6. Fischer — Porter vacuum tap

approximate, because the highest workable pressure of iodine was 8mm. Therefore reactants were introduced into the 'mixer' from constant temperature baths. A schematic diagram of the vacuum system is shown in fig.7. 7.2mm HMDS was used as a standard pressure as this is the vapour pressure at $0^{o}C$. The iodine reservoir was thermostatted in the same way as the 'mixer' and the injecting temperature derived from the vapour pressure plot. It was found necessary to allow up to three minutes for a vapour pressure to build up in this way.

The pressure of HMDS was expanded into the 'mixer' through T_1. It was then frozen into the sample U and held there whilst the iodine pressure was allowed to build up in the 'mixer'. Both components were then frozen down into the pip and allowed to warm up together. After pre-mixing for 30 minutes the reactants were expanded into the vessel through T_2. Clearly, one has to guard against the presence of cold spots in the system during such a procedure. These were easily detected by the collection of iodine on the tube walls.

Sampling Procedure.

The reaction was quenched by freezing into the Sample U through T_3 and T_4. After warming, the whole sample was injected into the gas chromatograph by manipulation of T_5, T_4, and T_7. The carrier gas was by-passed through a capillary tube when these taps were closed.

Initially a steel sampling valve, similar to that developed by Pratt and Purnell[60], was used. The products of the reaction were found to attack the metal of the value and therefore this was rejected in favour of an all-glass sampling system. At first difficulties were experienced in the sampling procedure but eventually the system described above was built up and this proved very effective.

Identification and Analysis of Products.
By Gas Chromatography.

The products of the reaction were analysed and identified by passage through a gas chromatograph. The chromatograph consisted of a packed column and a Gow-Mac (Model 091) hot wire gas density balance, both housed in a furnace which was thermostatted at about $90^{\circ}C$.

The Column.

The reaction products were found to attack both copper and nylon columns and therefore an all-glass version was introduced. This consisted of four coils packed separately and joined together to a length of about 10ft. Thus the whole reaction and analysis system up to the mouth of the detector was built from pyrex glass and was kept completely free from grease. The column packing was 5% silicone oil on embacel.

The Detector.

The eluted gasses passed into the detector, which was coupled to a Honeywell-Brown recorder fitted with a disc integrator. The integrator measured the areas of the peaks as they were recorded. Ideally the peak area of a component taken in conjunction with the areas of all the other constituents of the sample, gives a good measure of the concentration of that component.

The carrier gas was oxygen - free nitrogen dried by passage through molecular sieve. This gas was divided into two streams; the reference stream, which flowed directly to the detector, entering at A (fig.8) and the sample stream, which went via the sample injection point and the column entering the detector at C. Inside the detector the reference stream divided again, flowing upwards past the detector element B_1 and dow nwards past B_2;B_1 and B_2 were heated by a 150 ma current and were built into a Wheatstone bridge circuit, which was balanced when only the carrier gas was flowing. When a sample was introduced at C it either rose or fell depending on its density relative to nitrogen. This caused the reference gas flowing past one detector element to slow down, leading to an increase in the temperature of the element, which in turn caused an out-of-balance signal, appearing as a peak on the recorder. A big advantage here is that the samples are never allowed to come into contact with the elements.
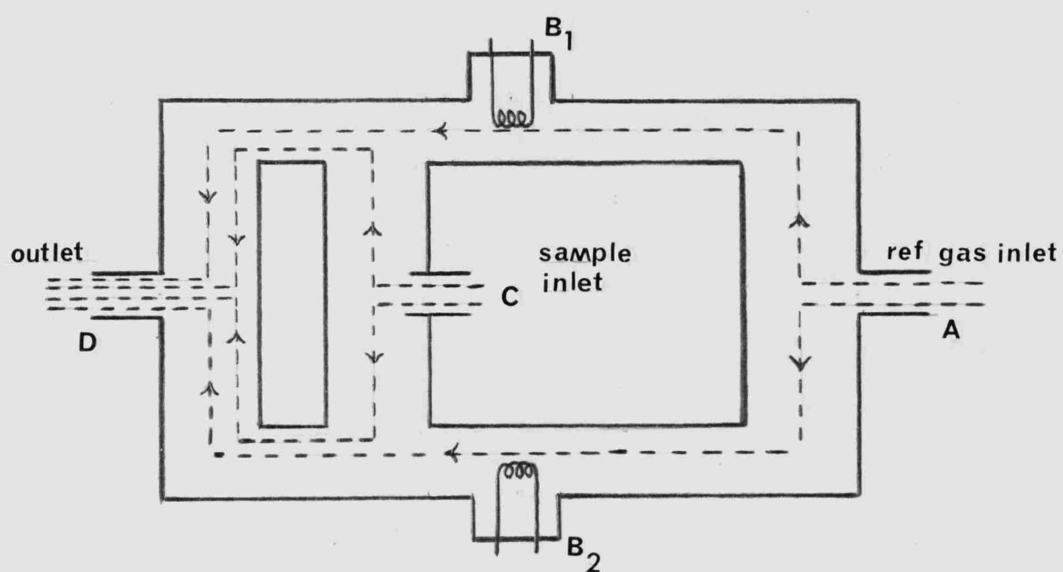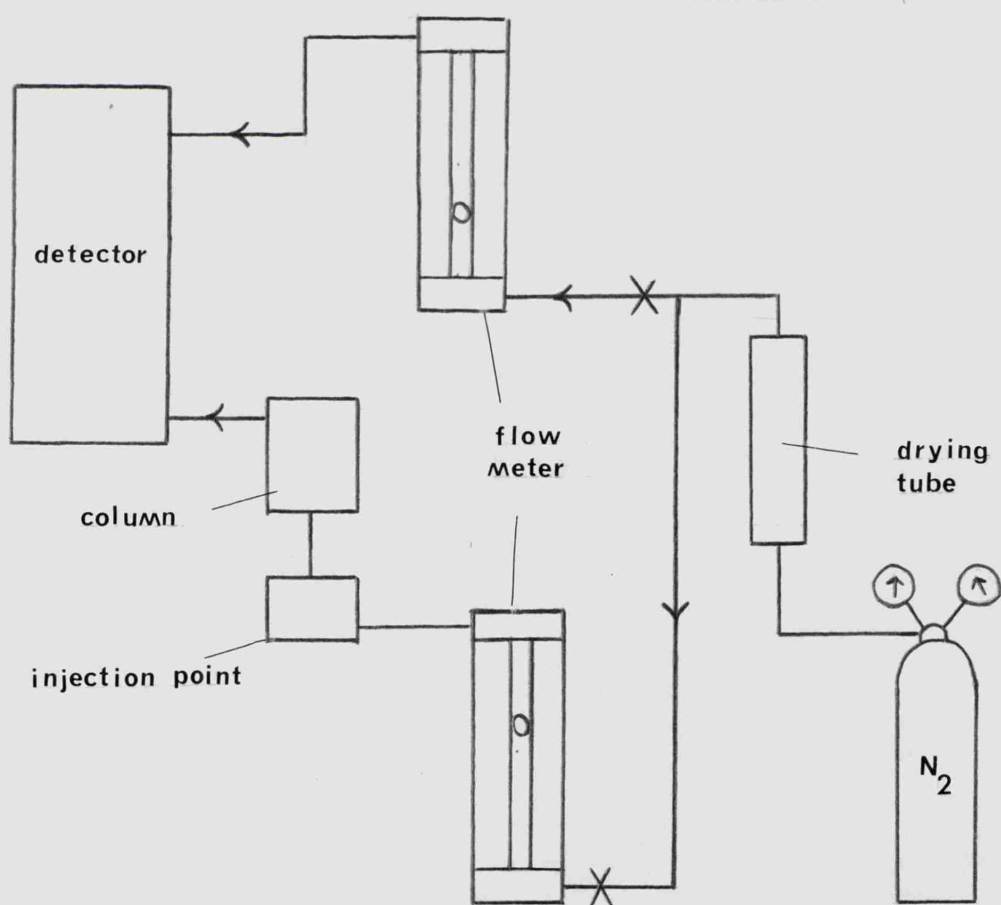
B₁

outlet

sample inlet

ref gas inlet

C

D

A

B₂

FIGURE 8. Detector.

detector

flow meter

drying tube

column

injection point

N₂

By Mass Spectrometry.

Reaction products were also identified by use of the M.S.9 mass spectrometer, which was able to detect very tiny concentrations of components present in the sample mixture. Run products were collected in the sampling reservoir and introduced to the source via the all-glass inlet.

Variation in Sensitivity of g.l.c.Detector.

Because of the procedure used, considerable time passed before a full decay plot could be built up. The sensitivity of the detector to the effluents tended to vary even throughout a day. To overcome this a zero reaction HMDS peak was passed through the column after every run and the corresponding peak areas corrected by comparison to this. Consequently, it was not necessary to obtain a plot all in one day. Indeed one decay curve was made up from points taken several weeks apart.

RESULTS SECTION

Part I - Electron Impact Studies

The Trimethylsilyl Halides

The mass spectral cracking patterns of all trimethylsilyl compounds are characterised by the strength of their m/e 73 peak from the trimethylsilyl ion, Me_3Si^+. This is almost invariably the base peak, having a much greater intensity than the other peaks present. When introduced through the conventional cold inlet of the mass spectrometer the bromo- and iodosilane spectra contained variable parent and parent minus methyl peaks of low intensity. This was due to the rapid hydrolysis of these compounds on the metal walls of the mass spectrometer to form hexamethyldisiloxane, $Me_3SiOSiMe_3$, which contains the extremely strong Si-O bond. The chloride spectrum contained little evidence of siloxane and in fact this compound is only hydrolysed when boiled with water.

The characteristic siloxane peaks at 147 and 162 were largely eliminated when the halides were introduced to the
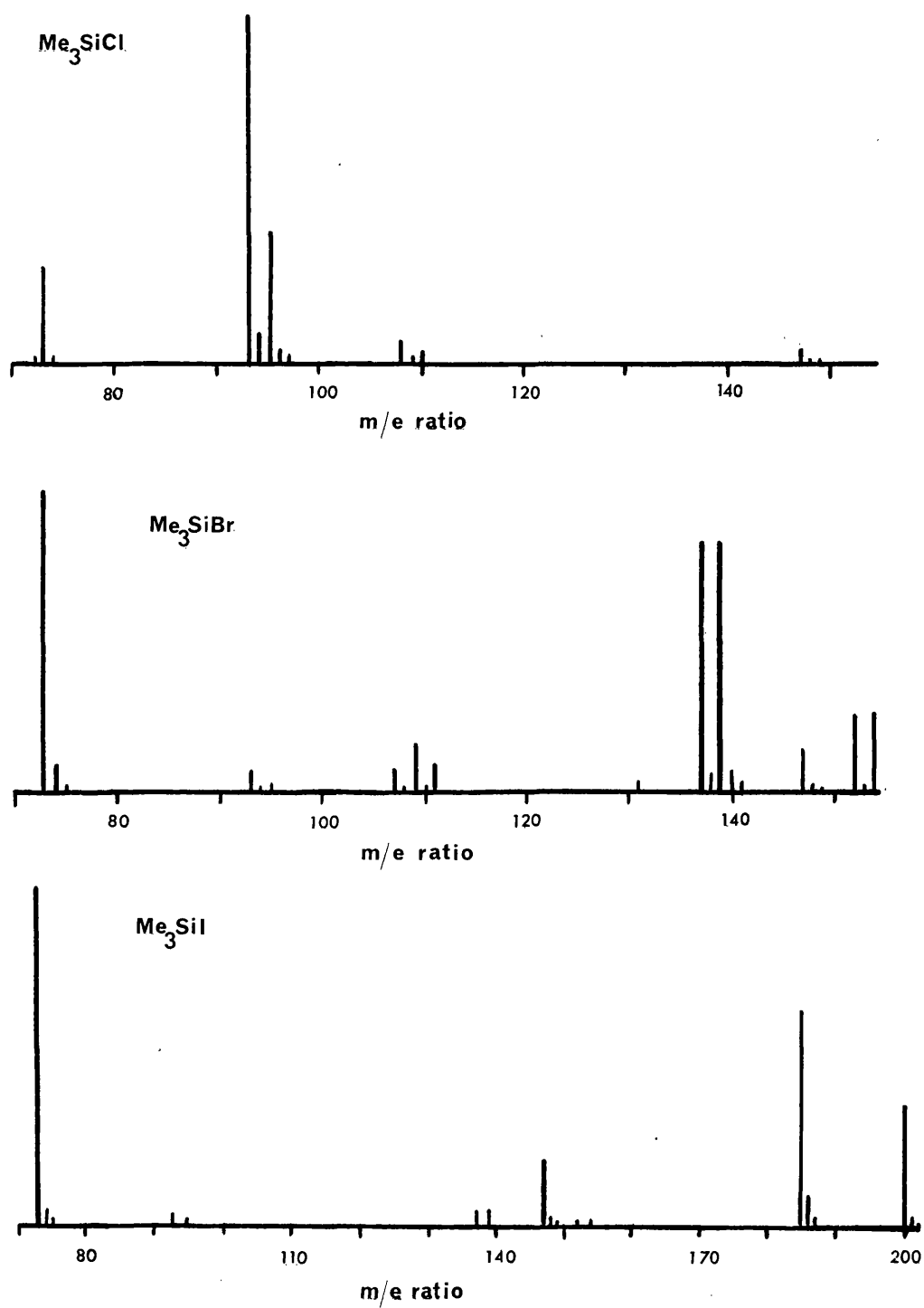
FIGURE 9. Mass spectra of the trimethylhalosilanes.

source through the all-glass inlet. The halide ion peaks be-
came correspondingly stronger and were of good intensity if
the source was 'seasoned' before a run by allowing the compounds
to flow through the system for some time. 70e.v. (strength of
ionising electron beam) mass spectra obtained in this way for
the three trimethylsilyhalides (X = Cl,Br and I) are shown in fig.9.
It can be seen that characteristic ions present in all three
mass spectra are m/e 73, the molecule (or parent) ion and the
ion formed from the radical produced by loss of a methyl group
from the molecule.

Despite the precautions taken the peaks of m/e 73 almost
certainly contained a small contribution from the siloxane.
Fortunately the appearance potential value for m/e 73 from
hexamethyldisiloxane is several electron volts higher than the
halosilane figures, and it is unlikely that the small amounts
present interfered with the results obtained. Before every run
it was necessary to check the background of the spectrum in
the region of the two ions to be considered in order to ascertain
that no peaks were present of the same m/e as either of these
ions.

Source temperatures were particularly important in
measurements on the bromide and iodide for it was found that
at higher temperatures inconsistent results were obtained and

sometimes the halide ion failed to disappear at all. Therefore all measurements were made at source temperatures below $100^{\circ}C$ where repoducible figures were recorded.

Appearance Potential Measurements.

Because of the need to keep the m/e and appearance potential values of the sample and reference ions close together it follows that a wide range of reference compounds will have to be employed in order to study a series of ions of differing mass and appearance potential. The measurements on the trimethylsilylhalides were carried out in all cases against compounds with well established ionisation potentials. Appearance potentials obtained in this way for the m/e 73, parent and parent minus methyl ions from the trimethylsilyl halides are listed in table V together with the published data presently available. At least six determinations were carried out on each ion and provided the conditions recorded above were adhered to all these determinations agreed to within one step (i.e 0.05ev). Variation of sample and reference pressure did not affect the results in any way. Typical ionisation. efficiency curves for a sample and reference ion are shown in fig.10.

The molecular ion i - $C_5H_{12}^{+}$ from iso-pentane was used as reference in the m/e 73 measurements as it has a m/e of 72.

Table V

Appearance Potentials from the Trimethylsilylhalides

Compound	Ion	Standard	This work	ref. 18	ref. 25
Me_3SiCl	Me_3SiCl^+	$PhC_2H_5^+$	9.9 ± 0.1	10.58	10.2
	Me_3Si^+	$i\text{-}C_5H_{12}^+$	10.9 ± 0.1	12.4	12.16
		$n\text{-}C_3H_7Cl^+$			
	Me_2SiCl^+	$PhCH_3^+$	10.6 ± 0.1	11.0	
Me_3SiBr	Me_3SiBr^+	$PhBr^+$	9.8 ± 0.1	10.24	10.04
	Me_3Si^+	$i\text{-}C_5H_{12}^+$	10.5 ± 0.1	10.69	
	Me_2SiBr^+	CH_3I^+	10.7 ± 0.1	10.97	
Me_3SiI	Me_3SiI^+	PhI^+	8.9 ± 0.1		
	Me_3Si^+	$i\text{-}C_5H_{12}^+$	10.1 ± 0.1		
	Me_2SiI^+	$n\text{-}C_4H_9I^+$	10.3 ± 0.1		

Also Haszeldine et al record $A(Me_3Si^+) = 11.5\pm0.2$ ev in ref. 20.
from Me_3SiCl.

Table VI

Thermochemical Data Derived from the Above Appearance Potentials (kcal mole^{-1}).

	$D(Me_3Si\text{-}X)$	$\Delta H_f^0(Me_3SiX)_g$	$\Delta H_f^0(Me_2SiX^+)_g$
Me_3SiCl	88 ± 2	-84.7 (lit)	126 ± 4
Me_3SiBr	78.5 ± 2	-77 ± 2	136 ± 4
Me_3SiI	69 ± 2	-69 ± 2	135 ± 4
$Me_3Si.$	—	-25.6 ± 2	

From the relationship:

$$I(Me_3Si.) = \Delta H_f^0(Me_3Si^+) - \Delta H_f^0(Me_3Si.) \quad \text{derived}$$

from the ionisation

$$Me_3Si. \longrightarrow Me_3Si^+ + e^-$$
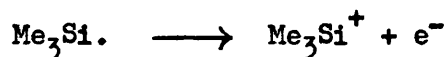
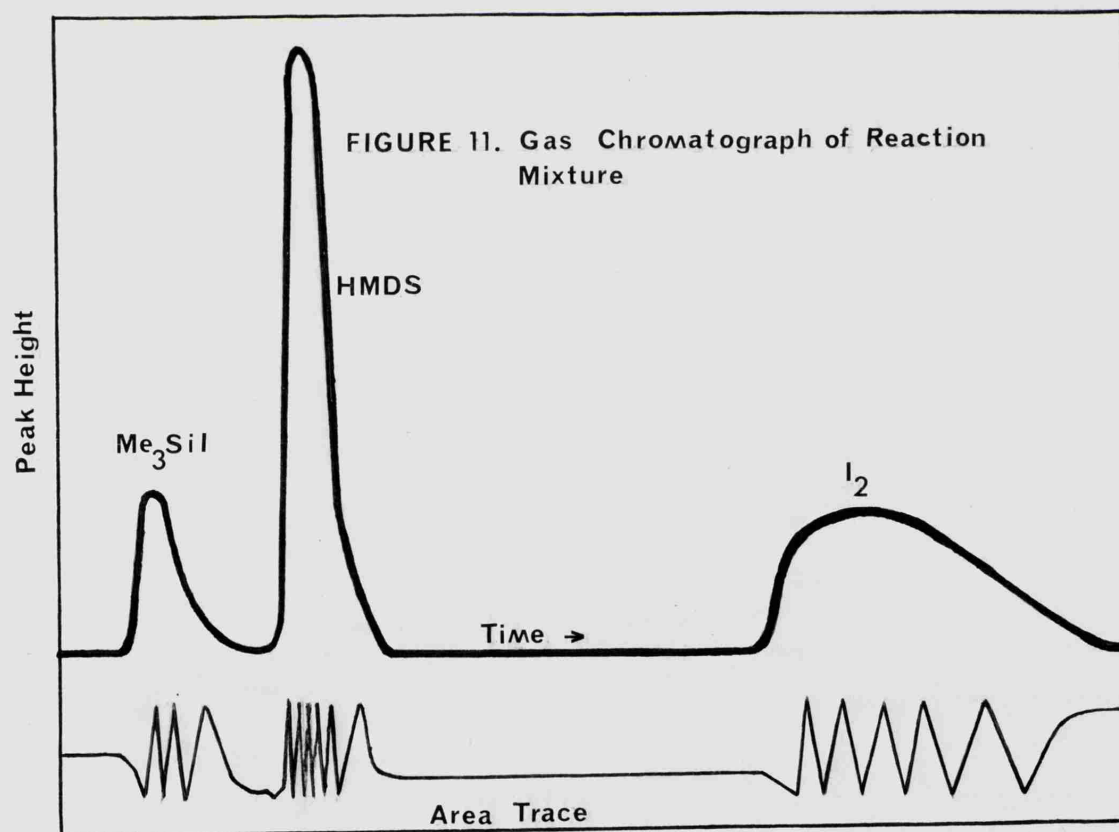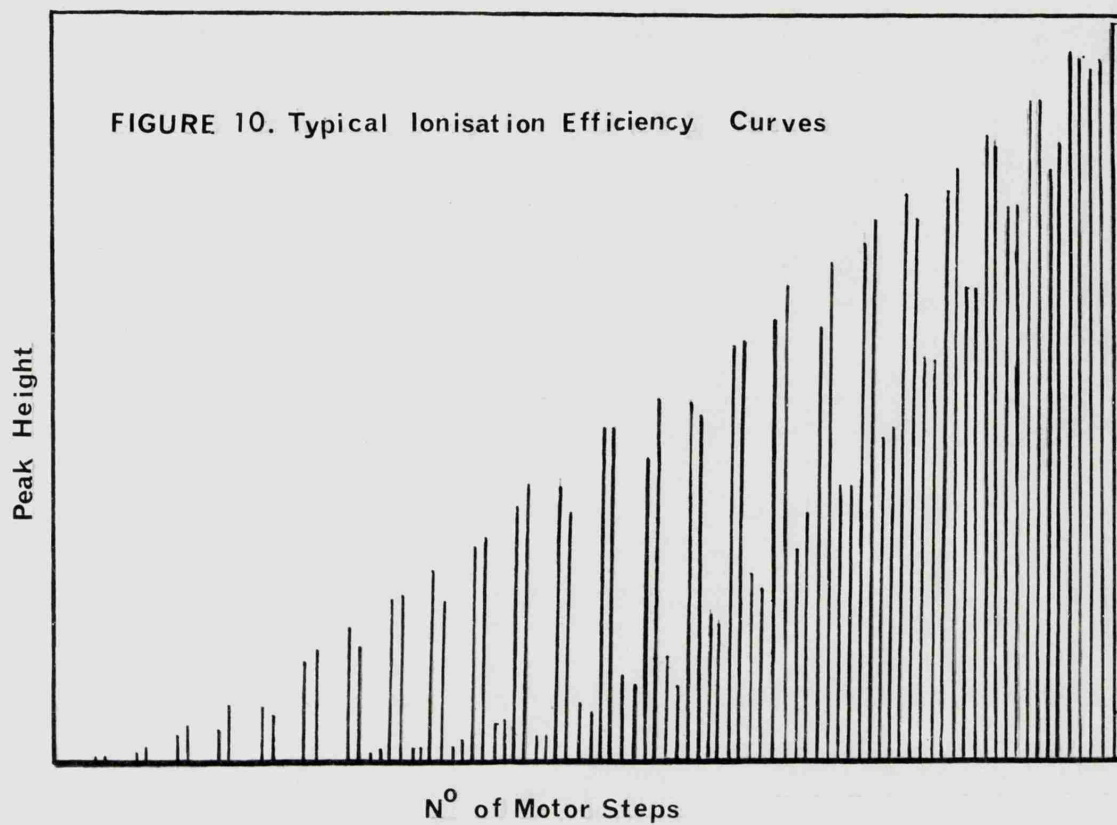we can also deduce a value of 138 ± 4 kcal mole^{-1} for $\Delta H_f^0(Me_3Si^+)_g$.

This ion also has a small isotope peak at m/e 73 and therefore

any sample ions of higher or approximately the same appearance

potential as $i\text{-}C_5H_{12}^+$ (i.e. 11.0 ev) will clearly be suspect if

measured against it. The value for m/e 73 from the chlorosilane

was 10.9 ev and therefore this ion was checked against $n\text{-}C_3H_7Cl^+$

(m/e 78) and the figure confirmed. All the reference compounds

used were tested alone to ascertain that the background of

their cracking patterns were clean in the region of the sample

ion.

Bond Dissociation Energies.

B.D.E's, $D(Me_3Si\text{-}X)$, were derived for the silicon-halogen

bonds in the trimethylsilyl halides (Table VI) by substitution of

the m/e 73 appearance potentials in the relationship:

$$D(Me_3Si\text{-}X) = A(Me_3Si^+) - I(Me_3Si\cdot) \tag{1}$$

together with the figure of 7.1 ± 0.1 ev obtained by Davidson and

Stephenson[19] for $I(Me_3Si\cdot)$, the ionisation potential of the tri-

methylsilyl radical. As stated previously this value for $I(Me_3Si\cdot)$

was derived by combining a kinetic determination of $D(Me_3Si\text{-}SiMe_3)$

with a figure for $A(Me_3Si^+)$ from HMDS in the relationship (1)

above.

FIGURE 10. Typical Ionisation Efficiency Curves

Peak Height

N° of Motor Steps

FIGURE 11. Gas Chromatograph of Reaction Mixture

Peak Height

HMDS

Me₃SiI

I₂

Time →

Area Trace

Molecular Heats of Formation, $\Delta H_f^O(Me_3SiX)_g$.

For the dissociation:
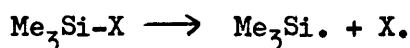
$$Me_3Si-X \longrightarrow Me_3Si. + X.$$

we have $\Delta H = D(Me_3Si-X) = \Delta H_f^O(Me_3Si.)_g + \Delta H_f^O(X)_g - \Delta H_f^O(Me_3SiX)_g$.

$\Delta H_f^O(Hal)_g$, the heats of formation of the halogen atoms, are

available from the literature[4]. A recent figure for $\Delta H_f^O(Me_3SiCl)_g$

of -84.7 kcal mole^{-1} has been reported by Beezer and Mortimer[28]

and this was substituted in the relationship above to give

$\Delta H_f^O(Me_3Si.)_g = -25.6\pm2$ kcal mole^{-1} and hence the molecular heats

of formation for the other halosilanes (see Table VI).

Ionic Heats of Formation, $\Delta H_f^O(Me_2SiX^+)_g$.

Combining molecular and radical heats of formation with

the appropriate appearance potentials led to heats of formation

for the parent minus methyl radical ions (Table VI).

Thus for:

$$Me_3SiX + e^- \longrightarrow Me_2SiX^+ + Me. + 2e^-$$
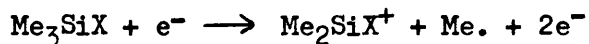
$$\Delta H = A(Me_2SiX^+) = \Delta H_f^O(Me_2SiX^+)_g + \Delta H_f^O(Me.)_g - \Delta H_f^O(Me_3SiX)_g$$

$\Delta H_f^O(Me.)_g$ is available and therefore the ionic heats of formation,

$\Delta H_f^O(Me_2SiX^+)_g$, can be obtained.

Part II - Kinetic Studies.

The results of kinetic studies on the system HMDS + iodine are presented in this section, together with a brief account of the exploratory work carried out on other organosilane halo-genations. The kinetic experiments were performed in a static system and analysis was by g.l.c and mass spectrometry.

The System HMDS + Iodine.

The thermal decomposition of HMDS has been shown to proceed via a free radical process, either chain[20,21] or non-chain[19] depending on the severity of the conditions used. This evidence, in conjunction with the fact that all the alkane iodinations studied to date proceed via an atomic mechanism[44], would lead one to expect the reaction of HMDS with iodine to follow a free radical path initiated by homolytic fission of the relatively weak I - I bond. If there is quantitative formation of the iodosilane, i.e. $(Me_3Si)_2 + I_2 \longrightarrow 2Me_3SiI$, as in the liquid phase reaction[51] then ΔH for the process is given by the difference in B.D.E's of the bonds formed and broken:

i.e. $\Delta H = -2D(Me_3Si-I) + D(Me_3Si-SiMe_3) + D(I-I)$.

Using the D value for Me_3Si-I obtained earlier in this work by electron impact, together with Davidson and Stephenson's[19]

figure for $D(Me_3Si-SiMe_3)$ we have:

$$\Delta H = -(2\times69) + 67 + 36 = -35 \text{ kcal mole}^{-1}$$

making the overall reaction quite strongly exothermic and therefore energetically favourable.

Preparation of the Reaction Vessel.

The vessel used was a 100 cc pyrex sphere, joined to the remainder of the system via Fischer-Porter teflon vacuum taps. Before any kinetic studies were carried out this vessel was baked at about 500°C and pumped for several days in order to remove moisture and impurities adsorbed on the vessel surface.

Seasoning of the Vessel.

The seasoning of vessels in gas kinetic studies is not an unusual problem. Silicon containing compounds especially are well known for their tendency towards heterogeneous behaviour and, in view of the careful seasoning procedure that was found necessary in the work on the pyrolysis of HMDS[19], it seemed only sensible to proceed with extreme care in these halogenation studies. For this reason a metal-free reaction system, consisting wholly of pyrex glass, was used and this system was kept completely grease free because of the tendency of the compounds used to

attack tap grease. The reactants were rigorously purified
and thoroughly dried before use.

The vessel surface was 'seasoned' by repeated contact with
the reaction mixture. This procedure removed the active sites
which are always present on 'fresh' vessel surfaces, the evidence
of this fact being the gradual decrease in the reaction rate
as the surface became increasingly inert. The iodide, Me_3SiI,
formed in the reaction proved to be extremely susceptible to
hydrolysis and therefore its presence in the vessel helped to
remove any remaining traces of moisture. It was found necessary
to repeat this baking and ' seasoning' procedure whenever there
was a need to let the reaction vessel down to atmospheric
pressure. In this event the reaction rate always re-attained
its old value, some indication that the reaction was proceeding
homogeneously. The remainder of the reaction system, including
the g.l.c column, was also 'seasoned' by contact with the
reaction mixture.

Siloxane Formation.

The pyrolysis of HMDS was complicated somewhat by the
ready formation of hexamethyldisiloxane, $(Me_3Si)_2O$, in the
presence of traces of moisture[19]. The same problem was
encountered in this work, the siloxane being formed by

hydrolysis of the iodosilane, Me_3SiI, as well as by direct radical combination.

Separation of Me_3SiI and $(Me_3Si)_2O$.

The formation of hexamethyldisiloxane was complicated somewhat by the fact that both it and the iodosilane were eluted from the g.l.c. column with precisely the same retention time. This was because the column packing used was (5%) silicone oil on embacel, a packing which separates components on volatility alone. Me_3SiI and $(Me_3Si)_2O$ are two compounds with equal volatilities over a considerable temperature range and although the variables of the column (i.e. temperature and flow rates) were changed considerably there was no resulting separation. A pre-column of 10% carbowax 400 on 100/110 acid washed celite was introduced because of its properties as a halogen retainer, but no separation resulted and it had to be removed as the reaction mixture discoloured the packing.

The major problem was to determine whether the product peak eluted from the silicone oil column was iodosilane, siloxane or a mixture of both. If siloxane formation occurs by hydrolysis one ought to see HI in the reaction products. Unfortunately a prepared sample of HI could not be detected by g.l.c. or mass spectrometry even after considerable 'seasoning' and therefore the presence of this compound in the reaction mixture would not be noticeable anyway.

The production of siloxane during the reaction was incon-
sistent with the use of a dry, leak-free vessel, but neverthe-
less run products were collected in the sample reservoir and anal-
ysed in the mass spectrometer by injection through the all-glass
inlet. 70 e.v. mass spectra were obtained from the samples
after 'seasoning' the mass spectrometer by allowing the run
products to flow through the system for some time. Characteristic
siloxane peaks were very small, consistent with its formation with-
in the mass spectrometer. Therefore the production of any
siloxane in the kinetic runs was likely to be via hydrolysis of
the iodosilane on the column and this in itself, would not
interfere with the kinetics of the reaction. Addition of an
atmosphere of the column carrier gas to the reaction mixture
however did not affect the rate in any way, confirming that the
gas was inert to the reaction studied and giving a further
indication that the reaction was proceeding homogeneously.

Identification of Products
By Gas Chromatography.

Only one product peak, corresponding to $Me_3SiI/(Me_3Si)_2O$
was found on the gas chromatogram. This and the HMDS peak
were quite sharp and well resolved but iodine gave a diffuse,
Variable peak at long retention time. A typical gas chromatograph
of the reaction mixture is shown in fig.11. The reaction was

extremely clean from the temperatures used in the kinetic

studies (185 - 250°C) right up to the softening point of the

vessel, (~515°C). No deposit collected on the vessel walls in

the course of the work, a further indication that no 'heavy'

products were formed, and no pressure change occured during the

course of the reaction.

By Mass Spectrometry.

Characteristic HMDS and Me_3SiI peaks were present in mass

spectra of the reaction mixture, together with small peaks

produced by fragmentation of hexamethyldisiloxane. No I^+ or

I_2^+ peaks were observed and in fact a spectrum of pure iodine

was also completely clean. It was found that halogens and

hydrogen halides generally did not respond to the mass spectro-

meter. A typical cracking pattern for HMDS is shown in fig 12.,

together with a mass spectrum obtained from the reaction

products. The spectrum of Me_3SiI has already been discussed

(see fig.9)

Quantitative Estimation of Product.

It was difficult to measure the product iodosilane

quantitatively because of the hydrolysis problem both on the

g.l.c column and in the mass spectrometer. A standard semi-

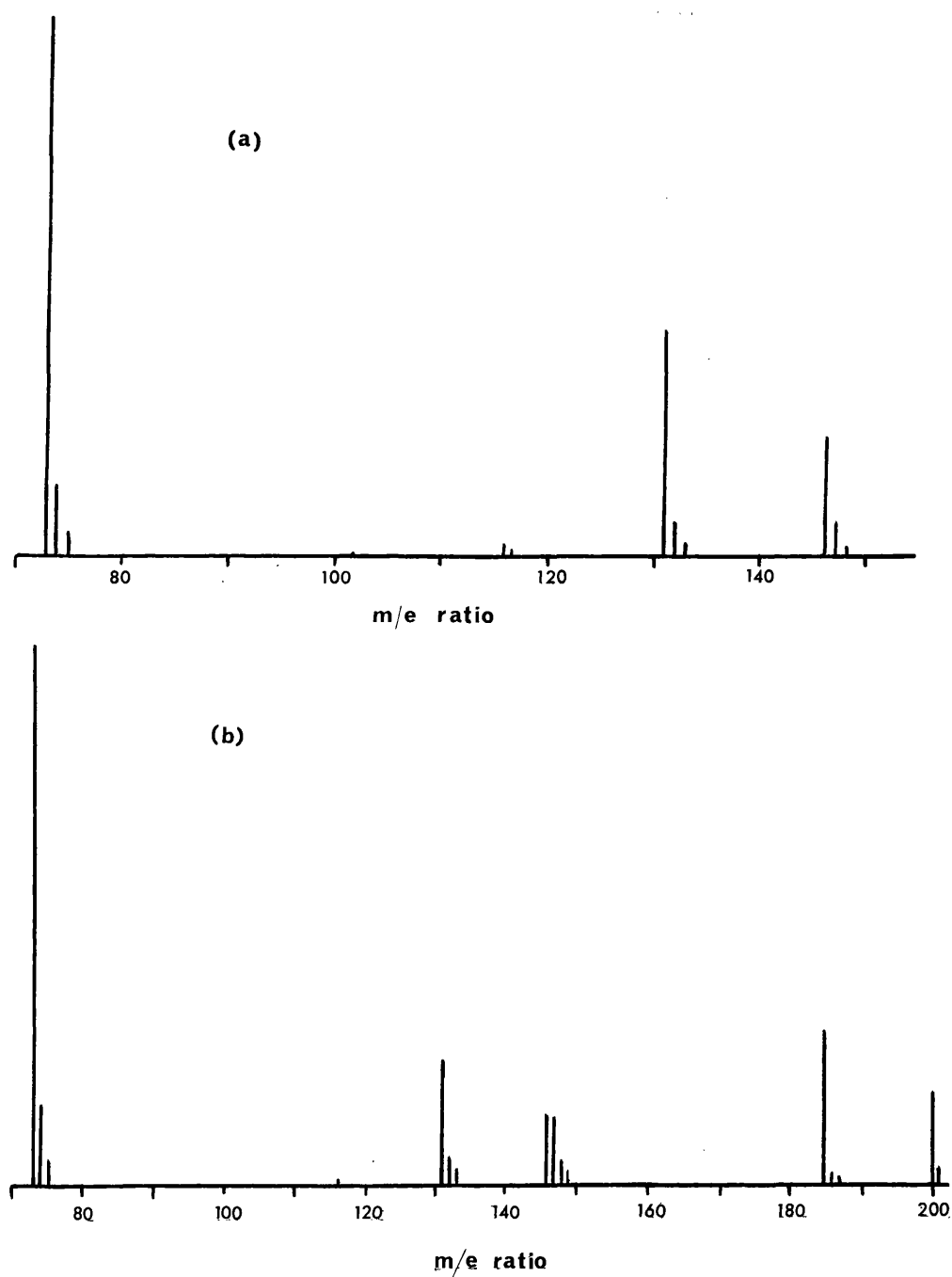logarithmic vapour pressure plot was not available for this

FIGURE 12. Mass spectra of (a) hexamethyldisilane and (b) reaction mixture.

compound. An estimated plot was constructed using the boiling

point of trimethylsilyl iodide and the fact that alkyl halide

plots are essentially parallel for a fixed alkyl group.[61] As

expected this line was virtually co-incident with that for

hexamethyldisiloxane.

Reactions between HMDS and iodine were allowed to proceed

to completion and the product area compared to the area of an

iodosilane sample with the expected concentration. Agreement

was reasonable taking into account the slight variation in the

product and reference iodosilane peak areas resulting from

hydrolysis.

Product Stability.

The halosilane, Me_3SiI, was stable thermally up to the

softening point of the vessel. Thus a 1.1 mixture at initial

reactant pressures of 5.4 mm Hg, left in the reaction vessel

overnight at $500^{\circ}C$, contained only Me_3SiI when analysed by

g.l.c. This is consistent with the B.D.E of 69 kcal mole^{-1}

obtained for $D(Me_3Si - I)$ earlier in this work.

Variation of Reactant Pressures.

Varying the pressure of the reactants produced no change in

the products formed. 1.1 mixtures reacted to completion unlike

the corresponding alkane systems which proceed to an equilibrium.

When either component was present in excess the reaction stopped
after a 1:1 mixture was used up. Therefore the stoiceiometry of
the reaction under the conditions used here was quite simply:

$$(Me_3Si)_2 + I_2 \longrightarrow 2Me_3SiI.$$
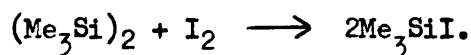
Analysis of Results.

An attempt to use the disc integrator to the full by measur-
ing the areas of all the components in the reaction mixture (thus
enabling each area to be expressed as a direct measure of that com-
ponent's concentration in the original sample) proved unsuccessful
because of the unreliability of the iodine and iodosilane peaks.
Therefore reactant decay curves were obtained by measuring the peak
area of HMDS only and adjusting this for changes in sensitivity of
the detector by passing a zero reaction peak of HMDS through the
column after each run. The area of a constant amount of sample
was reproducible to $\pm\frac{1}{2}\%$ and points on the decay curves to $\pm 1\%$.

Determination of $V_{R.V.}/V_{Mixer}$

The actual volumes of the reaction vessel and mixer were
not accurately known. Therefore in order to express component
concentrations absolutely the ratio of the volume of the reaction
vessel to that of the 'mixer' was calculated by using the 'mixer'

spiral gauge as a null deflection device with both vessels at room temperature. Repeated determinations were accurate to ± 0.003 and a mean value of 0.473 was taken.

Calculation of Component Pressure.

For most kinetic runs initial 1:1 'mixer' pressures of 7.2 mm Hg of reactants were used. Then with the mixer at 85°C and the reaction vessel at 250°C, say,

we have in the 'mixer'

$$7.2 \, V_{mixer} = n \, R \, 358$$

On expansion into the reaction vessel

$$P_1 \, V_{mixer} = n_1 \, R \, 358 \text{ in the 'mixer'}$$

and

$$P_1 \, 0.473 \, V_{mixer} = n_2 \, R \, 523 \text{ in the reaction}$$

vessel, where P_1 is the new pressure and $n_1 + n_2 = n$.

$$\therefore \frac{P_1}{R \, 358} = \frac{n_1}{V_{mixer}} \quad \text{gives concentration in 'mixer' and}$$

$$\frac{P_1}{R \, 523} = \frac{n_2}{0.473 \, V_{mixer}} \quad \text{gives concentration in the R.V.}$$

$$\therefore P_1\left(\frac{1}{358} + \frac{0.473}{523}\right) = \frac{n_1 + n_2}{V_{mixer}} = \frac{n}{V_{mixer}}$$

or $P_1 = \dfrac{\dfrac{7.2}{358}}{\left(\dfrac{1}{358} + \dfrac{0.473}{523}\right)}$ mm $= 5.44$ mm

The equivalent calculation with the reaction vessel at 185°C

gives $P_1 = 5.25$ mm and therefore there is only 0.2 mm pressure

FIGURE 13. Calibration Plots.

a. At 250° C

Conc HMDS x 10^4 (moles I^{-1})

b. At $195\frac{1}{2}°$C

Conc. HMDS x 10^5 (moles I^{-1})
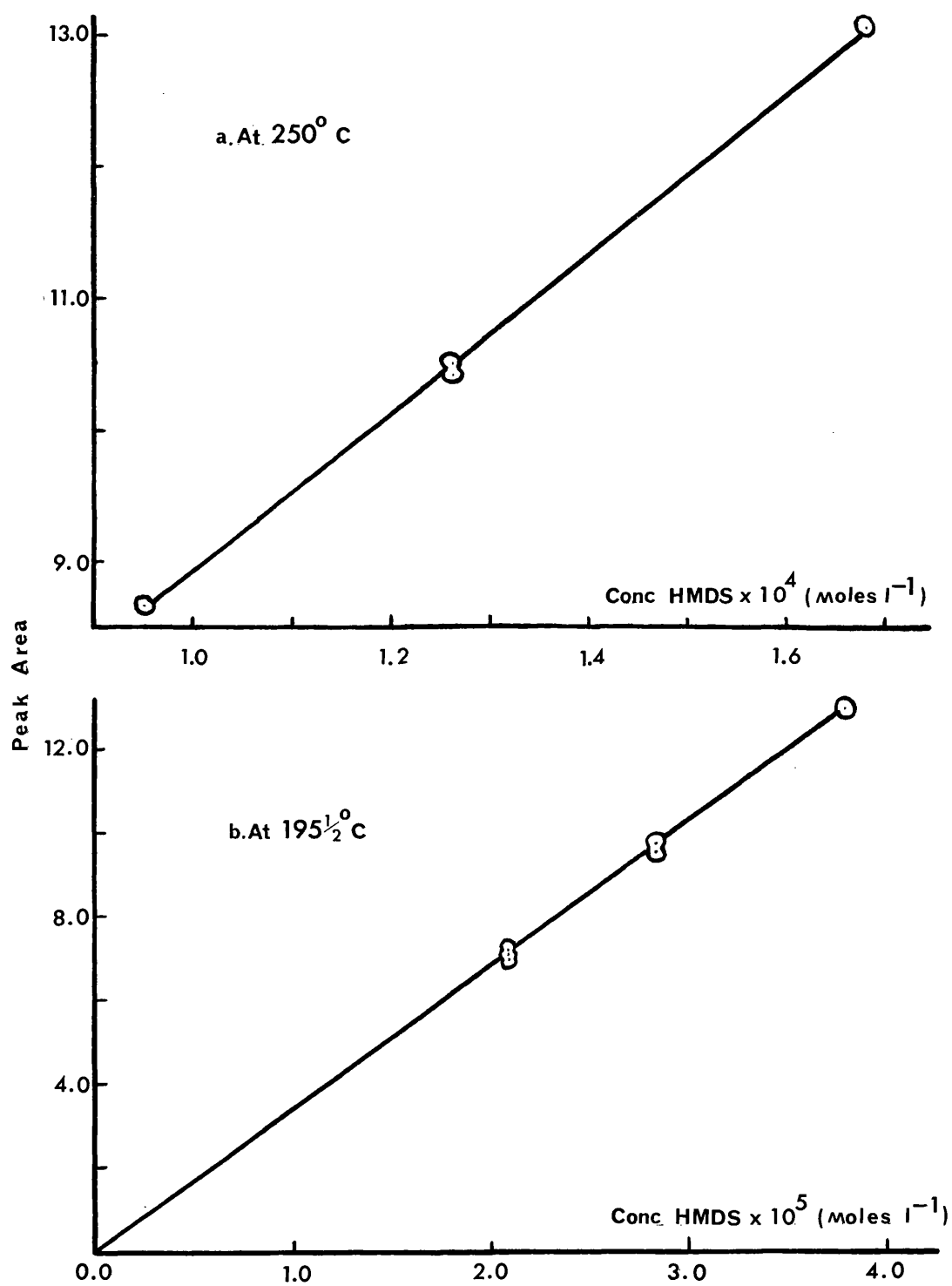
Peak Area

change over the whole temperature range.

A concentration v.s peak area plot for HMDS was built up by measuring the areas of three consecutive samples expanded from the 'mixer' into the reaction vessel. Each value was repeated three times (see table VII in part III) and the relation proved to be linear over the range studied (fig.13). Each set of areas were corrected to an arbitrary standard at the setting used of 5.44 mm = area of 13.0

Build-Up of Decay Curves.

The reaction mixture was sampled at varying reaction times and the area of HMDS corrected as described. Decay curves were constructed fairly slowly as the whole reaction mixture had to be 'quenched' for every point on the curve. Typical decay plots for 1:1 mixtures of reactants can be seen in fig.15. On all plots the reaction was followed to approximately 10% decomposition.

Order Measurements.

The technique used was not sufficiently accurate to permit the direct determination of reaction orders by fitting the data to standard decay curves. Therefore the initial concentrations of the reactants were varied substantially and the orders deduced from the changes prod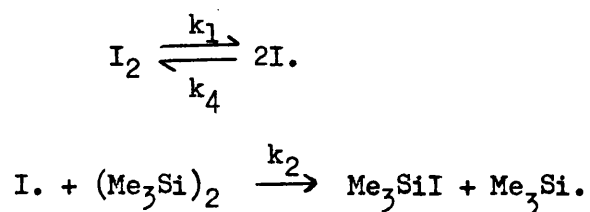uced in the initial reaction rates. Thus if we consider $A + B \rightarrow 2C$ we have $-\dfrac{d(A)}{dt} = -\dfrac{d(B)}{dt} =$
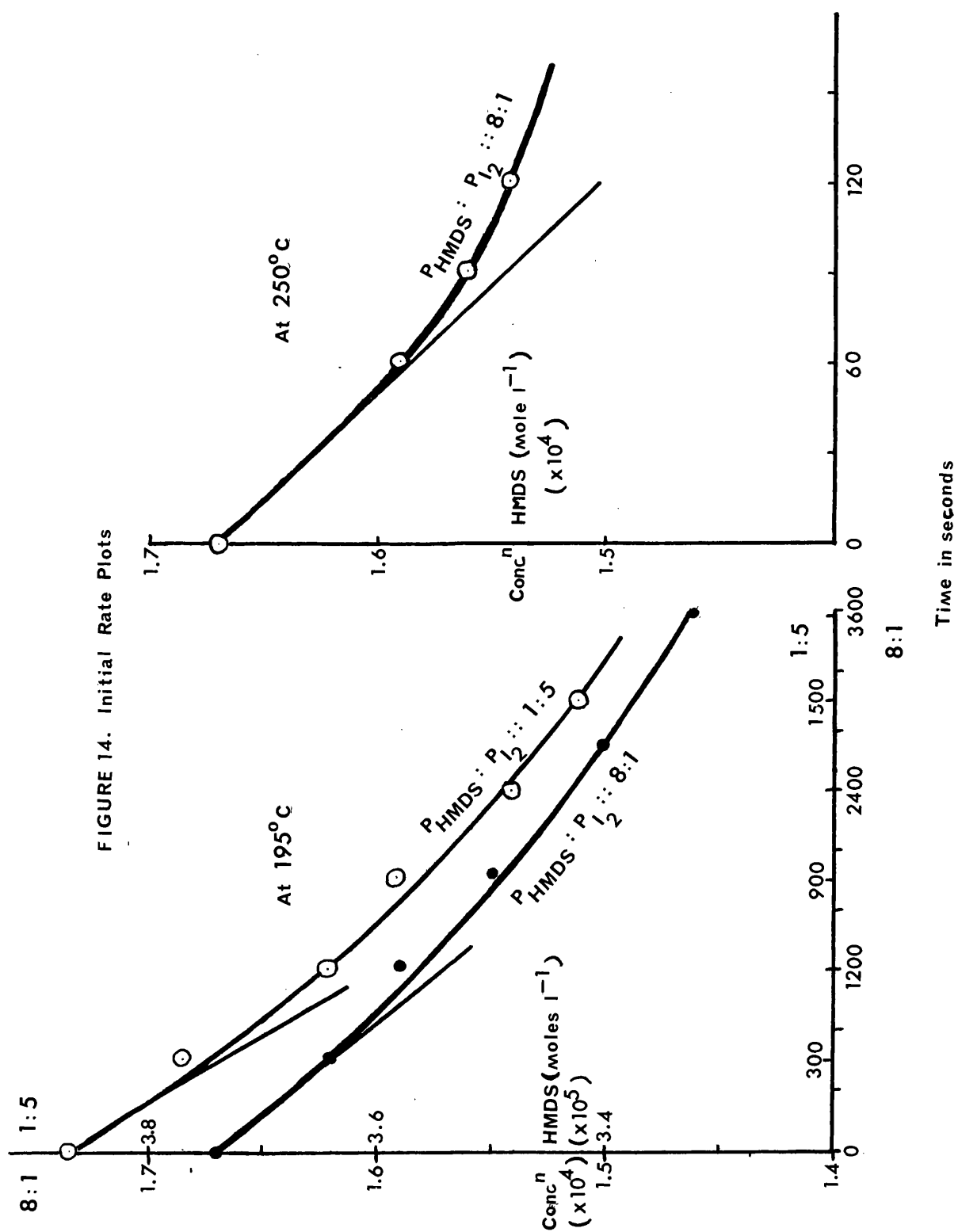
$k \, [A]^m \, [B]^n$, where m and n are reaction orders with respect to A

and B. A five fold increase in the concentration of A should then

change the reaction rate by $(5)^m$, e.g. for m = $\frac{1}{2}$, the rate change

is $\sqrt{5}$; for m = 1, the rate change is five fold and so on.
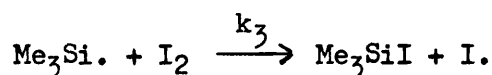
The order with respect to iodine was determined at both ends

of the temperature range over which the reaction was studied. An

eight fold variation in the initial concentration at both tempera-

tures produced initial rate changes of 2.9 and 3.0 and since

$\sqrt{8}$ = 2.8 we may deduce that the reaction is half order with respect

to iodine throughout the temperature range considered (fig. 14).

A five fold variation in the concentration of the disilane at the

lower temperature produced a five fold initial rate change (fig. 14).

Therefore the reaction is first order in disilane and $1\frac{1}{2}$ order

overall.

Derivation of the Rate Equation.

The product analysis, together with the evidence that the

reaction was first order in HMDS and half order in iodine, suggests

reaction according to the simple chain mechanism:

$$I_2 \underset{k_4}{\overset{k_1}{\rightleftharpoons}} 2I \cdot$$

$$I \cdot + (Me_3Si)_2 \xrightarrow{k_2} Me_3SiI + Me_3Si \cdot$$

FIGURE 14. Initial Rate Plots

$$Me_3Si. + I_2 \xrightarrow{k_3} Me_3SiI + I.$$

The fact that reaction went to completion indicates that -2 and -3 are unimportant. This is a simple chain reaction initiated by thermal dissociation of iodine; thus we can say directly that the rate equation is dependent on $K_c^{\frac{1}{2}}[I_2]^{\frac{1}{2}}$, where K_c is the equilibrium constant for the iodine dissociation, and in fact we find that use of the steady state approximation on the reactant decay equation:

$$-d\frac{[HMDS]}{dt} = k_2[I][HMDS]$$

yields the relationship

$$-d\frac{[HMDS]}{dt} = k_2\left(\frac{k1}{k_4}\right)^{\frac{1}{2}}[I_2]^{\frac{1}{2}}[HMDS]$$

i.e. $$-d\frac{[HMDS]}{dt} = k_2 K_c^{\frac{1}{2}}[I_2]^{\frac{1}{2}}[HMDS]$$

Arrhenius Plots.

Overall Reaction.

Separation of variables and integration of the rate equation above in the normal way gives:

$$k't = -\frac{1}{(b-a)^{\frac{1}{2}}}\log\frac{(a-b) + (b-x)^{\frac{1}{2}}(b-a)^{\frac{1}{2}}}{(a-b) - (b-x)^{\frac{1}{2}}(b-a)^{\frac{1}{2}}}$$

where $k' = k_2 K^{\frac{1}{2}}_{I_2}$, (a-x) is the concentration of HMDS and (b-x) the concentration of iodine. However, if a = b integration yields:

$$k't = \frac{2}{(a-x)^{\frac{1}{2}}} - \frac{2}{a^{\frac{1}{2}}} \qquad \text{if } a = b;$$

i.e. the standard equation for A $\rightarrow$ products for $1\frac{1}{2}$ order in A.

FIGURE 16. 3/2 Order Plots

FIGURE 15. 1:1 Decay Plots
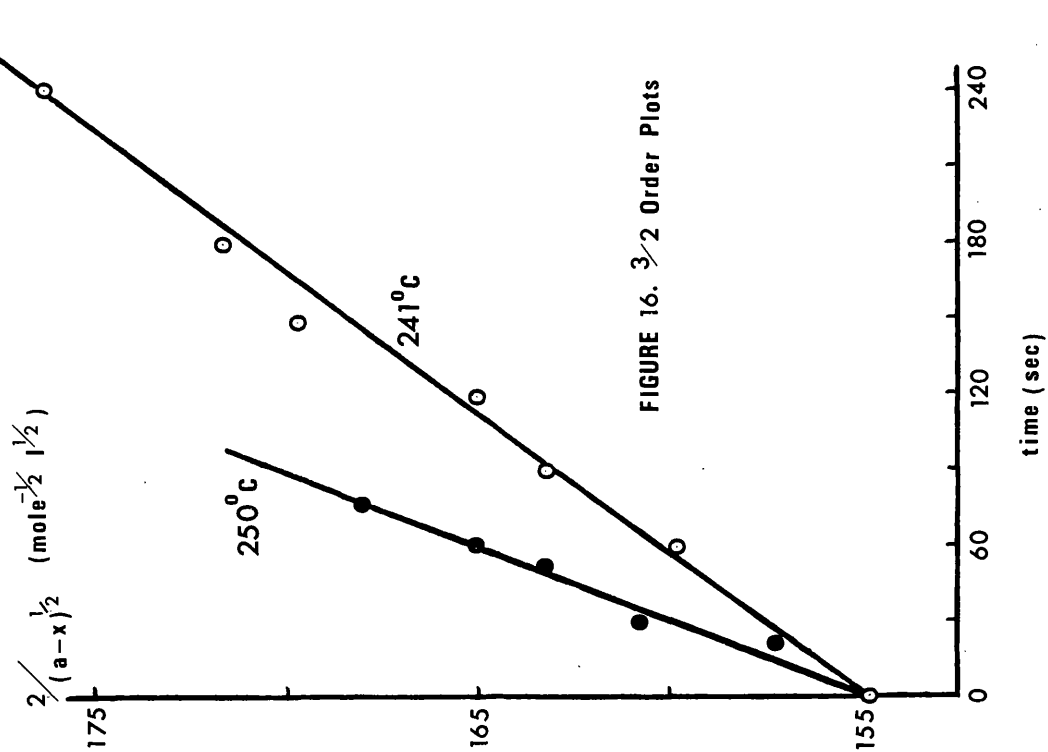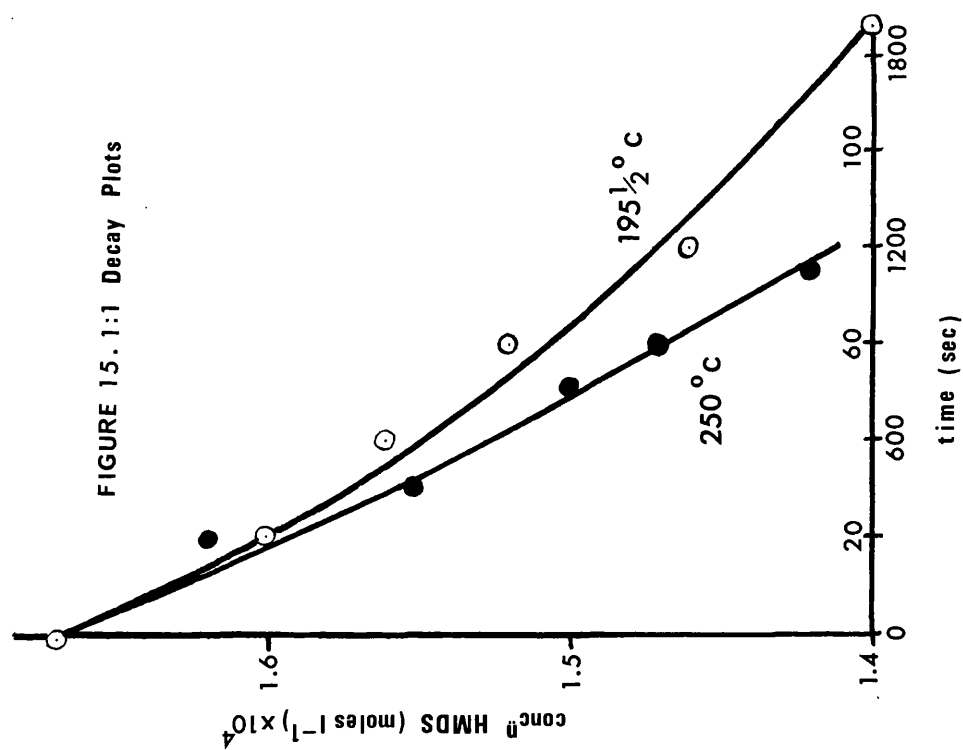
Therefore 1:1 decay curves were obtained at 7° intervals

between 188 and $250^\circ C$ and drawing the best straight lines through

plots of t.v.s $2/_{(a-x)^{\frac{1}{2}}}$ yielded the complex rate constants

$k_2 K^{\frac{1}{2}}_{I_2}$ (see fig.16). These $1\frac{1}{2}$ order plots were effectively

linear up to about 10% reaction. A graph of log k' v.s 1/T was

constructed using the least mean squares method to find the best

straight line and from this the velocity constants were seen to

obey the Arrhenius equation (fig.17):

$$k' = 1.16 \times 10^{10} \exp(-26,100 \pm 1,100)/RT \quad \text{where } k' \text{ is}$$

in $l^{\frac{1}{2}} mole^{-\frac{1}{2}} sec^{-1}$ and energies are in cal $mole^{-1}$

$Me_3 Si$. Radical Displacement Reaction.

The equilibrium constant K_{I_2} was derived from thermochemical

data[62] on the iodine equilibrium at one temperature $(500^\circ K)$ within

the range studied and the k_2 value deduced from $k_2 \, K^{\frac{1}{2}}_{I_2}$ at this

temperature. Then, from the fact that the activation energy E_2

is given by the overall activation energy minus one half of that

for the iodine dissociation (i.e. $E_2 = 26.1 - 18.0 = 8.1$ kcal $mole^{-1}$)

we obtain A_2 by substitution in the Arrhenius relationship. Thus

we find that the values of k_2 the velocity constant for the

radical reaction,

$$I + (Me_3 Si)_2 \xrightarrow{k2} Me_3 SiI + Me_3 Si$$
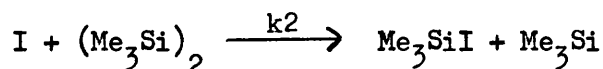
are governed by the Arrhenius equation:

$$k_2 = 1.70 \times 10^{11} \exp(-8,100 \pm 1,100)/RT$$

where k_2 is in cc $mole^{-1} sec^{-1}$ and energies are in cal $mole^{-1}$.

FIGURE 17. Arrhenius Plot for Reaction of HMDS
with iodine

From which:

$$\log k' = 13.1 - (26,100 \pm 1,100)/2.303\,RT$$

where k' is in $cc^{\frac{1}{2}} mole^{-\frac{1}{2}} sec^{-1}$ and E_a is in cals $mole^{-1}$

from 'packed' vessel

$\frac{1}{T} \times 10^3$

Log k'
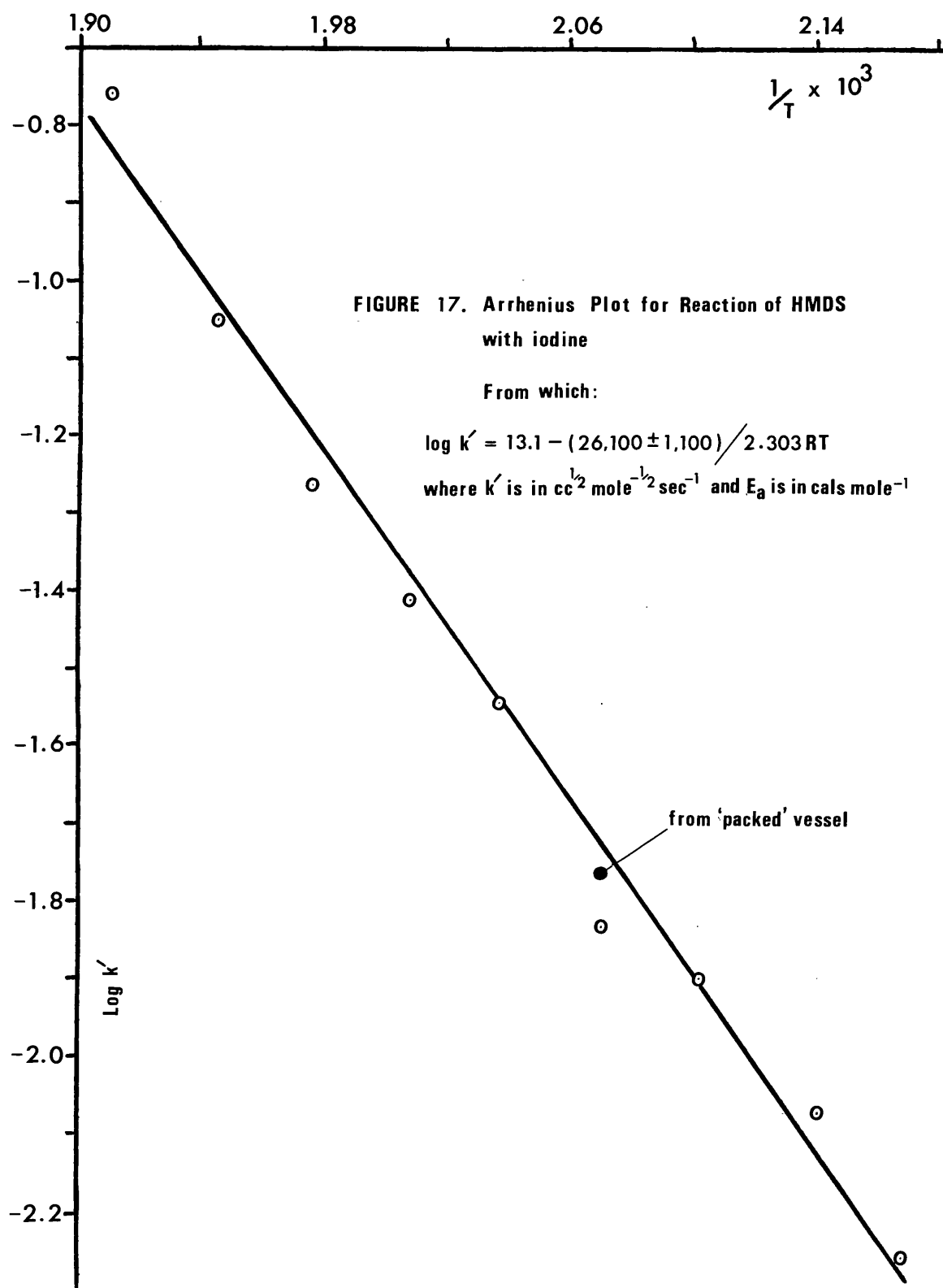
Calculation of $K_{I_2}^{\frac{1}{2}}$

Using data available in the JANAF[62] tables for the iodine

equilibrium at $500^{\circ}K$, we have

$$\Delta S^{\circ} = 2S^{\circ} (I.)_g - S^{\circ} (I_2)_g = 24.627 \text{ cal mole}^{-1}$$

$$\Delta H^{\circ} = 2\Delta H^{\circ}f (I.)_g - \Delta H^{\circ}f (I_2)_g = 36,360 \text{ cal mole}^{-1}$$

now

$$\Delta G^{\circ} = - RT \ln Kp$$

and $\quad \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

$\therefore \quad \Delta H^{\circ} - T\Delta S^{\circ} = - RT\ 2.303 \log Kp$

$$36,360 - 500 \times 24.627 = - 4.5758 \times 500 \log Kp$$

$\therefore \quad \log Kp = - 10.508$

$$= \overline{11}.492.$$

$\therefore \quad Kp = 3.1046 \times 10^{-11} \text{ atm}$

and $\quad K_c = \dfrac{3.1046}{0.082055 \times 500} \times 10^{-11} \quad \text{moles l}^{-1}$

$\quad K^{\frac{1}{2}}_c = 8.6986 \times 10^{-7}$

From the Arrhenius plot $k_2 K_{I_2}^{\frac{1}{2}} = 0.0456\ 1^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}} \text{ sec}^{-1}$

at $500^{\circ}C$ and $\therefore k_2 = 5.243 \times 10^4\ 1 \text{ mole}^{-1} \text{ sec}^{-1}$.

Substitution in the Arrhenius equation gives

$$\log k_2 = \log A_2 - \frac{E_2}{2.303\ RT}$$

from which $A_2 = 1.70 \times 10^{11} \text{ cc mole}^{-1} \text{ sec}^{-1}$.

Variation of Surface to Volume Ratio.

The reaction vessel was packed with fire-polished pyrex glass tubes and this gave a seven fold increase in surface to volume ratio (S/V). The packed vessel was 'seasoned' in the usual way and a 1:1 decay curve obtained at $210^{\circ}C$ as in the empty vessel. This agreed well with that previously obtained in the unpacked reaction vessel (see page 84) and confirmed that the iodination was proceeding homogeneously in the kinetic studies.

Full kinetic results are tabulated in part III of this section.

Other Halogenations Studied.
The System Me$_3$SiH + I$_2$

The same experimental difficulties were encountered in this study as in the HMDS iodination. Once again the only product identified by g.l.c and mass spectrometry was trimethyliodosilane. The formation of HI is therefore inferred by the absence of any other peaks and the simple stoic eiometry

$$Me_3SiH + I_2 = Me_3SiI + HI$$
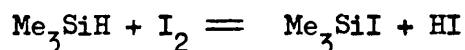
seems likely. This is supported by the fact that there was no pressure change in the course of the reaction. Unlike the disilane system this reaction was extremely fast and even at $70^{\circ}C$ conversion to the iodosilane took place in a few minutes.

Bromination of HMDS and Me$_3$SiH

Again experimental problems were much the same as in the

iodination reactions because the bromosilane, Me$_3$SiBr, is also

highly susceptible to hydrolysis to the siloxane. The major

product was Me$_3$SiBr but these reactions tended to be more complex

than the iodinations and a peak was present in the gas chromatograph

which corresponded to MeBr. The formation of MeBr was supported

by equal intensity peaks in mass spectra of the reaction mixtures

at 93 and 95 which were probably from -CH$_2$Br, the two equal peaks

being formed because the 79 and 81 isotopes of bromine are

present to approximately the same extent. Once again, there was

no pressure change in either reaction. With both systems the

bromination was extremely rapid and only the HMDS reaction had

any appreciable lifetime at room temperature.

Part III - Full Kinetic Results.

TABLE VII

Concentration v.s Area Calibration for HMDS at 250°C

Pressure in R.V (mm)	[HMDS] (moles 1^{-1})	Peak Areas			Peak Areas (corr)		
		A	B	C	A	B	C
5.45	1.67×10^{-4}	12.9	13.3	13.5	13.0	13.0	13.0
4.10	1.26×10^{-4}	10.5	10.7	10.9	10.6	10.5	10.5
3.10	0.95×10^{-4}	8.6	8.9	9.0	8.7	8.7	8.7

For calibration plot see fig. 13(a).

Table Vlll

Concentration v.s Area Calibration for HMDS at $195\frac{1}{2}^\circ$C

[HMDS] (mole 1^{-1})	Peak Areas			Peak Areas (corr)		
	A	B	C	A	B	C
3.87×10^{-5}	16.0	16.4	15.8	13.0	13.0	13.0
2.84×10^{-5}	11.9	12.0	11.8	9.7	9.5	9.7
2.09×10^{-5}	8.8	8.8	8.2	7.1	7.0	6.8

This calibration was linear and passed through the origin (see

fig. 13(b)).

Initial Rate Determinations for Order Measurements.

At Low Temperature($195\frac{1}{2}^{\circ}$C).

(a) For initial P_{I_2} = 0.68 mm and P_{HMDS} = 5.44 mm in the reaction vessel, i.e. an eight fold change in iodine concentration.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^4$ (mole l^{-1})
0	13.1	13.1	13.0	1.67
600	12.8	13.1	12.7	1.62
1200	11.8	12.2	12.5	1.59
1800	11.6	12.2	12.3	1.55
2700	11.3	12.2	12.0	1.50
3600	11.2	12.3	11.8	1.46

(b) For initial P_{I_2} = 5.44 mm and P_{HMDS} = 1.13 mm in the reaction vessel, i.e. a five fold change in HMDS concentration.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^5$ (mole l^{-1})
0	15.0	15.0	13.0	3.87
300	14.7	15.0	12.7	3.77
600	13.5	14.3	12.3	3.64
900	13.8	15.0	12.0	3.58
1200	12.9	14.3	11.7	3.48
1500	13.4	15.1	11.5	3.42

For plots derived from this data and the corresponding initial rate determinations see fig. 14.

At High Temperature(250°C). Initial pressures as in (a) above.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^4$ (mole 1^{-1})
0	11.5	11.5	13.0	1.67
60	10.5	10.9	12.5	1.59
90	10.5	11.1	12.3	1.56
120	10.8	11.5	12.2	1.54
150	10.1	11.1	11.8	1.47

For initial rate plots see fig. 14.

Data For Constructing $1\frac{1}{2}$ Order Plots For 1:1 Mixtures of Reactants.

At 250°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^4$ (mole 1^{-1})	$2/(a-x)^{\frac{1}{2}} \times 10^{-2}$ (mole$^{-\frac{1}{2}} 1^{\frac{1}{2}}$)
0	11.3	11.3	13.0	1.67	1.548
20	11.0	11.3	12.7	1.62	1.572
30	12.7	13.4	12.3	1.55	1.608
50	10.7	11.6	12.0	1.50	1.632
60	11.4	12.6	11.8	1.47	1.650
75	9.4	10.6	11.5	1.42	1.680

At 241°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^4$ (mole 1^{-1})	$2/(a-x)^{\frac{1}{2}} \times 10^{-2}$ (mole$^{-\frac{1}{2}} 1^{\frac{1}{2}}$)
0	11.8	11.8	13.0	1.67	1.548
60	11.3	11.8	12.4	1.57	1.598
90	10.9	11.8	12.0	1.50	1.632
120	10.4	11.5	11.8	1.47	1.650
150	9.8	11.3	11.3	1.39	1.698
180	9.7	11.4	11.1	1.36	1.716
240	8.6	10.5	10.7	1.29	1.762

At 233°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	[HMDS] X 10^4 (mole l^{-1})	$2/(a-x)^{\frac{1}{2}}$ X 10^{-2} (mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$)
0	12.1	12.1	13.0	1.67	1.548
60	11.7	12.1	12.6	1.60	1.582
90	11.2	11.7	12.4	1.57	1.598
120	11.2	11.8	12.3	1.55	1.608
180	10.7	11.8	11.8	1.47	1.650
240	10.2	11.6	11.4	1.40	1.692
300	10.0	11.6	11.2	1.37	1.710

At 225°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	[HMDS] X 10^4 (mole l^{-1})	$2/(a-x)^{\frac{1}{2}}$ X 10^{-2} (mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$)
0	11.5	11.5	13.0	1.67	1.548
60	11.2	11.5	12.7	1.62	1.572
120	11.0	11.5	12.4	1.57	1.598
180	10.6	11.5	12.0	1.50	1.632
300	10.6	11.7	11.8	1.47	1.650
420	10.2	11.9	11.5	1.42	1.680
600	9.9	11.4	11.3	1.39	1.698

At 217½°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	[HMDS] X 10^4 (mole l^{-1})	$2/(a-x)^{\frac{1}{2}}$ X 10^{-2} (mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$)
0	12.3	12.3	13.0	1.67	1.548
120	11.8	12.4	12.4	1.57	1.598
300	11.3	12.3	11.9	1.49	1.638
600	10.5	12.3	11.1	1.36	1.716
900	10.2	12.3	10.8	1.32	1.742
1200	10.6	13.2	10.4	1.24	1.796

At 210°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[\text{HMDS}] \times 10^4$ (mole l^{-1})	$\dfrac{2}{(a-x)^{\frac{1}{2}}} \times 10^{-2}$ (mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$)
0	13.0	13.0	13.0	1.67	1.548
120	11.2	11.4	12.8	1.64	1.562
300	12.5	13.0	12.5	1.58	1.592
420	10.8	11.5	12.2	1.54	1.612
600	10.5	11.5	11.9	1.49	1.638
720	10.4	11.4	11.8	1.47	1.650
900	10.2	11.6	11.4	1.40	1.692

At 203°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[\text{HMDS}] \times 10^4$ (mole l^{-1})	$\dfrac{2}{(a-x)^{\frac{1}{2}}} \times 10^{-2}$ (mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$)
0	13.1	13.1	13.0	1.67	1.548
300	12.6	13.0	12.6	1.60	1.582
420	12.2	12.9	12.3	1.55	1.608
600	12.6	13.5	12.1	1.52	1.622
720	11.9	13.0	11.9	1.49	1.638
900	12.2	13.5	11.8	1.47	1.650
1800	10.6	13.1	10.5	1.26	1.782

At 195½°C.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[\text{HMDS}] \times 10^4$ (mole l^{-1})	$\dfrac{2}{(a-x)^{\frac{1}{2}}} \times 10^{-2}$ (mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$)
0	13.4	13.4	13.0	1.67	1.548
300	13.4	13.8	12.6	1.60	1.582
600	12.4	13.1	12.3	1.56	1.602
900	11.9	12.8	12.1	1.52	1.622
1200	11.6	12.9	11.7	1.46	1.656
1860	10.9	12.4	11.4	1.40	1.692

At $188\frac{1}{2}°C.$

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^4$ (mole 1^{-1})	$2/(a-x)^{\frac{1}{2}} \times 10^{-2}$ (mole$^{-\frac{1}{2}}$ $1^{\frac{1}{2}}$)
0	13.6	13.6	13.0	1.67	1.548
600	13.3	13.6	12.7	1.62	1.572
900	11.4	12.0	12.4	1.57	1.598
1200	11.3	12.0	12.2	1.54	1.612
1800	10.9	12.0	11.8	1.47	1.650
2700	10.4	12.0	11.3	1.39	1.698

Values of the Complex Rate Constants, $k_2K^{\frac{1}{2}}I_2$, Obtained from

the $1\frac{1}{2}$ Order Plots.

$t°C$	$1/T \times 10^3 (deg^{-1})$	$k'(1^{\frac{1}{2}} mole^{-\frac{1}{2}} sec^{-1})$	Log. k'
250	1.912	0.172	-0.764
241	1.946	0.0894	-1.049
233	1.976	0.0545	-1.263
225	2.008	0.0386	-1.413
$217\frac{1}{2}$	2.037	0.0287	-1.542
210	2.070	0.0148	-1.830
203	2.101	0.0126	-1.900
$195\frac{1}{2}$	2.139	0.00850	-2.070
$188\frac{1}{2}$	2.165	0.00551	-2.258

Data for 1:1 Mixture at $210°C$ in Packed Reaction Vessel.

Time (sec)	Peak Area	Standard Area	Corrected Area	$[HMDS] \times 10^4$ (mole 1^{-1})	$2/(a-x)^{\frac{1}{2}} \times 10^{-2}$ (mole$^{-\frac{1}{2}}$ $1^{\frac{1}{2}}$)
0	13.6	13.6	13.0	1.67	1.548
180	12.4	12.8	12.6	1.60	1.582
300	13.1	13.6	12.5	1.58	1.592
420	11.4	12.3	12.0	1.50	1.632
600	11.6	12.8	11.8	1.47	1.650
700	11.4	12.7	11.7	1.46	1.656

From which $k' = 0.0173$ $1^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec^{-1}.

DISCUSSION.

Part I - Electron Impact Measurements.

The appearance potentials of the ions Me_3SiX^+, Me_2SiX^+ and

Me_3Si^+ have been measured for the trimethylsilyl halides (X = Cl,

Br and I) by electron impact. From these measurements B.D.E's,

$D(Me_3SiX)$, for the silicon halogen bonds have been derived by use of

the relationship:

$$D(Me_3Si-X) = A(Me_3Si^+)_{Me_3SiX} - I(Me_3Si.)$$

assuming that the radicals and radical ions are produced in their

ground states. The figure used for $I(Me_3Si.)$ was that derived by

Davidson and Stephenson[19] who substituted their kinetic value for

$D(Me_3Si - SiMe_3)$, together with their electron impact figure for

$A(Me_3Si^+)_{HMDS}$ in the above equation.

The heat of formation of the trimethylsilyl radical,

$\Delta H_f^o(Me_3Si.)_g$, was derived by combining Beezer and Mortimer's[28]

recent figure for $\Delta H_f^o(Me_3SiCl)_g$ with $D(Me_3Si-Cl)$ obtained in this

work. From this the molecular heats of formation of the bromo-

and iodosilane were also evaluated. The radical ion heats of

formation, $\Delta H_f^0(Me_2SiX^+)_g$, were determined from the values of

$A(Me_2SiX^+)_{Me_3SiX}$.

Appearance Potentials.

The appearance potentials measured in this work were con-

sistently lower than those reported by earlier workers on these

compounds (Table V.)[18,20,25]. Although no previous measurements

have been carried out on the iodosilane, the figures obtained here

can be seen to fit the trend expected from the chloro- and bromosilane

results.

In view of the fact that ions formed by electron impact may

be produced with excess energy, it is reasonable to suggest that

the lower values reported here are the more acceptable. For most

of the ions considered the disagreement with earlier work is not

great (within 0.4 e.v.) but the value for m/e 73 from Me_3SiCl is

some 0.6 e.v. lower than any earlier estimate. From a consideration

of the values recorded for this quantity, i.e. 12.4 e.v.[18], 11.5

e.v.[20] and now 10.9 e.v. it is clear that some peculiarity exists

here. The answer seems to lie in the fact that the ionisation

efficiency curve for this ion has an extremely long 'tail', and

the threshold region is an area which is virtually ignored by the

more conventional methods of extrapolation.

The lowering of the m/e 73 appearance potentials may also be attributable to the use of the all-glass inlet on our mass spectrometer. Hess, Lampe and Sommer[18] commented on the difficulties involved in obtaining siloxane-free halosilanes in the mass spectrometer. They assumed that the presence of hexamethyldisiloxane did not affect the m/e 73 appearance potentials for the halosilanes, as the corresponding value for the siloxane ion is relatively high ($>$15 e.v. compared to approx. 11 e.v. for the halosilanes). However, it seems likely that appreciable quantities of the siloxane would tend to obscure the true values for the halosilane Me_3Si^+ appearance potentials, leading to misleadingly high results.

Earlier mention has been made of the difficulties involved in obtaining parent and parent minus methyl peaks of reasonable intensity for these halosilanes. Thus it seems probable that the earlier workers in this field[18,25] carried out their measurements at low ion concentrations, with a corresponding loss of accuracy.

Appearance Potentials from Related Compounds.

Other workers in this laboratory[63] have measured appearance potentials of related trimethylsilyl compounds (viz X = H, Me and $SiMe_3$) by the same method as that reported here. These results

are summarised in Table IX, together with earlier figures for the same compounds. The value for m/e 73 from HMDS agrees with that reported previously by Haszeldine et al[20], who used a different mass spectrometer and a more rigorous method of extrapolation. Thus one may submit this as further evidence for the reliability of our method. It is also encouraging that Kerr et al[22], in their work on radical abstraction reactions in organosilanes, estimated a figure of 81 ± 5 kcal mole^{-1} for $D(Me_3Si-H)$ and 81 ± 2 kcal mole^{-1} is the value obtained from $A(Me_3Si^+)_{Me_3SiH}$ recorded in Table IX.

Independence of Sample Pressure.

Although the step counting procedure used in this work resembles the pressure dependent 'initial upward break' method[59], results were in fact found to be independent of the sample pressure. The explanation would seem to lie in the simultaneous recording of reference and sample ionisation efficiency curves and the use of high sensitivities. The former adaptation is useful because it leads to rapid determination of appearance potentials and therefore eliminates over-heating in the source region and decreases errors due to variation of the sample pressures during measurement.

Our method was inconclusive for the Me_3SiH^+ion from tri-

Table IX

Results from Electron Impact Studies on some Trimethylsilanes

Compound	Ion	Standard	Appearance potentials (ev)			
			Ref. 63	Ref. 18	Ref. 49	Ref. 20
Me_6Si_2	Me_3Si^+	$i\text{-}C_5H_{12}^+$	10.0	10.69		10.0
		$n\text{-}C_3H_7Cl^+$				
Me_4Si	Me_4Si^+	$c\text{-}C_6H_{12}^+$	9.9	9.9		
	Me_3Si^+	$i\text{-}C_5H_{12}^+$	10.4	10.63	11.3	10.5
Me_3SiH	Me_3SiH^+	$i\text{-}C_5H_{12}^+$	9.6 (10.2)			
	Me_3Si^+	$i\text{-}C_5H_{12}^+$	10.6	10.78	10.9	10.7
	Me_2SiH^+	$C_2H_5Cl^+$	11.2	11.70	11.9	

From which we may derive the following data:

	$Me_3SiSiMe_3$	Me_3SiMe	Me_3SiH
$D(Me_3Si\text{-}X)$ (kcal mole^{-1})	(67 ± 2)	76 ± 2	81 ± 2
$\Delta H_f^o(Me_3SiX)_g$ "	-118 ± 2	-68 ± 2	-55 ± 2

FIGURE 18. Comparison of B.D.E's, D(R—X)
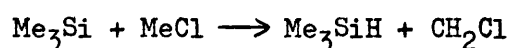(kcal mole^{-1})
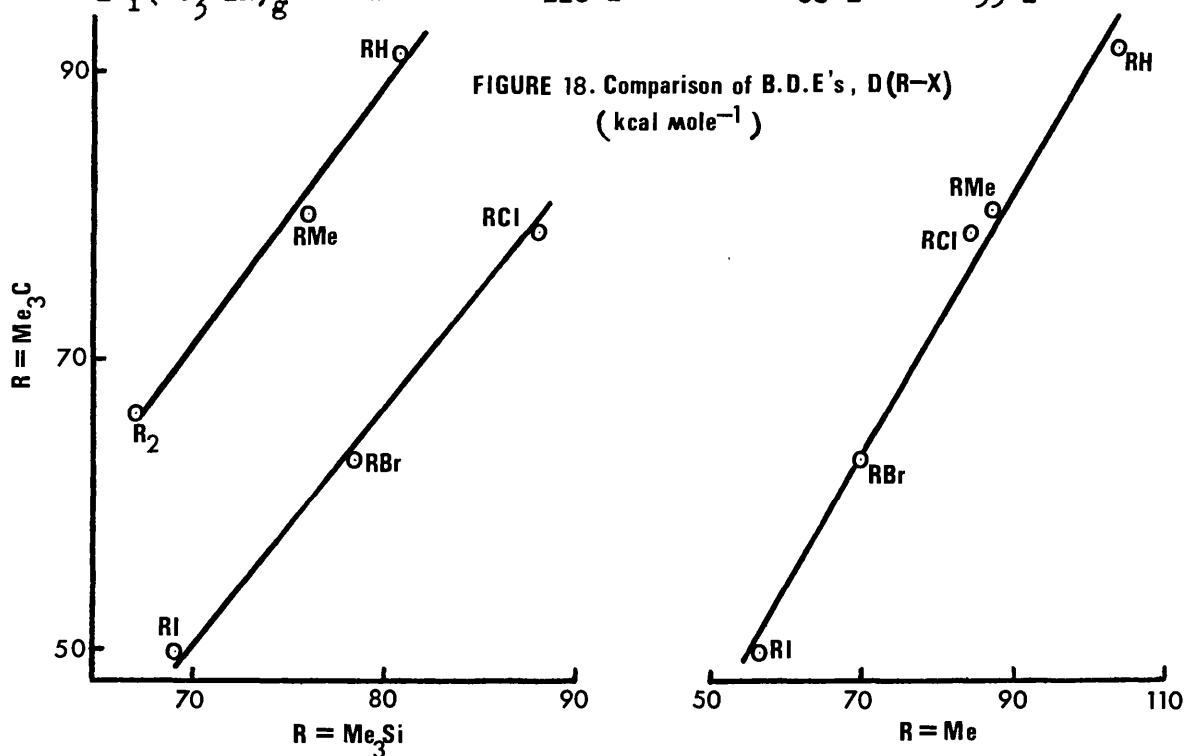
methyl silane, which is present in very low abundance: values of

9.6 e.v. and 10.2 e.v. were recorded and it was not possible to

say with confidence which of these figures was correct. This may

be explained by the reasoning above together with the fact that

this m/e undoubtedly contains a significant contribution from the

C^{13} isotope from Me_3Si^+, which would tend to increase the appearance

potential of the parent ion as $A(Me_3Si^+)_{Me_3SiH} = 10.6$ e.v. There

is also a possibility that this appearance potential is affected

by the presence of a low lying excited state for the Me_3SiH mole-

cule.

Bond Dissociation Energies.

The values for the B.D.E's reported here are considerably higher

than the corresponding alkyl halide D values[7]. This relative

strength of the silicon-halogen bonds in silyl halides is res-

ponsible for the preferential halogen abstraction reactions (as

opposed to hydrogen abstraction) of silyl radicals. Thus, using

the B.D.E's reported here for attack of trimethylsilyl radicals on

methyl chloride, the chlorine abstraction reaction:

$$Me_3Si + MeCl \longrightarrow Me_3SiCl + Me$$
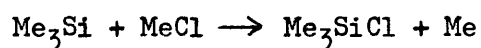
is 8 kcal mole^{-1} exothermic, whereas hydrogen abstraction,

$$Me_3Si + MeCl \longrightarrow Me_3SiH + CH_2Cl$$

is some 20 kcal mole^{-1} endothermic.

Factors Influencing D(Me$_3$Si-Cl).

If D(Me$_3$Si-X) is plotted against D(Me$_3$C-X)[7] for the three

halides, the silicon D values can be seen to vary regularly with

their carbon analogues (fig. 18). If the other B.D.E's, obtained

in this laboratory for related trimethylsilyl compounds[63], are

included in the plot (X = H, Me and SiMe3) they also show this

regular variation but lie on a different straight line. On the

other hand the analogous plot for D(Me-X) v.s. D(Me$_3$C-X) is a

straight line throughout (fig. 18). Fig. 18 exhibits the expected

trend that the organosilane B.D.E's are weaker than the carbon

analogues whereas Si-Hal bonds are stronger than C-Hal. This

implies that there is an added factor present in the bonding of

the silyl halides which stabilises the Si-Hal bonds. We have sug-

gested[65] that this stabilisation could well be the result of (p-d)π

bonding between the silicon and halogen atoms, but it has been

pointed out that the effect may be caused by ionic factors arising

from the difference in electronegativity between silicon and the hal-

ogens[66].

We have suggested that the methyl group is a closer analogue

to Me_3Si. than is Me_3C^{67} and certainly molecular models indicate that this is true on steric grounds. Thus it ought to be more fruitful to compare the halosilanes to the corresponding methyl halides[7]. It is a reasonable approximation to treat these halides as quasi diatomic molecules $(Me_3Si)-X$ and $(Me-X)$; then if we define $\delta = D(Me_3Si-X) - D(Me-X)$ this quantity ought to remain constant on simple electronegativity grounds[68]. In fact $\delta = 4$ for $X = Cl$, 8.5 for $X = Br$ and 13 for $X = I$. Of course, δ should strictly be derived from bond energies[66] to fit in with Pauling's original ideas. Thus we can adopt the same approach as Beezer and Mortimer[28], who have estimated a series of E values for Si-X bonds by substitution of their heat of formation data in the relationship:

$$\sum E(b) = -\Delta H_f^a(\text{compound})_g = \Delta H_f^o(\text{atoms})_g - \Delta H_f^o(\text{compound})_g.$$

$\sum E(b)$ is the sum of the bond energies in the molecule whose gas phase heat of formation is $\Delta H_f^o(\text{compound})_g$; $\Delta H_f^a(\text{compound})_g$ is the heat of formation of the compound from its atoms and $\Delta H_f^o(\text{atoms})_g$ is the sum of the gas phase heats of formation of the atoms which comprise the molecule.

Then for Me_3SiCl we have:

$$E(b) = E(Si-Cl) + 3E(Si-C) + 9E(C-H)$$

$$= \Delta H_f^o(Si)_g + \Delta H_f^o(Cl)_g + 3\Delta H_f^o(C)_g + 9\Delta H_f^o(H)_g$$

$$-\Delta H_f^o(Me_3SiCl)_g.$$

Of these quantities, $\Delta H_f^o(Si)_g$ has been estimated as 110 ± 5 kcal mole^{-1}

by Beezer and Mortimer[28], $\Delta H_f^o(Me_3SiCl)_g$ has also been evaluated

by these authors[28]. All the other quantities except $E(Si-Cl)$ and

$E(Si-C)$ are well established. $E(Si-C)$ can be found by using this

type of approach on the tetramethylsilane molecule, substituting

the value for $\Delta H_f^o(Me_4Si)_g$ obtained in this laboratory[63], whence

$E(Si-C) = 75.6$ kcal mole^{-1}, in good agreement with Beezer and

Mortimer's[28] value of 73.2 kcal mole^{-1} derived from Me_3SiCl.

$E(Si-Cl)$ can now be calculated to 90.1 kcal mole^{-1}, also in reason-

able agreement with Beezer and Mortimer's estimate of 97.2 from

$SiCl_4$. Using E values to determine δ we obtain, $\delta = E(Si-X)$

$- E(C-X)^4 = 17$ kcal mole^{-1} for $X = Cl$, 20 kcal mole^{-1} for $X = Br$

and 27 kcal mole^{-1} for $X = I$. Therefore δ can again be seen to

follow the trend observed for use of D values.

The Electronegativity of Silicon.

The B.D.E's of Me_3Si-Me and Me_3Si-H measured in this labora-

tory[63] can be used to determine the apparant electronegativity

of silicon by Pauling's method. The difference in electronegativity

between elements A and B is given by:

$$\Delta = D(A-B) - \left[D(A-A) \times D(B-B) \right]^{\frac{1}{2}}.$$

The equation has been used for polyatomic molecules by employing

average bond energies. In view of the uncertainty involved in

E values we may again suggest the direct use of D, treating the

silanes as quasi diatomics. Thus for Me_4Si:

$$\Delta = D(Me_3Si-Me) - \left[D(Me_3Si-SiMe_3) \times D(Me-Me)\right]^{\frac{1}{2}}$$
$$= 76 - (67 \times 88)^{\frac{1}{2}} = 0.8^{\pm}2 \text{ kcal mole}^{-1},$$

and for Me_3SiH

$$\Delta = D(Me_3Si-H) - \left[D(Me_3Si-SiMe_3) \times D(H-H)\right]^{\frac{1}{2}}$$
$$= 81 - (67 \times 104)^{\frac{1}{2}} = -1.9^{\pm}2 \text{ kcal mole}^{-1}.$$

If E values are used we have, for the difference in electronega-

tivity between silicon and carbon,

$$\Delta = E(Si-C) - \left[E(Si-Si) \times E(C-C)\right]^{\frac{1}{2}}.$$

E(Si-C) has been evaluated above and E(Si-Si) can be obtained by

a similar calculation using $\Delta H_f^0(HMDS)_g$ to give E(Si-Si) = 71.0

kcal mole^{-1}. Thus Δ = -0.5 kcal mole^{-1}. Use of E values for the

Si-H case yields Δ = -2.3 kcal mole^{-1}.

In all cases Δ is effectively zero implying that the electro-

negativity of silicon lies close to the values for carbon and

hydrogen, i.e. between 2.1 and 2.5 on Pauling's scale as opposed

to the original value of 1.8. This figure fits in well with that

of 2.44 obtained for silicon by the Mulliken approach[69,70]. If it

is accepted that the electronegativity of silicon lies close to

that for carbon then this diminishes the likelihood of ionic fac-

tors being responsible for the changes in δ.

The Effect of Ionic Factors on Other B.D.E's.

Some B.D.E's[4] for a series of halides M-X are shown in Table X. If we define $\delta_1 =$ D(M-Cl) - D(M-Br) and $\delta_2 =$ D(M-Br) - D(M-I) then δ_1 and δ_2 should remain constant when M is changed if there is effectively the same bonding in the new halides. δ_1 and δ_2 are small (3 to 8 kcal mole^{-1}) for the interhalogen compounds (where π-bonding is undoubtedly strong) compared to those for singly bonded covalent halides (e.g. methyl halides and hydrogen halides, which have δ_1 and δ_2 15 kcal mole^{-1}). In the more ionic halides, e.g. Na-X and K-X, the values of δ_1 and δ_2 are again about 15 kcal mole^{-1}, implying that there is no bond strengthening effect in passing from Cl to I in these ionic halides. δ_1 and δ_2 for Me$_3$Si-X are 9 kcal mole^{-1} suggesting the presence of an effect analogous to, but weaker than, that caused by the π-bonding in the interhalogens.

Baughan, Evans and Polanyi[71] first drew attention to the effect of variation of ionic contributions to B.D.E. variations in the series Me-X $\rightarrow$ tBu-X, but they varied the alkyl group rather than the halogen. If we take modern figures for some alkyl halide B.D.E's and tabulate δ_{RX}, where

$$\delta_{RX} = D(Me-X) - D(R-X) \text{ we obtain:}$$

	Et	nPr	iPr	tBu
Cl	3	2	3	5
Br	1	1	2	7
I	3	2	3	6

The horizontal variation represents the effect studied by Polanyi et al whereas the vertical columns are analogous to the δ values recorded above for δ = D(Me$_3$Si-X) - D(Me-X). These figures are essentially constant in contrast to the trend in the halosilane δ.

Evidence for Stability from Cl to I.

The B.D.E's tabulated in Table X indicate stabilisation of the interhalogen bonds in passing from the chlorides to the iodides. If the π-bonding was strongest in the chlorides, then δ_1 and δ_2 would be larger for π-bonded compounds than singly bonded covalent molecules. One would also expect $(p-d)\pi$ bonding to increase from Cl to I in the trimethylsilyl halides as the respective p and d orbitals are more conveniently placed in the iodide.

Some degree of bond shortening is indicated in the data for the Me$_3$Si-Hal compounds[72]. Goubeau and Sommer[73] compared the Raman spectra of these three halosilanes (X = Cl, Br and I) and suggested appreciable double bond character in the Si-I bond (force constant of 2.10 mdyne/Å as compared to a theoretical 1.58 mdyne/Å for singly bonded Si-I). They felt this also explained the very small increase in dipole moment in passing from the

bromo- to the iodo-compound (a sizeable π-contribution would

clearly decrease the effective dipole in the iodide due to back

donation from iodine to silicon).

It is difficult to say with conviction whether π-bonding gener-

ally increases on descending a group of the periodic table as

there appears to be well documented evidence for both sides of

the arguement. It is well known that replacement of methyl groups

to nitrogen by silyl groups leads to a widening of the pyramidal

bond angle and such increases have been thought to be a criterion

for $(p-d)\pi$ bonding in related compounds. Thus when Sheldrick et

al[74] showed by electron diffraction that both $(SiH_3)_3P$ and

$(SiH_3)_3As$ are pyramidal they assumed this precluded the possibility

of π contribution in the bonding, and in fact the Si-P and Si-As

bond lengths are close to those calculated from covalent radii[74].

However, Ebsworth[75] has demonstrared that π-bonding is still likely

even in pyramidal structures, the difference being that σ and π

contributions are not easily separated.

Perkins[76] has estimated the extent of $(p-d)\pi$ bonding in

$(SiH_3)_3N$ and also suggests the possibility of σ and π mixing

in pyramidal structures. Also the $p_\pi-p_\pi$ bond strength does not

decrease markedly down group III and hence by analogy we might

expect that the situation in Si-N could obtain for Si-P and Si-As.

Randall and Zuckermann[77] on the other hand take the view from their N.M.R experiments on the M.N.H skeleton that large $(p-d)\overline{\pi}$ in Si-N, Ge-N and Sn-N are unlikely and they also point out that the force constants for Si-N and Si-P are consistent with single bond character[78]. Thus at this stage in our knowledge it would be foolish to make any definite pronouncements about the bonding in halosilanes, although the trend in the halosilane D values reported here does indicate a strong possibility of $(p-d)\overline{\pi}$ bonding.

Heats of Formation.

Beezer and Mortimer's figure for $\Delta H_f^o(Me_3SiCl)_g$[28] has been confirmed by Lappert et al's work on the heats of hydrolysis of group IV compounds[79,66]. This latter work also yields a figure of 70.1 kcal mole^{-1} for $\Delta H_f^o(Me_3SiBr)_g$[66] which is in reasonable agreement with that of 77 kcal mole^{-1} obtained here. It is further encouraging that Hess, Lampe and Sommer's[18] calculated value of $\Delta H_f^o(HMDS)$, i.e. -126 kcal mole^{-1}, agrees well with that of -118 ± 2 kcal mole^{-1} obtained for the same quantity from electron impact studies in this laboratory[63].

Molecular Ionisation Potentials.

The molecular ionisation potentials of the three halosilanes
are recorded in Table XI together with those measured in this lab-
oratory for X = H and Me[63] and the corresponding alkyl compounds.

Table XI
Molecular Ionisation Potentials (e.v.)

	X = Me	H	Cl	Br	I
Me_3SiX	9.9	(9.6)	9.9	9.8	8.9
Me_3CX	10.3	10.6	10.2	9.0	9.0

As the molecular ions are present in the mass spectra of these
compounds in quite low abundance these measurements will not be
so accurate as those for the other characteristic ions. Morrison
and Nicholson[64] have found that the use of benzenoid standards in
appearance potential studies can lead to errors in measurement
due to the possibility of forming such compounds in low lying
excited states. Thus the ions measured here against benzenoid
standards (i.e. parent ions and $A(Me_2SiCl^+)_{Me_3SiCl}$) may have been
given appearance potentials which are a little low. Nevertheless,
the silicon ionisation potentials in Table XI can be seen to
exhibit a similar trend to their t-butyl analogues[58,80], being
generally the lower values, as would be expected from a comparison
of the ionisation potentials of carbon and silicon.

.

Table X

Bond Dissociation Energies for a Series of Halides, M-X.(kcal mole^{-1})

I - I	36 [*]	H - I	70.5 [*]
I - Br	41	H - Br	86.5
I - Cl	49.6	H - Cl	102.2
Br - I	41 [*]	Na - I	71 [*]
Br - Br	46	Na - Br	88
Br - Cl	52	Na - Cl	98
Cl - I	49.6 [*]	K - I	77 [*]
Cl - Br	52	K - Br	91
Cl - Cl	57	K - Cl	101
Me - I	56 [***]	Me$_3$Si - I	69 [**]
Me - Br	70	Me$_3$Si - Br	78.5
Me - Cl	84	Me$_3$Si - Cl	88

[*] ref. 4

[**] ref. 63

[***] ref. 7

Part II - Kinetic Studies

The system HMDS + iodine has been studied kinetically in the gas phase between 188 and 250°C at initial reactant pressures of 1.5 - 11.0 mm Hg. The reaction was found to be 3/2 order overall, being 1st order in HMDS and $\frac{1}{2}$ order in iodine. This information together with the product analysis suggested reaction via the simple chain mechanism:

$$I_2 \; \underset{4}{\overset{1}{\rightleftharpoons}} \; 2I$$

$$I + (Me_3Si)_2 \; \overset{2}{\longrightarrow} \; Me_3SiI + Me_3Si$$

$$Me_3Si + I_2 \; \overset{3}{\longrightarrow} \; Me_3SiI + I$$
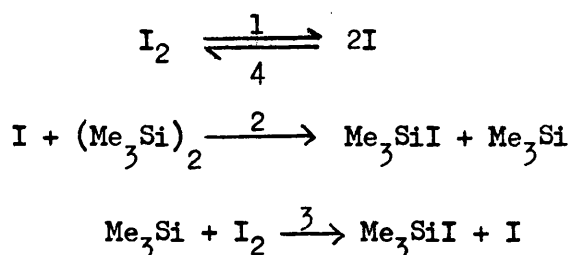
which led to the overall rate equation

$$-d \frac{[HMDS]}{dt} = k_2 \, K_{I_2}^{\frac{1}{2}} \, [I_2]^{\frac{1}{2}} \, [HMDS]$$

where K_{I_2} is the constant for the iodine equilibrium.

The decay of HMDS was monitored kinetically over the temperature range studied and the complex rate constants shown to obey the Arrhenius equation:

$$(cc^{\frac{1}{2}}mole^{-\frac{1}{2}}sec^{-1}) \; k_2 \, K_{I_2}^{\frac{1}{2}} = 1.16 \times 10^{13} \exp(-26,100 \pm 1,100)/RT.$$

obtained by a least mean squares fit on the computer. k_2 at one temperature was calculated by substitution of the value for $K_{I_2}^{\frac{1}{2}}$ in the complex rate equation. Then with $E_2 = E_{overall} - \frac{1}{2}E_1$

we have $E_2 = 8,100 \pm 1,100$ cal mole^{-1} and by substitution in

the Arrhenius relationship we obtain $A_2 = 1.70 \times 10^{11}$ cc/mole sec and

therefore the velocity constants k_2 obey the Arrhenius equation:

$$k_2 = 1.70 \times 10^{11} \exp(-8,100 \pm 1,100)/RT \text{ cc mole}^{-1}\text{sec}^{-1}$$

The reaction was shown to be homogeneous by addition of an inert

atmosphere (of nitrogen) to the reaction mixture and by alteration

of the surface to volume ratio (s/v). In both cases the reaction

rate was unaffected. The use of standard methods for verifying the

presence of radicals was complicated in this case; Strausz et al[81]

have shown that addition of NO to silane systems leads to siloxane

formation via a chain mechanism. The addition of other radical

traps, say toluene was also complicated by the fact that iodine

itself is a very efficient trapping agent.

The Reaction Mechanism.

a) Initiation.

Davidson and Stephenson[19] have shown that the thermal fission

of the Si-Si bond in ethylpentamethyldisilane Et $Me_2SiSiMe_3$, to

form the trimethylsilyl and ethyldimethylsilyl radicals only

occurs at temperatures above 500°C at the pressures used here,

and therefore it is reasonable to assume that HMDS, with a weakest

B.D.E value of 67 kcal mole^{-1}, is thermally stable at the temperatures

used in this study. Therefore initiation by homolytic fission of

iodine molecules is the only feasible suggestion. Iodine is
0.01% thermally dissociated at $510^\circ K$[83] and this would be sufficient
to initiate a chain mechanism of the type suggested.

Iodine is dissociated photolytically by visible light. The
absorption band is narrow[82] but even so some iodine atoms are
presumably formed in daylight even at room temperature. However,
the absence of any appreciable reaction between iodine and HMDS
at temperatures around $100^\circ C$ indicates that insufficient iodine
atoms are present to keep the reaction going. This seems to
suggest that this system proceeds to relatively short chain
lengths.

Evidence of a half order in iodine also indicates initiation
by this process and further support is given by the postulation
of the same step in all alkyl iodinations.

b) Me_3Si Radical Displacement.

Step 2 appears to be an S_H2 type of reaction, so called
because of the obvious similarity to S_N2 processes. S_H2 reactions
generally will be discussed later and for the moment we will
consider only the energetic requirements of the process.

$$I + (Me_3Si)_2 \longrightarrow Me_3SiI + Me_3Si\cdot$$
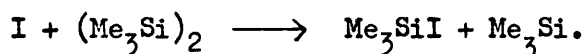
has ΔH given by the difference in D values for the bonds formed

and broken. i.e $\Delta H = - D(Me_3Si - I) + D(Me_3Si-SiMe_3) = - 2$ kcal mole^{-1}.

Therefore this step is almost thermoneutral and on energetic

grounds 2 and -2 are equally feasible.

The analogous step to alkyl iodinations would be.

$$I + (Me_3Si)_2 \longrightarrow HI + Me_3Si.Si Me_2CH_2.$$
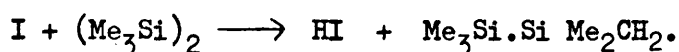
which is approximately 27 kcal mole^{-1} end othermic, similar to

methyl abstraction

$$I + (Me_3Si)_2 \longrightarrow MeI + Me_2Si SiMe_3$$

which is some 20 kcal mole^{-1} endothermic.

These latter processes are also ruled out by the absence of any

evidence for $Me_3SiSiMe_2{}^{\bullet}CH_2$, MeI or $Me_3SiSiMe_2$ in the product

analyses. Davidson and Stephenson[19] have shown that the radicals

$Me_3SiSi Me_2{}^{\bullet}CH_2$ and $Me_3SiSi^{\bullet} Me_2$ tend to undergo combination

reactions leading to tri and tetra silanes.

c) Iodine Abstraction.

The iodine abstraction step:

$$Me_3Si^{\bullet} + I_2 \longrightarrow Me_3SiI + I.$$
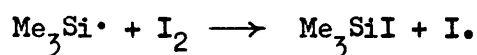
is the equivalent process to that in the corresponding alkyl

reactions[44] and is therefore not unusual in itself. The process

has a strong driving force, being some 33 kcal mole^{-1} exothermic

and, as the entropy of activation for such an abstraction reaction

ought not to be particularly unfavourable, it is reasonable to

suppose that this is quite a rapid step. The strong exothermicity

clearly precludes the other possible reactions i.e hydrogen and

methyl abstraction, as there is no evidence for such processes from the product formed.
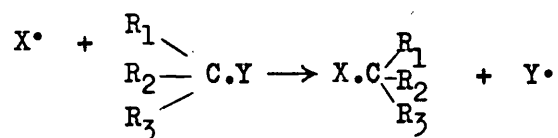
Absence of an Equilibrium.

The fact that the reaction studied went to completion would suggest that the back reactions - 2 and -3 are unimportant, probably due to the strong driving force of step 3. The corresponding alkyl iodinations, however, have all been found to proceed to an equilibrium[44]. The difference in behaviour can again be attributed to the change in energy requirements of the two systems.

Step 2 for the alkyl reactions is generally hydrogen abstraction[44] i.e $I + RH \longrightarrow HI + R$ for which $\Delta H \approx + 30$ kcal mole^{-1} e.g. 30 kcal mole^{-1} endothermic for R = Me, 25 for Et, 30 for Pr and 20 for t Br. This means that -2 has a strong driving force whereas 2 and-2 are approximately thermoneutral for HMDS + I_2. Step 3 for the alkyl iodinations is $R + I_2 \longrightarrow RI + I$ for which ΔH is 17 kcal mole^{-1} exothermic for R = Me and 15 for R = Et. Therefore -2 is actually more favourable than 3 and this leads to the setting up of an equilibrium rather than reaction to completion. Olefin formation by the breakdown of the alkyl iodides is also about 20-30 kcal mole^{-1} endothermic.

Radical Displacement Reactions

S_H2 on Carbon.

Radical displacement reactions, S_H2 are of type

$$X\bullet + \begin{array}{c} R_1 \\ R_2 \\ R_3 \end{array}\!\!\!\!-C.Y \longrightarrow X.C\!\!\begin{array}{c} R_1 \\ R_2 \\ R_3 \end{array} + Y\bullet$$

They are virtually unknown on 'saturated' sp^3 carbon atoms [84,85]

where atom abstraction is the more general reaction. In most of

the cases where S_H2 reactions do seem likely the attacked carbon

atom is under considerable strain and not strictly of sp^3 con-

figuration. Thus there is good reason to believe that opening

of the cyclopropane ring by halogens[33,86-9] occurs via radical displace-

ment by 'backside' attack on carbon

$$X\bullet \longrightarrow \triangle \longrightarrow X-\!\!\diagup\!\!\diagdown\bullet \xrightarrow{X_2} X(CH_2)_3X$$
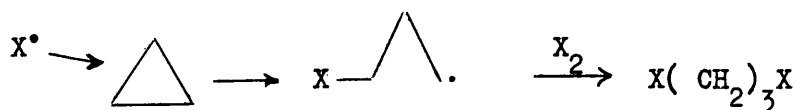
The suggestion of halogen addition followed by bond breaking between

the adjacent carbon atoms[84] seems unlikely due to the necessity

of expanding the carbon octet.

Friswell and Gowenlock[91] reported the reverse type of process

in which the heptyl radical cyclised to form cyclohexane and they

suggested S_H2 by displacement of a methyl radical. This

interpretation has been criticised[84] because the radicals were

produced under rather severe conditions, which could have caused

cyclohexane formation by some other process. Attempts to reproduce

this reaction[84] on the n-pentyl bromide radical led to the formation

of intermolecular products and only traces of cyclopentane.

Applequist and Searle[92] demonstrated fairly conclusively

that bromination of the 'Dewar benzene' system in 9,10 dehydro-

dianthracene proceeds by bromine atom attack on the cross link

with radical displacement and ultimate formation of the dibromide.
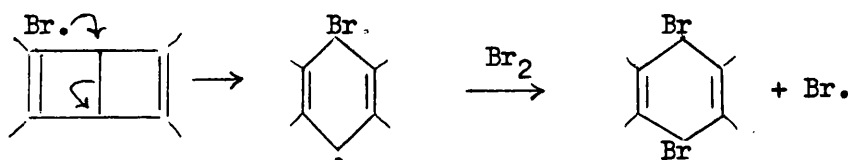
S_H2 attack on convential sp^3 carbon atoms has been claimed

for some iodine exchange reactions with alkyl iodides[93] . It is

also suggested that racemisation of optically active sec-butyl

iodide occurs by radical displacement[94] :

$$dRI \longrightarrow d,lR + I.$$

$$I + dRI \longrightarrow lRI + I. \quad etc$$
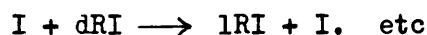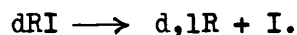
but the possibility of radical racemisation:

$$I + dRI \longrightarrow dR. + I_2$$

$$dR. \rightleftharpoons lR.$$

$$d,lR + I_2 \longrightarrow d,lRI + I.$$
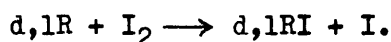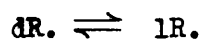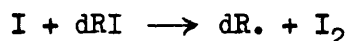
has not been excluded. Later work on this type of system merely

illustrated the difficulties involved in the study of these reactions[93,95-8].

Carbon Linked to Other Atoms.

The rarity of S_H2 reactions on sp_3 carbon atoms is partly due to the fact that these reactions are too slow to compete with other processes[85], such as atom abstraction. This is understandable when one considers the relative strength of the C-C bond and the necessary rigidity of the S_H2 transition state (and hence the lower probability factor). Radical displacement reactions ought to become more favourable in systems containing links between elements which produce lower D values. Thus the C-Hg bond in diaryl mercury compounds is cleaved by the $CCl_3 \cdot$ radical to form $RCCl_3$ and $RHgCl$, and the S_H2 process

$$CCl_3 \cdot + RHgR' \longrightarrow RCCl_3 + RHg'.$$
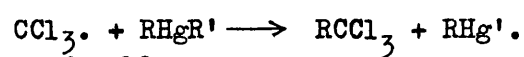
has been suggested[99,100,90].

The mechanism proposed by Davidson and Stephenson[19] for the decomposition of HMDS would seem to involve a radical displacement step on 'saturated' carbon,
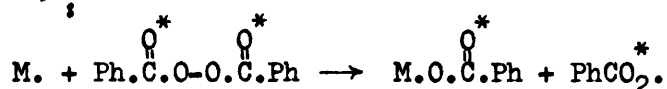
$$Me_3Si \cdot + Me_3SiSiMe_3 \longrightarrow Me_4Si + Me_2SiSiMe_3$$
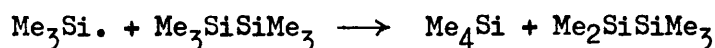
as it is unlikely that such a process would occur by prior addition followed by elimination.

S_H2 on Other Atoms.
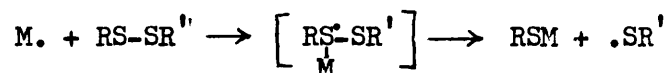
The relatively weak O-O bond in peroxides $\big[D(O-O) = 30$ kcal

mole^{-1} ^{4}] is rapidly cleaved by radicals at sufficient speed to

compete with other processes^{85} . It has been shown that O^{18} labelled

carbonyl oxygen retains its identity in radical attack on benzoyl

peroxide$^{101-3}$:

$$M. + Ph.\overset{\overset{*}{O}}{\underset{}{C}}.O-O.\overset{\overset{*}{O}}{\underset{}{C}}.Ph \longrightarrow M.O.\overset{\overset{*}{O}}{\underset{}{C}}.Ph + Ph\overset{*}{C}O_2.$$

and therefore the mechanism probably involves S_H2 attack on the

peroxide oxygen. Disulphides are cleaved at equivalent rates by

a reaction that could be direct displacement,

$$M. + RS-SR' \longrightarrow MSR + .SR'$$
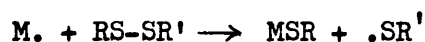
but could involve radical addition:

$$M. + RS-SR' \longrightarrow \left[R\underset{M}{\overset{|}{S}}-SR' \right] \longrightarrow RSM + .SR'$$

due to the possibility that sulphur could extend its electronic octet.

The Mechanism of Radical Displacement.

The stereochemistry of S_H2 reactions is still unknown but it

has been generally assumed to occur by 'backside' attack as this

would seem the most unhindered mode of approach. Wolfgang et al^{104} ,

however, studied the reaction of recoil tritium atoms from nuclear

reactions with organic compounds and found that the hydrogen atom

on the assymetric carbon of 2-butanol was displaced with $91 \pm 6\%$

retention and therefore the attack was unambiguously 'frontside'.

This is clearly a special case as these 'hot' atoms react with some

2 to 10 ev of kinetic energy.

Prior and Pickering[85] studied S-S and O-O bond fission by radicals

in disulphides and peroxides, because of the facility of reaction,

the evidence for S_H2 processes in both and the fact that S_N2

reactions in disulphides are known to be 'backside'. They

concluded that the process was mostly 'frontside' across the

S-S (O-O) bond and in fact this can be seen to be the least hind-

ered approach. It was also possible that sulphur (oxygen) atom

attack occured by a 'quasi backside' process in which the in-

coming radical chose the least hindered route. This latter mode

of reaction becomes less important as R and R' become more bulky.

Me$_3$Si Radical Displacement.

It is unlikely that

$$(Me_3Si)_2 + I \longrightarrow Me_3SiI + Me_3Si.$$
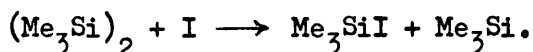
occurs by iodine addition to silicon followed by elimination

because of the steric difficulties involved. Therefore it seems

reasonable to assume that this step occurs by 'frontside' or

'backside' radical displacement. 'Frontside' would involve

attack across the Si-Si bond and molecular models indicate that

this is only possible when the SiMe$_3$ groups are 'eclipsed'.

On the other hand 'backside' attack is less hindered and there

is no barrier to rotation about Si-Si in the transition state:

$$I\ldots\ldots\ldots Si\ldots\ldots\ldots SiMe_3$$
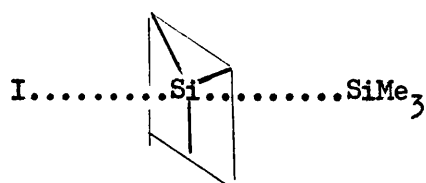
It would clearly be of interest to study the effect of different alkyl groups around silicon as 'frontside' attack would be less dependent on steric factors than 'backside'.

The Frequency Factor.

The calculated collision number for bimolecular reactions is of the order of 10^{14} cc mole^{-1} sec^{-1}. A probability factor of about 10^{-2} has been estimated for the reaction between an atom and a non linear polyatomic molecule[105];
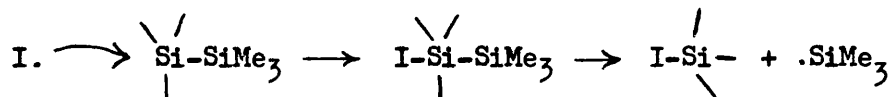
$$A + BC \longrightarrow AB + C$$
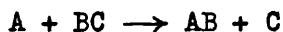
Thus for an S_H2 type of process, the attack of I. atoms on HMDS

$$I + Me_3SiSiMe_3 \longrightarrow Me_3SiI + SiMe_3$$
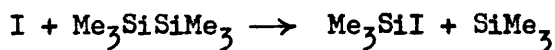
would be expected to have a pre-exponential factor of around 10^{12} cc mole^{-1}sec^{-1}. The figure of 1.70×10^{11} cc mole^{-1} sec^{-1} obtained in this work is therefore in good agreement with such an estimate.

Whilst the possibility of radical addition followed by elimination:

$$I. \longrightarrow \overset{\diagup}{\underset{|}{Si}}-SiMe_3 \longrightarrow I-\overset{\diagup}{\underset{|}{Si}}-SiMe_3 \longrightarrow I-\overset{\diagup}{\underset{\diagdown}{Si}}- + .SiMe_3$$

cannot be dismissed completely, one would expect the higher degree of steric hinderance involved in such a process to result in a

substantial lowering of the frequency factor.

The frequency factor is derived for only one proposed S_H2 displacement reaction[88,33]. Fortuitously this reaction - the iodination of propane - also involves attack by iodine atoms and therefore ΔS, the entropy of activation, should be similar to that measured here. The opening of the cyclopropane ring by iodine was studied both thermally and photolytically in the gas phase by Ogg and Priest[88]. They postulated a mechanism containing the step:

$$I + C_3H_6 \longrightarrow ICH_2CH_2CH_2 \cdot$$
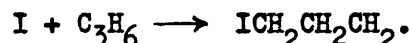
for which they suggested radical displacement,
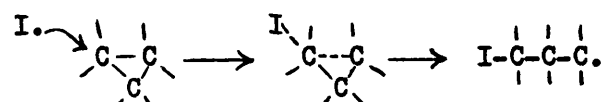
The rate constant was given by:

$$k = 7.36 \times 10^{12} e^{-17,280/RT} \text{ cc mole}^{-1}\text{sec}^{-1}$$

The reaction was essentially homogeneous and the slow iodine catalysed isomerisation to propylene was the only important side reaction. There was considerable error involved in their work as they were only able to follow the kinetics over a 30°C temperature range (the side reaction became too important at higher temperatures).

More recently Benson[33] has studied the same reaction and re-

corded the relationship:

$$k = 4.17 \times 10^{12} e^{-17,500/RT} \quad \text{in good agreement}$$

with the earlier estimate.

Both of these figures are fairly close to that obtained in this work for displacement of the trimethylsilyl radical. The lower figure for the latter reaction can be rationalised in view of the increased hindrance experienced by the incoming iodine atom.

Atom abstraction reactions would be expected to have a 'looser' transition state with a correspondingly smaller entropy change between the reactants and the transition state. In fact the frequency factors for hydrogen abstraction by iodine in alkyl iodinations are all close to the collision number, indicating that the transition states involve almost free rotation of the iodine atom around the hydrocarbon molecules.

The Activation Energy.

The Arrhenius plot obtained for the overall reaction was linear throughout and indicated no tendency to flatten out at lower temperatures, thus further verifying that the reaction was proceeding homogeneously. The activation energy E_2 fell within

the range of second order radical reactions of approximately the same enthalpy change (e.g. activation energies for hydrogen abstraction by methyl radicals cover the range 4.4 - 11.8 kcal mole^{-1} and all these reactions are slightly exothermic) but was considerably lower than those obtained for abstraction of hydrogen by iodine in alkyl iodinations (20 - 25 kcal mole^{-1}). This is not surprising as these latter processes are 20 - 30 kcal mole^{-1} endothermic.

Whilst it is tacitly assumed that a correlation exists between the activation energy of a reaction and the corresponding heat change no simple equation exists to link the two parameters accurately. Evans and Polanyi[106] noted that the change in activation energy in a homologous series of exothermic abstraction reactions

$$A + BC \longrightarrow AB + C \quad \ldots\ldots\ldots\ldots\ldots(1)$$

was related to the change in the heat of reaction by:

$$\Delta E_{act} = \alpha \Delta H_{act}$$

where α is a constant for a given series. More recent results have, however, placed limits on the quantitative value of this rule. Voevodskii[107] has proposed rules for the calculation of bond energies in hydrocarbons and has combined these with Evans and Polanyi's in an attempt to calculate the activation energies of abstraction reactions. As yet there is insufficient data

available to estimate the validity of the results.

Other empirical rules have been suggested for calculation of activation energies from the energies of the bonds involved in the reaction. Thus Hirschfelder[108] proposed that for exothermic reactions between atoms and molecules (as in (1) above) the activation energy is approximately 5% of the energy of the bond being broken; i.e. $3\frac{1}{2}$ kcal mole^{-1} for attack of iodine atoms on HMDS (if we again use D values for bond energies). Whilst this rule is only approximate (± 5 kcal) it is further verification that the activation energy obtained in this work is in the right region.

## Other Systems Studied.

Iodination of Trimethylsilane.

This reaction proceeds rapidly at temperatures as low as 70°C even though it is some 7 kcal mole^{-1} less favourable energetically than HMDS + I_2 (i.e. 25 kcal mole^{-1} exothermic). Assuming iodine initiation the most likely second step is:

$$I + Me_3SiH \longrightarrow HI + Me_3Si.$$
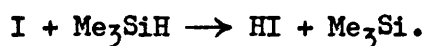
which is about 10 kcal mole^{-1} endothermic. Methyl abstraction is about 23 kcal mole^{-1} endothermic. In the light of this one would

expect a slower reaction for this system. It is unlikely that the rapid reaction was caused by heterogeneous factors as the same precautions were taken here as in the HMDS iodination. The explanation would seem to lie in the dissociation of iodine by visible light[82] This small degree of dissociation could well be sufficient to allow the reaction to proceed even at quite low temperatures, provided this system reacts with longer chains than the HMDS iodination. One would expect longer chains here because step 2 is a hydrogen abstraction and not a radical displacement. Therefore, although the process is less favourable energetically than attack on HMDS, the transition state would be considerably 'looser' and the probability of reaction (i.e. chain propagation) correspondingly higher.

In view of these factors and the fact that the only product detected was trimethylsilyliodide one may tentatively suggest the reaction mechanism:

$$I_2 \rightleftharpoons 2I$$

$$I + Me_3SiH \longrightarrow HI + Me_3Si$$

$$Me_3Si + I_2 \longrightarrow Me_3SiI + I$$
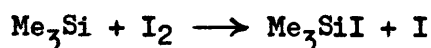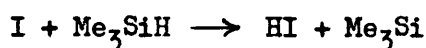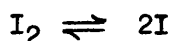
as HI was not detectable, either by g.l.c. or mass spectrometry.

Bromination Reactions.

The reactions of bromine with HMDS and trimethyl-silane at initial pressures of about 20 mm Hg were both fast, even at room temperature; the Me_3SiH reaction being completed in a few seconds, whilst the bromination of the disilane occupied about 30 minutes. Bromine is less read-ily dissociated by daylight than iodine as its absorption band is weaker[82] and its B.D.E. higher. Nevertheless, Whittle has found that brominations in carbon systems are frequently light sensitive[109], and therefore it seems likely that these reactions proceed to longer chains than the corresponding iodinations. The vessel used in the org -anosilane reactions was virtually light-free but a little probably entered around the vessel vacuum tap. The Me_3SiH/Br_2 system has since been re-examined in a light-free vessel[110] but it was found difficult to obtain a measurable rate and it is likely that heterogeneous factors were involved.

These reactions were less 'clean' as would be expected in a more energetic system where side reactions become more probable. Some of the expected side reactions are only slightly endothermic anyway and therefore quite favourable.

References.

(1) For discrepancies in molecular heats of formation:

    (a) S. R. Gunn and L. G. Green, J. Phys. Chem., 65, 779 (1961);

    (b) F. Feher, G. Jansen and H. Rohmer, Angew. Chem., 75, 859 (1963);

    (c) R. Thompson, J. Chem. Soc., 1908 (1953);

    (d) K. B. Goldblum and L. S. Moody, Ind. Eng. Chem., 47, 847 (1955);

    (e) W. F. Lautsch, Chem. Tech.(Berlin), 10, 419 (1958);

    (f) S. Tannenbaum, J. A. C. S., 76, 1027 (1954).

(2) For variations in bond energies:

    (a) H. Gilman and G. E. Dunn, Chem. Rev., 52, 77 (1953);

    (b) Ref. 16.

(3) W. D. Good, J. L. Lacina, B. L. DePrater and J. P. McCullough, J. Phys. Chem., 68, 579 (1964).

(4) T. L. Cottrell, 'The Strengths of Chemical Bonds', 2nd Edn., 1958, Butterworths, London.

(5) M. Szwarc, Chem. Rev., 75, 47 (1950).

(6) A. H. Sehon and M. Swarcz, Ann. Rev. Phys. Chem., 8, 439 (1957)

(7) J. A. Kerr, Chem. Rev., 66, 465 (1966).

(8) G. Jaffe, Z. Phys., 87, 535,(1934).

(9) E. Hylleraas, Z. Phys., 71, 739 (1931).

(10) J. A. Kerr and A. F. Trotmann-Dickenson, Prog. React. Kinetics,

1, 113 (1961).

(11) E. L. Metcalfe, J. Chem. Soc., 3560 (1963).

(12) M. Szwarc, J. Chem. Phys., 17, 505 (1949).

(13) H. J. Eméléus and C. Reid, J. Chem. Soc., 1021 (1939).

(14) H. J. Eméléus, A. G. Maddock and C. Reid, J. Chem. Soc., 353,

(1941).

(15) K. Stokland, Trans. Farad. Soc., 44, 545 (1948).

(16) W. C. Steele, L. D. Nichols and F. G. A. Stone, J. A. C. S.,

84, 4441 (1962).

(17) W. C. Steele and F. G. A. Stone, J. A. C. S., 84, 3599 (1962).

(18) G. G. Hess, F. W. Lampe and L.H. Sommer, J. A. C. S., 87, 5327

(1965).

(19) I. M. T. Davidson and I. L. Stephenson, J. Chem. Soc.(A), 282,

(1968).

(20) J. A. Connor, G. Finney, G. J. Leigh, R. N. Haszeldine, P. J.

Robinson, R. D. Sedgwick and R. F. Simmons, Chem. Comm., 178

(1966).

(21) J. A. Connor, R. N. Haszeldine, G. J. Leigh and R. D. Sedgwick,

J. Chem. Soc.(A), 768 (1967).

(22) J. A. Kerr, D. H. Slater and J. C. Young, J. Chem. Soc.(A),

134 (1967).

(23) V. H. Dibeler and F. L. Mohler, J. Res. Natl. Bur. Std.,

40, 25 (1948).

(24) D. P. Stevenson, Disc. Farad. Soc., 10, 35 (1951).

(25) M. F. Lappert, J. B. Pedley and P. N. K. Riley, Chem. Soc.

Autumn Meeting, (1966).

(26) J. L. Franklin, Ind. Eng. Chem, 41, 1070 (1949).

(27) S. Tannenbaum, J. A. C. S., 76, 1027 (1954).

(28) A. E. Beezer and C. T. Mortimer, J. Chem. Soc.(A), 514 (1966).

(29) I. M. T. Davidson and I. L. Stephenson, J. Organomet. Chem.,

7, 24 (1967).

(30) J. Curtice, H. Gilman and G. S. Hammond, J. A. C. S., 79,

4754 (1957).

(31) S. W. Benson and P. S. Nangia, J. A. C. S., 86, 2770; 2773 (1964).

(32) S. W. Benson and H. Teranishi, ibid, 85, 2887; 2890 (1963).

(33) S. W. Benson, J. Chem. Phys., 34, 521 (1961).

(34) S. W. Benson and A. Bose, ibid, 37, 2935 (1962).

(35) S. W. Benson and A Amano, ibid, 36, 3464, (1962).

(36) S. W. Benson, ibid, 38, 1945 (1963).

(37) S. W. Benson and H. Teranishi, ibid, 40, 2946 (1964).

(38) S. W. Benson and A. Bose, ibid, 37, 1081 (1962).

(39) S. W. Benson and E. O'Neal, ibid, 34, 514 (1961).

(40) M. C. Flowers and S. W. Benson, ibid, 38, 882 (1963).

(41) D. M. Golden, R. Walsh and S. W. Benson, J. A. C. S., 87, 4053 (1965).

(42) J. H. Sullivan, J. Phys. Chem., 65, 722 (1961).

(43) C. A. Goy and H. O. Pritchard, ibid, 69, 3040 (1965).

(44) J. H. Knox and R. G. Musgrave, Trans. Farad. Soc., 63, 2201 (1967).

(45) B. G. Gowenlock and K. E. Thomas, J. Chem. Soc., 931, 5068 (1965).

(46) R. N. Haszeldine and J. C. Young, ibid, 4503 (1960).

(47) J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson and J. C. Young, ibid (A), 510 (1968).

(48) A. Taketa, M. Kumada and K. Tarama, Nippon Kagaku Z., 78, 999 (1957); Chem Abs. 52, 8942 (1958).

(49) B. G. Hobrock and R. W. Kiser, J. Phys. Chem., 65, 2186 (1961); 66, 155 (1962).

(50) G. R. Wilson and A. G. Smith, J. Org. Chem., 26, 557 (1961).

(51) M. Kumada, K. Shiina and M. Yamaguchi, J. Chem. Soc. Japan, Ind. Chem. Sect., 57, 230 (1954); Chem. Abst., 49, 11542 (1955).

(52) M. G. Voronkov, B. N. Dolgov and N. A. Dmitrieva, Doklady Akad. Nauk. S.S.S.R., 84, 959 (1952).

(53) E. J. Gallegos and R. F. Klaver, J. Sci. Instr., 44, 427 (1967).

(54) E. G. Johnson and A. O. Nier, Phys. Rev., 91, 10 (1953).

(55) R. E. Honig, J. Chem. Phys., 16, 105 (1948).

(56) F. P. Lossing, A. W. Tickner and W. A. Bryce, J. Chem. Phys.,
19, 1254 (1951).

(57) J. W. Warren, Nature, 165, 810 (1950).

(58) R. W. Kiser, 'Introduction to Mass Spectrometry and its Appli-
cations', Prentice-Hall, Englewood Cliffs, N. J.,(1965), p162.

(59) J. Waldron and K.Wood, 'Mass Spectrometry', Institute of Petro-
leum, London, (1952), p16.

(60) G. Pratt and J. Purnell, Analyt. Chem., 32, 1213 (1960).

(61) Handbook of Chemistry and Physics, p. D120, 49th
Edn.,(1968/9), Chemical Rubber Publishing Co., Ohio.

(62) JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan
(1965).

(63) S. J. Band, I. M. T. Davidson and C. A. Lambert, J. Chem. Soc.(A),
(1968).

(64) J. D. Morrison and A. J. C. Nicholson, J. Chem. Phys., 20,
1021 (1952).

(65) S. J. Band, I. M. T. Davidson and C. A. Lambert, J. Organomet.
Chem., 12, P3 (1968).

(66) B. G. Gowenlock and J. Stevenson, ibid, 13, P13 (1968).

(67) I. L. Stephenson, PhD thesis, Univ. of Leics., 1967.

(68) L. Pauling, 'Nature of the Chemical Bond', Cornell University Press, New York, p58 (1944).

(69) H. A. Skinner and H. O. Pritchard, Trans. Farad. Soc., 49, 1254 (1953).

(70) H. A. Skinner and H. O. Pritchard, Chem. Rev., 55, 745 (1955).

(71) E. C. Baughan, M. G. Evans and M. Polanyi, Trans. Farad. Soc., 37, 377 (1941).

(72) 'Interatomic Distances', Chem. Soc. Special Publication, N° 11 (1958).

(73) J. Goubeau and H. Sommer, Z. Anorg. U. Allgem. Chem., 289, 1-4 (1957)

(74) B. Beagley, A. G. Robiette and G. M. Sheldrick, Chem. Comm., 601 (1967).

(75) E. A. V. Ebsworth, Chem. Comm., 530 (1966).

(76) P. G. Perkins, Chem. Comm., 268 (1967).

(77) E. W. Randall and J. J. Zuckermann, Chem. Comm., 732 (1966).

(78) a. E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. Mc-Kean, N. Sheppard and L. A. Woodward, Spectrochim. Acta, 13, 202 (1958).

   b. G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick and L. A. Woodward, Spectrochim Acta., 22, 67 (1966).

(79) J. C. Baldwin, M. F. Lappert, J. B. Pedley and J. A. Treverton,
J. Chem. Soc.(A), 1980 (1967).

(80) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Med-
vedev and Ye. L. Frankevich, 'Bond Energies, Ionisation Poten-
tials and Electron Affinities', Arnold, London, p151 (1966).

(81) M. A. Nay, G. N. C. Woodall, O. P. Strausz and H. E. Gunning,
J. A. C. S., 87, 179 (1965).

(82) R. M. Keefer and L. J. Andrews, J. A. C. S., 74
1891 (1952).

(83) Z. G. Szabo, 'Advances in the Kinetics of Homogeneous Gas
Reactions', p191.

(84) W. S. Trahanovsky and M. P. Doyle, J. Org. Chem., 32, 146 (1967).

(85) W. A. Pryor and T. L. Pickering, J. A. C. S., 84, 2705 (1962).

(86) C. A. Walling and P. S. Fredricks, J. A. C. S., 84, 3326 (1962).

(87) D. E. Applequist, G. F. Fanta and B. W. Henrikson, ibid, 82,
2368 (1960).

(88) R. A. Ogg Jr and W. J. Priest, J. Chem. Phys., 7, 736 (1939).

(89) M. S. Kharasch, M. Z. Fineman and F. R. Mayo, J. A. C. S., 61,
2139 (1939).

(90) R. F. Jensen and H. E. Guard, ibid, 90, 3250 (1968).

(91) N. J. Friswell and B. G. Gowenlock, Chem. Comm., 277 (1965).

(92) D. E. Applequist and R. Searle, J. A. C. S., 86, 1389 (1964).

(93) J. E. Bujake Jr., M. W. T. Pratt and R. M. Noyes, ibid, 83,
1547 (1961).

(94) R. A. Ogg Jr. and M. Polanyi, Trans. Farad. Soc., 31, 482
     (1935).

(95) R. A. Herrman and R. M. Noyes, J. A. C. S., 78, 5764 (1956).

(96) S. W. Benson, J. Chem. Phys., 38, 1945 (1963).

(97) C. C. Price and M. Schwarcz, J. A. C. S., 62, 2891 (1940).

(98) D. Clark, H. O. Pritchard and A. F. Trotman-Dickenson, J. Chem.
     Soc., 2633 (1954).

(99) A. N. Nesmeyanov, A. E. Borisov, E. T. Golubeva and A. I.
     Kovredov, Tetrahedron, 18, 683 (1962).

(100) A. E. Borisov, Izv. Akad. Nauk SSR. Otd. Khim. Nauk., 524
      (1951).

(101) E. H. Drew and J. C. Martin, Chem. and Ind., 925 (1959).

(102) D. B. Denney and G. Feig, J. A. C. S., 81, 5322 (1959).

(103) W. Doering, K. Okamoto and H. Krauch, ibid, 82, 3579 (1960).

(104) M. Henchman and R. Wolfgang, ibid, 83, 2991 (1961).

(105) S. W. Benson, 'The Foundations of Chemical Kinetics', Mc-
      Graw Hill, New York, p276 (1960).

(106) M. G. Evans and M. Polanyi, Trans. Farad. Soc., 32, 1333
      (1936); 34, 22 (1938).

(107) V. V. Voevodskii, Doklady Akad. Nauk., S. S. S. R., 79, 455
      (1951).

(108) J. D. Hirschfelder, J. Chem. Phys., 9, 645 (1941).

(109) See for eg. E. Buckley and E. Whittle, Trans. Farad. Soc.,
      58, 529 (1962); 58, 536 (1962).

(110) I. M. T. Davidson and P. Ellis, University of Leicester,
      Unpublished Work.