THE UNIVERSITY OF MANITOBA

THE REACTION OF XENON DIFLUORIDE WITH ORGANOMETALLIC COMPOUNDS. SOME STUDIES OF RAPID FLUORINE EXCHANGE IN SOLUTION BY THE NUCLEAR MAGNETIC RESONANCE TECHNIQUE.

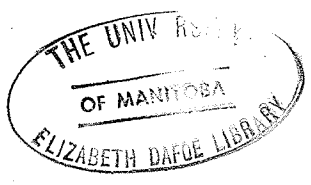
by

JAMES ANDREW GIBSON

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

WINNIPEG, MANITOBA
May 1973



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BY: JAMES ANDREW GIBSON

A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

The reaction of xenon difluoride with a number of organosilicon compounds was investigated. In particular, the reaction of xenon difluoride with organosilicon chlorides produced fluorosilanes, chlorine and xenon; evidence is presented for the initial production of atomic rather than molecular chlorine in these reactions. A reaction pathway is suggested based on the known chemistry of xenon difluoride and on kinetic evidence. A nucleophilic displacement of chlorine by an S_N2 - Si or an S_N2 - Si mechanism seems most reasonable.

Reactions of xenon difluoride with other main group compounds are also reported. For example reaction with methyl iodide appears to produce the novel compound methyliodine(III) difluoride,(CH_3IF_2). Phosphorus(III) compounds were readily oxidised to phosphorus(V) compounds by xenon difluoride.

The second section of the thesis deals with the study of fluorine exchange by the n.m.r. method. The rapid, reversible, base catalysed hydrolysis of trimethylfluorosilane was studied by the collapse of the doublet due to ^1H-^{19}F coupling in the proton n.m.r. spectrum. A rate expression was derived and mechanisms consistent with the experimental data are presented.

A reinvestigation of the reported intermolecular exchange found in the pentafluorosilicate (SiF_5^-) moiety was made and the exchange was shown to be due to the presence of traces of moisture in the solvent methylene chloride. Some of the arguments surrounding both inter- and intramolecular exchange mechanisms were reviewed and the interaction of bases with pentafluorosilicate and phosphorus pentafluoride was studied. A mechanism of intramolecular exchange based on Lewis acid-Lewis base interactions is discussed.

ACKNOWLEDGEMENTS

The author wishes to thank Dr.A.F.Janzen for his continued help and guidance throughout the course of this work and for the patience shown during more difficult times.

Thanks are expressed to Mr.M.Arneson for running the mass spectra and assisting with the gas chromatography. I would also like to thank the members of the laboratory who made the days of failure considerably brighter, particularly S.N.Kay and D.G.Ibbott. For help and interest in ^{19}F n.m.r. spectroscopy I would like to thank Dr.T. Schaefer and his group and I would also like to thank Dr.G.Burchill for help with the kinetics. The "four-site" line shape analysis computer programme was kindly provided by Mr.B.Goodwin whose assistance was greatly appreciated.

My wife Pauline is thanked most deeply for understanding an ill-tempered chemist and for typing this thesis. Dr.J.B.Westmore is thanked for the loan of the typewriter.

The financial support of the National Research Council of Canada and the Aluminum Company of Canada is gratefully acknowledged. Finally the Great Canadian Shield is thanked for unforgettable peace and solitude during periods of academic strife.

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CHAPTER 1

GENERAL INTRODUCTION

Fluorine chemistry has received a continuing interest during recent years and there are now extensive publications in the areas of both perfluoroalkyl-[1] and metallic[2] fluoride chemistry. The commercial availability of bottle fluorine has alleviated the necessity for temperamental electrolytic fluorine generators and the handling of gaseous fluorine in the laboratory is becoming much more common.

In 1962 it was fluorine chemistry that finally terminated the notion that the noble gases were truly inert and incapable of forming any chemically definable compounds. In Bartlett's famous experiment[3] it was found that the very powerful oxidising agent PtF_6 was capable of facile reaction with xenon to yield a bright orange compound, then thought to be $Xe(PtF_6)$. The development of inert gas chemistry was initially rapid and in very little time it was discovered that simple fluorides of xenon could be synthesised by the direct action of fluorine on the element and also by a number of other related methods.[4-7] The di-, tetra- and hexafluorides have been synthesised by these methods and tentative claims have been laid for the formation of an octafluoride.[8] An intensive study of the xenon/fluorine system by several workers showed that each of the fluorides could be synthesised in high yield simply by changing the reaction conditions employed.[9,10]

After the initial surge of interest in noble gas chemistry

subsided it appeared that research diverged into two broad areas, aqueous xenon chemistry (xenates, perxenates etc.) and the reaction of xenon fluorides with other suitable reagents in an attempt to form further xenon derivatives. Aqueous xenon chemistry is of no interest to this thesis and will not be discussed further; an interested reader is directed to some of the literature in this area.[11–14]

The reaction of xenon fluorides with various heavy metal fluorides has been studied in some detail. Good fluoride ion acceptors appear to form stable ionic compounds; some examples are given below.

$$XeF_2 + SbF_5 \longrightarrow XeF^+[SbF_6]^- \quad [15]$$

$$XeF_2 + 2SbF_5 \longrightarrow XeF^+[Sb_2F_{11}]^- \quad [15–17]$$

$$2XeF_2 + SbF_5 \longrightarrow Xe_2F_3^+[SbF_6]^- \quad [15]$$

$$2XeF_2 + AsF_5 \longrightarrow Xe_2F_3^+[AsF_6]^- \quad [18]$$

Crystal structures have been completed for $Xe_2F_3^+[AsF_6]^-$,[18] $XeF^+[Sb_2F_{11}]^-$[17] and $XeF^+[RuF_6]^-$.[19] Many other complexes, probably of an ionic nature, have also been reported.[20–22] Xenon difluoride also appears to form molecular adducts involving no ionisation to XeF^+ or related species.

$$XeF_2 + IF_5 \longrightarrow XeF_2 \cdot IF_5$$

$$XeF_2 + XeOF_4 \longrightarrow XeF_2 \cdot XeOF_4$$

($XeOF_4$ is isostructural with IF_5)

X-ray and Raman data have been presented for molecular complexes showing that, although some fluorine bridging appears present, the xenon difluoride bond distances are almost indistinguishable from those in pure crystalline xenon difluoride.[23,24]

Xenon hexafluoride forms a similar, well known, series of 1:1 adducts with metal fluorides yielding the XeF_5^+ ion.[25-31] X-ray data have been presented for two of them confirming the existence of XeF_5^+.[30,31]

In contrast, xenon tetrafluoride is a poor fluoride ion donor, only with antimony pentafluoride[32] and with very powerful fluoride acceptors does it seem to form stable compounds. The existence of XeF_3^+ has however been recently shown by X-ray and n.m.r. studies.[33,34] The relative ion donor abilities of the simple xenon fluorides have been investigated semi-quantitatively by several workers and have been rationalised in a series of articles by Bartlett and co-workers.[24,27,35]

donor ability

$$XeF_6 > XeF_2 \gg XeF_4$$

The high donor abilities of XeF_6 and XeF_2 have provided a useful

method of purification of XeF_4.[27]

Xenon difluoride has been found to be quite kinetically inert in many of its reactions despite its low average bond energy of 32 kcal $mole^{-1}$. For example, although the hydrolysis of xenon difluoride is thermodynamically very favourable the rate is in fact quite slow ($t_{\frac{1}{2}} \sim 7$ hours at 0^{o}).[36] Similarly iodine, which should be readily oxidised by xenon difluoride, is stable for some time in CH_3CN solutions of XeF_2.[37] Addition of traces of Lewis acids however considerably increases the reactivity of xenon difluoride, presumably via an initial ionisation step:[37]

$$XeF_2 + A \longrightarrow XeF^+....AF^-$$

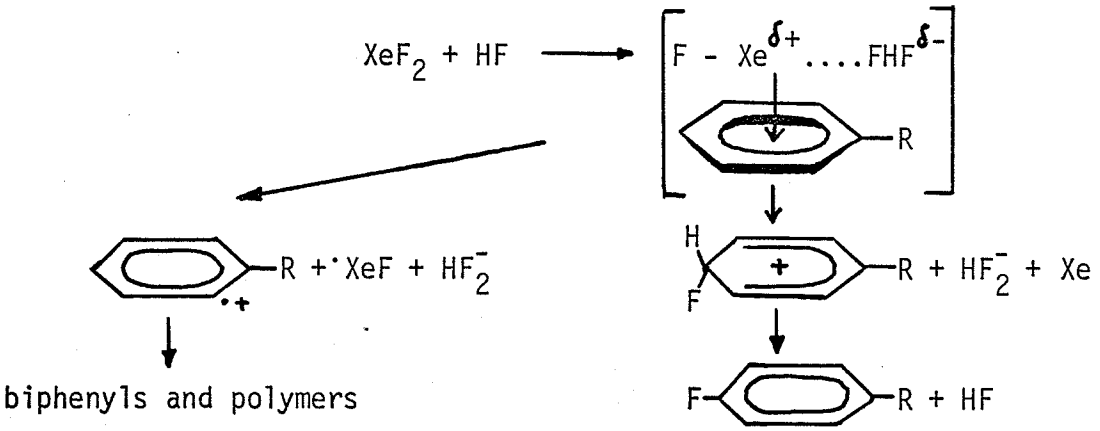
$$\text{or} \quad 2XeF_2 + A \longrightarrow Xe_2F_3^+....AF^-$$

Reactions of xenon difluoride with organic compounds have been studied. Reactions with olefins are limited; for example, Chernick and co-workers have studied the reaction of xenon difluoride with several olefins.[38] Perfluoro-olefins are quite unreactive while hydrocarbon olefins add fluorine across the double bond. The mechanism of these reactions is uncertain but may involve initial ionisation of xenon difluoride to give the XeF^+ species due to the presence of traces of hydrogen fluoride. A series of papers from Shaw and coworkers have appeared in the literature describing an extensive study

of the fluorination of aromatic compounds by xenon difluoride.[39–43] No reaction occurred before hydrogen fluoride was added and some considerable speculation as to the path of the reactions has resulted. E.s.r. studies showed that during the course of the reactions aromatic radical cations were produced; the final products were fluorine substituted aromatics along with some polymerisation products such as biphenyls, etc. The initial step appeared once again to be ionisation or "polarisation" of the xenon difluoride by the added HF.

$$XeF_2 + HF \longrightarrow F - Xe^{\delta+} \ldots . FHF^{\delta-}$$

However, in an extensive argument supported by some experimental observations the authors suggest that the XeF^+ moiety is not the reactive species but rather that the ion pair or "polarised pair" forms a π complex with the aromatic molecule which then reacts via a radical pathway.



MacKenzie and Fajer have also studied the vapour phase fluorination of aromatic compounds to give fluorine substituted products.[44] At the temperatures used (100-200°), the reactions may involve free radical attack or may be due to the formation of small quantities of HF in the system followed by reactions similar to those described by Shaw and co-workers.

The reaction of xenon difluoride with carbon, silicon, tin and titanium tetrachlorides has very recently been reported.[45] Whereas the silicon, tin and titanium chlorides reacted readily, the xenon difluoride was found to be partially soluble in carbon tetrachloride without reaction. However addition of traces of group five metal fluorides led to rapid reaction to give freons, carbon tetrafluoride, chlorine and xenon.

Xenon difluoride has also been used by several workers as a source of further xenon compounds. A variety of these reactions are summarised below:

$$XeF_2 + CF_3COOH \longrightarrow Xe(OOCCF_3)_2 \ , \ FXe(OOCCF_3) \qquad [46,49,50]$$

$$XeF_2 + HNO_3 \longrightarrow Xe(NO_3)_2 \ , \ FXe(NO_3) \qquad [46]$$

$$XeF_2 + HOSO_2F \longrightarrow Xe(OSO_2F)_2, \ FXe(OSO_2) \qquad [46,54]$$

$$XeF_2 + HOTeF_5 \longrightarrow Xe(OTeF_5)_2, FXe(OTeF_5) \xrightarrow{+AsF_5} Xe(OTeF_5)^+AsF_6^- \qquad [47,48,49]$$

$$XeF_2 + P_2O_3F_4 \longrightarrow Xe(OPOF_2)_2,\ FXe(OPOF_2) \longrightarrow {}^{\cdot}OPOF_2 \quad [52]$$

$$XeF_2 + HOSO_2F + AsF_5 \longrightarrow (FXe)_2O_2SOF^+AsF_6^- \quad [51]$$

$$XeF_2 + HOSeF_5 \longrightarrow FXe(OSeF_5)\ ,\ Xe(OSeF_5)_2 \quad [53]$$

$$XeF_2 + HClO_4 \longrightarrow Xe(ClO_4)_2\ ,\ FXe(ClO_4) \quad [51]$$

Although not all the above compounds have been fully characterised there seems sufficient evidence that they exist; an X-ray structural determination has been completed for $FXe(OSO_2F)$ which shows the molecule to be linear with covalent Xe-O and Xe-F bonds.[54]

Attempts have been made to prepare Xe(IV) and Xe(VI) derivatives with some success[55] but these will not be reported here, (early results reporting Xe(IV) derivatives have not been found to be reproducible and the situation at present is not clear).

Besides fluorine and oxygen only two other elements have been claimed to form bonds with xenon. Xenon dichloride, albeit unstable, seems to be fairly well established[56,57] while claims of a compound containing a xenon-boron bond have not yet been substantiated by other workers.[58]

This thesis reports and speculates on a number of reactions of xenon difluoride with organometallic compounds. Here an attempt is made to utilise both the strong fluoride ion donor abilities of xenon difluoride together with its powerful oxidising potential as a fluor-

inating agent. No reports have appeared in the literature in this area apart from an unrelated reaction of xenon difluoride with zinc tetraphenylporphyrin to yield one electron oxidation products.[59]

Some of the reactions described in this thesis are proposed to occur via xenon bonded intermediates and in some cases xenon compounds were hoped for, unfortunately without any positive success.

Another area of great importance and interest to fluorine chemists is the ability of many main group and transition metal fluorides to undergo rapid fluorine exchange processes. The fluorine-19 nucleus, having a spin of ½ and a natural abundance of 100% lends itself to convenient study by the nuclear magnetic resonance (n.m.r.) technique.[60-62] Exchange of nuclei with a nuclear spin can alter in a predictable and calculable manner the observed resonances in a particular spectrum.[60-63] The rates that may be studied are in the range of the frequency separation of the spectral lines in question and may vary considerably (10^{-1}-10^{-5} s^{-1}). For example, rapid exchange of nuclei can lead to collapse of spin-spin multiplets or the loss of magnetic non-equivalence of two or more nuclei giving a time averaged single line.[64,65] Considerable kinetic information can be obtained concerning the exchange of various nuclei from a complete line shape analysis of the observed spectra.[66,67] The effects of chemical exchange may also be artificially induced by, for example, double resonance techniques which are becoming increasingly important for the study of nuclei of low natural abundance.[68]

Two types of exchange are of particular interest to this thesis;

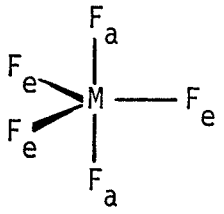
they are, by the names in general usage, inter- and intramolecular fluorine exchange.

Intermolecular exchange is a process that is normally considered to involve a bond breaking step, e.g.

$$M - F \rightleftharpoons M^+ + F^-$$

However the above does not imply that all intermolecular exchange processes are dissociative ionisation steps ; on the contrary, evidence in many cases points to other mechanisms.

A second type of exchange which has been, and still is, the subject of considerable controversy is the permutational or site exchange of ligands called intramolecular exchange. For example, in the trigonal bipyramidal MF_5 molecule shown below this would mean that the non-equivalent fluorines F_a and F_e, as shown, would be exchanging sites <u>without</u> a bond breaking (M - F) step occurring.



All fluorines equivalent by ^{19}F n.m.r.

Both inter- and intramolecular exchange will be looked at much more fully, with suitable references, in chapter 5. However it is worth adding here that nuclear magnetic resonance may be used to dest ingu-

ish easily between inter- and intramolecular exchange where the central atom M has a convenient spin. Intermolecular exchange will result in loss of spin-spin coupling between M and F while intramolecular exchange will retain such a coupling.

It seems appropriate at this stage to review briefly the types of exchange in main group fluorides that have been encountered and studied by the dynamic n.m.r. technique. The interpretations listed below represent the current state of the art; some simplification has been indulged in in an effort to convey in a concise manner the wide range of studies that have been reported in the literature.

Examples of fluorine exchange observed on the n.m.r. time scale.

Group No.	Element	System or Compound	Type of Exchange	Ref.
III	B	BF_4^-	no exchange	69
	Al	H_2O/AlF_4^-		70
		H_2O/AlF_2^+ etc.	intermolecular	
IV	C	C-F	no exchange kinetically very stable bond	
	Si	Me_3SiF/SbF_5	intermolecular (via bridged intermediates?)	71
		SiF_5^-	inter- and intramolecular	72
		$RSiF_4^-$	inter- and intramolecular	72
	Sn	Me_3SnF	polymeric or ionic	73

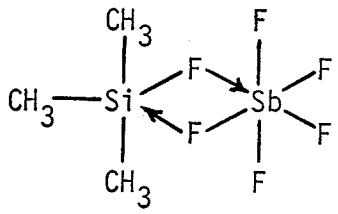
V	N	NF_3	no exchange	74
		FNO_2	no exchange	75
	P	PF_5	intramolecular	74, 76
		RPF_4	intramolecular	77
		R_4PF	intermolecular (ionic?)	78, 79
	As	$C_6H_5AsF_4$	inter- and/or intramolecular	78
	Sb	SbF_5	intermolecular via bridged polymeric intermediates	80, 81, 82
	Bi	$(C_6H_5)_3BiF_2$	no exchange or inter- and/or intramolecular?	78
VI	O	R_f-O-F	no exchange	83
	S	SF_4	intra- and/or intermolecular (impurity catalysed)	84,74, 85,87
		RSF_3	intra- and/or intermolecular (impurity catalysed)	87,86, 88,89
	Se	R_2SeF_2	intermolecular dissociative (impurity catalysed)	90
		SeF_4	associative intermolecular?	74
	Te	TeF_4	rapid exchange	74
VII	Cl	ClF_3	inter- and/or intramolecular, impurity catalysed	91
		ClF_5	no exchange, AB_4 spectrum	92

	Br	BrF_3	rapid, intramolecular?	93
		BrF_5	no exchange, AB_4 spectrum	91, 93
	I	IF_5	at high temp. inter- and/or intramolecular, impurity catalysed	66, 74
VIII	Xe	XeF_2/HF	intermolecular (dissociative ionic?)	94
		XeF_4/HF	no exchange	94
		XeF_6/HF	rapid intermolecular	94

During the course of the investigations of the reactions of xenon difluoride with organosilicon compounds, it was accidentally discovered that when untreated commercial diethylamine was added to a solution of trimethylfluorosilane in acetonitrile, then rapid exchange of fluorine took place leading to collapse of the spin-spin proton doublet. This thesis presents a kinetic investigation of this phenomenon proving that fluorine exchange of this type is due to an intermolecular hydrolysis mechanism, traces of water being sufficient to cause rapid exchange of fluorine in the presence of a suitable base. This study forms part of a continuing interest by this laboratory into the mechanisms of inter- and intramolecular exchange in a number of main group fluorides.[87–89]

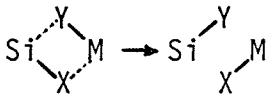
Only one instance has been reported in the literature concerning the collapse of the proton doublet of trimethylfluorosilane, (except for one implied occurrence: see Ref.68). Olah and co-workers,[71] in an

attempt to extend their vast work on carbonium ions, studied the ^{1}H and ^{19}F n.m.r. spectra of trimethylfluorosilane in SbF_5/SO_2ClF solutions. Collapse of the spin-spin doublet in the ^{1}H spectrum was observed but no evidence was found for trimethylsilicenium ions. The authors concluded that exchange might result from the formation of a transient fluorine bridged complex.



However the reactions, and in particular the hydrolyses, of organosilicon compounds have received considerable attention in the literature. Excellent reference books have been written on the reactions of organosilicon compounds by Eaborn[95], Ebsworth[96], and Sommer.[97] Sommer in particular has studied the mechanisms of reactions of many organosilicon compounds and his work on optically active derivatives is exemplary[98,99]. To attempt to give even a concise account of this work would be beyond the scope of this thesis, however some points are of considerable general importance and will be mentioned here.

The notation first devised and used by Sommer for organosilicon reaction pathways will be used throughout this thesis, briefly this is as follows:

Notation	Stereochemistry and Description	
S_N1 - Si	Racemisation, ionisation	$Si\text{-}X \longrightarrow Si^+ X^-$
S_N2 - Si	Inversion, substitution	$Y^- + Si\text{-}X \rightarrow Y\text{-}Si + X^-$
S_Ni - Si	Retention, four centre	
S_N2^* - Si	Racemisation, formation of 5 coord. intermediate	$R_3SiX + Y^- \rightarrow$ fast $R_3S\bar{i}XY$ $R_3S\bar{i}XY \rightarrow$ slow $R_3SiY + X^-$
S_N2^{**} - Si	Inversion, formation of 5 coord. intermediate	$R_3SiX + Y^- \rightarrow$ slow $R_3S\bar{i}XY$ $R_3S\bar{i}XY \rightarrow$ fast $R_3SiY + X^-$

The hydrolysis of organosilicon halides is rapid compared with their carbon analogues ; this has been attributed to the availability of empty d orbitals on silicon participating in substitution transition states and/or formation of five coordinate intermediates.

sp^3 ⟶ sp^3d

4 coordinate, tetrahedral ⟶ 5 coordinate, trigonal bipyr.

Although hydrolysis of optically active organosilicon chlorides has been studied there have been no similar studies of the hydrolysis of organosilicon fluorides. Hydrolysis of the chlorides goes by a predominantly S_N2 - Si mechanism giving inversion of configuration. The S_N2 - Si mechanism is common for many organosilicon chloride

displacement reactions.

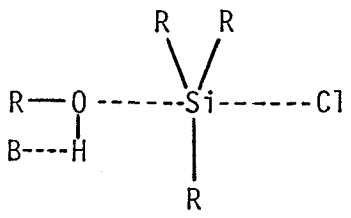
e.g.

$$R_3Si^*Cl + MeOH \xrightarrow[\text{pentane}]{C_6H_{11}NH_2} R_3Si^*OMe \quad 90\% \text{ inversion}$$

Chlorides have been shown to racemise rapidly in polar media such as acetonitrile, nitromethane and nitrobenzene. This was assumed in 1965 to be an S_N1 - Si ionisation racemisation. Racemisations of similar fluorosilanes are very slow.[97] However fluorosilanes do racemise in pentane solution in the presence of methanol, this is assumed to be an S_N2^* - Si "expanded octet return" mechanism.[100] Reactions of fluorosilanes have also been shown in many instances to occur via S_Ni - Si mechanisms.

Many studies have been made of the hydrolysis and alcoholysis of non-optically active chlorosilanes by a variety of workers.[101—105] The hydrolyses are generally rapid and are characterised by unusually high kinetic orders with respect to water; similar alcoholysis reactions have also shown very high orders with respect to alcohol concentration.

Transition states shown below have been suggested by most authors where B is <u>any</u> nucleophile capable of assisting proton removal (e.g. $(H_2O)_n$, ROH, etc.).



Studies on organosilicon fluoride hydrolyses are less frequent in the literature. However an early study[106] did indicate a high order with respect to water and a powerful catalytic effect by base. Szmant studied the hydrolytic condensation of triphenylfluorosilane to hexaphenyldisiloxane and noticed that the reaction was rapid in the presence of sodium hydroxide.[107] It was realised that fluorosilane hydrolysis yielded an equilibrium system.[97]

$$R_3SiF + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R_3SiOH + HF$$

$$K_{eq} = \frac{[R_3SiOH][HF]}{[R_3SiF][H_2O]} \sim 10^{-2} \text{ to } 10^{-4}$$

Sommer did not study any base catalysed hydrolyses of fluorosilanes and concluded that k_f was rather small, ~ 0.05 min^{-1}. The order with respect to water was not determined accurately but was ~ 1.3 over a very narrow water concentration range. No work has been carried out on the hydrolysis of optically active fluorosilanes so

a comparison with the well established inversion reaction for chlorosilane hydrolysis cannot be made.

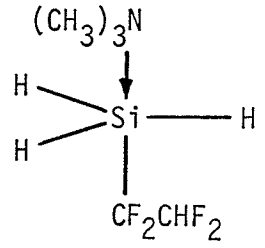
In recent years the hydrolysis of organosilicon fluorides has been studied almost exclusively by the Japanese group of Ishikawa. In a series of publications the base catalysed hydrolysis of a wide range of fluorosilanes have been reported.[108–113] However the rate of silanol formation was not of prime interest; the formation of siloxanes and polysiloxanes by the condensation of intermediate silanols was the main result of their researches.

$$R_3SiOH + R_3SiOH \longrightarrow R_3SiOSiR_3 + H_2O$$

No dynamic n.m.r. studies are reported in any of the articles although exchange of the type to be discussed in this thesis must have been occurring in many of the systems studied.

Despite Sommer's early reservations[97] the evidence for "stable" five (or six) coordinate intermediates has been growing in recent years. In a 1969 paper on the racemisation of optically active fluorosilanes there is good evidence for the formation of a five coordinate intermediate,[100] (rather than a simple five coordinate <u>transition</u> state). Six coordinate transition states have been postulated for the racemisation of chlorosilanes[114] while six coordinate silicon tetrafluoride adducts have been known for some time.[115,116] A bridgehead silicon compound containing a nitrogen atom in the ring has been suggested to be five coordinate.[117] There is n.m.r. evidence that trimethylamine forms a

trigonal bipyramidal adduct with the compound $H_3SiCF_2CHF_2$ [118]



However, of interest to the final section of this thesis is the work of Muetterties and Klanberg on the formation of stable five coordinate fluorosilicates.[72] Several of the compounds described were resynthesised and the exchange processes discussed by Muetterties were re-examined in the light of the work completed on the trimethylfluorosilane exchange reactions. Evidence is presented that intermolecular exchange in the SiF_5^- ion is a hydrolysis process while the rapid intramolecular exchange is discussed in view of some experimental results on the intramolecular exchange of phosphorus pentafluoride dissolved in diethylether.

The work was undertaken in view of the results found by D.G.Ibbott of this laboratory on the effects of traces of water on the ^{19}F n.m.r. spectra of sulphur fluorides.[87-89] The barriers to inter- and/or intramolecular exchange in these species were found to be much higher than previously reported when examined under rigourously anhydrous conditions. The possibility that this observation may

be more general was considered and is a basis for much of the work reported here.

The organisation of the thesis thus falls conveniently into two sections. The first half describes the work with xenon difluoride. The aims of the research were to demonstrate the selectivity of xenon difluoride as a fluorinating agent towards organometallic compounds, particularly where such compounds are good fluoride acceptors (Lewis acids). To understand the reactions more fully kinetic investigations were undertaken and are reported in the appropriate sub-sections.

The second half of the thesis reports on n.m.r. studies of fluorine exchange. The aims of the research were to show that the dynamic n.m.r. method may be utilised to derive rate expressions in an analogous manner to other rapid reaction techniques. The second aim was to demonstrate that traces of water commonly present in many systems may, under suitable conditions, lead to rapid inter- and/or intramolecular fluorine exchange.

CHAPTER 2

REACTIONS OF XENON DIFLUORIDE - EXPERIMENTAL

2.1 GENERAL

CAUTION. Xenon compounds have been found in many cases to be explosive.[49,119] Hydrolysis of the fluorides (except absolutely pure XeF_2) may lead to the formation of highly dangerous shock sensitive xenon oxides. During the course of this work detonations occurred, particularly during the reaction of xenon difluoride with silicon-nitrogen derivatives. The following safety precautions were taken at all times:

(a) Small reaction quantities of xenon difluoride were used in solution in acetonitrile where possible. (This was also desirable due to the high cost of producing or purchasing xenon difluoride.)

(b) Asbestos gloves were used to handle all pieces of apparatus; all reactions were carried out behind plexiglass or safety glass shielding. Reactions monitored by n.m.r. spectroscopy were carried out at least once beforehand in the laboratory to ensure they were safe.

(c) Glassware that had been exposed to xenon difluoride was washed with dilute alkali and the residues were rinsed well and disposed of.

Fluorine and powerful fluorinating agents were handled in a monel vacuum line. The design and operation of this line may be found elsewhere.[120] All monel equipment was prefluorinated by the following

technique,

(a) washing with acetone followed by dichloroethylene to ensure complete removal of organic materials,

(b) pumping out to $\sim 10^{-4}$ mm. at 300-400°,

(c) gradual fluorination by gaseous fluorine, (20°, 50 mm. F_2 to begin; 200°, 2 atm. F_2 to finish).

All glassware used throughout (except for e.s.r. studies) was pyrex; drying was thorough and, where indicated, silylation was carried out prior to introduction of reactants. Most of the compounds described are air and moisture sensitive, conventional vacuum line techniques were used at all times. Where possible, manual transfers were made under a dry nitrogen atmosphere. Analyses were performed by the Dr. Alfred Bernhard Mikroanalytisches Laboratorium, Elbach, W. Germany.

2.2 INSTRUMENTAL

Nuclear magnetic resonance spectra were recorded on a Varian A 56/60 instrument using 60 Mc/s and 56.4 Mc/s for proton and fluorine respectively. Reference sidebands for fluorine spectra were generated by a Hewlet Packard model 200 CD wide range oscillator coupled to a Hewlet Packard model 521 C electronic counter. Fluorine chemical shifts are reported relative to internal $CFCl_3$ where possible. Internal tetramethylsilane was not used for proton spectra since many organosilicon compounds absorb in this region. The chemical shifts in p.p.m. (downfield shift -ve) were recorded using the following definition:

$$\delta = \delta_{(\text{relative to } CH_3CN)} - 2.00$$

A dilute solution of tetramethylsilane in acetonitrile gave the chemical shift of acetonitrile as exactly - 2.00 p.p.m.

Infra red spectra were recorded on a Perkin Elmer 337 Grating Spectrophotometer, spectra were calibrated against polystyrene film. The infra red spectra of volatile reactive fluorine containing compounds (e.g. XeF_2) were recorded using a monel cell fitted with silver chloride windows. The design of the cell is shown in figure [1].

Mass spectra were run on a Hitachi RMU 6D instrument or on a Finnigan 1015. Vapour phase chromatography was carried out on a Varian Aerograph 90P instrument or on a Varian Series 1700 unit. Combined V.P.C./M.S. were run on the Varian 1700 coupled to the Finnigan 1015.

Electron spin resonance investigations were carried out on a Varian E-3 E.P.R. instrument with dewar attachments. Ultra violet spectra were recorded on a Unicam SP 600B spectrophotometer.

2.3 CHEMICALS

Trimethylchlorosilane, triethylchlorosilane, dimethyldichlorosilane, phenylmethylchlorosilane, allyldimethylchlorosilane, triphenylsilane, allyltrimethylsilane, hexamethyldisiloxane, hexachlorodisilane and hexaphenyldisilane were all obtained from Penninsular Chem. Research, their purities were checked by n.m.r. and they were used without

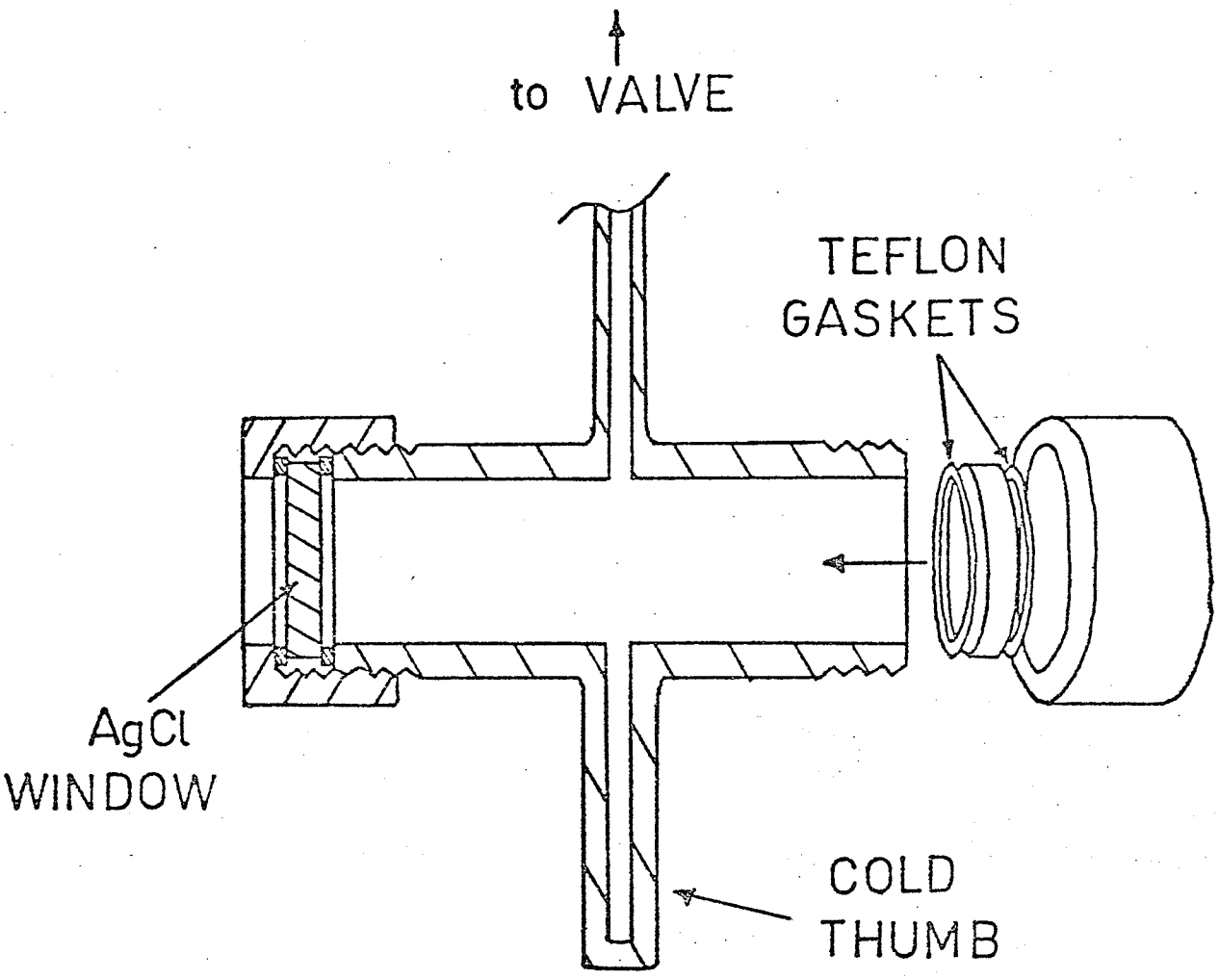


Figure [1]. Monel Infra Red Cell

further treatment. Diethylaminotrimethylsilane (P.C.R.) was found to be particularly sensitive to exposure even to dry air, only fresh bottles were used, redistillation did not appear to improve the quality.

Diethoxydimethylsilane (Alfa Inorganics) was redistilled prior to use to remove traces of polysiloxanes, similarly phenylmethylchlorosilane (Aldrich Chemicals) was redistilled to remove what were probably siloxane polymers. Trimethylgermanium bromide (Alfa Inorganics) was used without further purification. Hexamethyldisilazane (Alfa Inorganics) was redistilled before use as a reactant; crude hexamethyldisilazane was used as a silylating agent. Di-tert-butyldisulphide (P.C.R.) was obtained for comparison purposes and was not purified further.

Trimethylfluorosilane, dimethyldifluorosilane and methyltrifluorosilane (P.C.R.) were gaseous samples and were redistilled in the vacuum manifold before use.

For some of the reactions described commercial xenon difluoride (P.C.R.) was used. Purity by i.r., n.m.r. and mass spectrometry was identical to xenon difluoride synthesised in the laboratory.

Triphenylphosphine (Matheson, Coleman, Bell) was used from a freshly opened bottle, diphenylchlorophosphine and phenyldichlorophosphine (M.C.B.) were used without further purification.

Acetonitrile (99% Fisher certified grade) was refluxed for 5 hours over phosphorus pentoxide and then distilled onto fresh phosphorus pentoxide for storage in the vacuum manifold. Tetrahydrofuran was

refluxed over lithium tetrahydroaluminate for 12 hours and redistilled prior to use. Hexafluoroacetone (Matheson Canada) was redistilled at low temperature prior to use to remove traces of the hydrate. Methyl iodide (Eastman Ltd.) was redistilled and checked by n.m.r. and mass spectrometry.

Xenon (Canadian Liquid Air, 99.9%) was used as received. Fluorine (Matheson Canada) was purged of hydrogen fluoride by passage over dry potassium fluoride and handled in the monel vacuum line.

Trimethylsilane was prepared by the treatment of trimethylchlorosilane by lithium tetrahydroaluminate in dioxane[121]. The mixture was allowed to reflux gently and trimethylsilane, which distilled through a cold water reflux condenser, was collected in a trap held at -78°. Yields were ~60%. The product was purified by repeated distillation until the n.m.r. spectrum showed no spurious peaks, the purity was also checked by mass spectrometry.

Tert-butylthiotrimethylsilane was kindly supplied by Dr.O.C.Vaidya, the compound was checked to be free of tert-butylthiol.

Dimethylaminotrimethylsilane was prepared by treating trimethylchlorosilane with a 1:2 excess of dimethylamine in xylene[122]. The ratio of reactants was critical to the formation of the correct product in good yield. The crude product was redistilled to remove all traces of xylene, however a trace of gelatinous white precipitate always formed in the distillate. Repeating the reaction omitting the solvent gave an identical product. The proton n.m.r. spectrum showed only 2 peaks

with a relative intensity of 2:3. Di-isopropylaminotrimethylsilane was prepared in an analogous manner, even more difficulty was experienced in obtaining a pure product since it appeared that an equilibrium system was established rather than the reaction going to completion.

2.4 EXPERIMENTAL DETAILS

Synthesis of Xenon Difluoride

Xenon difluoride was prepared according to the method of Holloway[6] by exposing mixtures of xenon and fluorine to ultra violet irradiation or sunlight. This method is entirely satisfactory for the synthesis of xenon difluoride provided an excess of xenon is used.[6,4 6] Typically xenon was condensed into a 1 litre pyrex flask (prefluorinated for 24 hours and evacuated to 10^{-5} mm at 150-200^{o}) through a cold trap held at -78^{o} to remove any possible traces of moisture. The quantity of xenon was calculated to produce approximately 500 mm when the flask was warmed to room temperature. Fluorine was metered into the flask by pressure drop from a known volume to give a partial pressure of approximately 400 mm. The flask was sealed by an autoclave valve attached via a glass to metal seal.

The mixture of fluorine and xenon was exposed to ultra violet irradiation from a Hanovia mercury lamp while one side of the flask was cooled with a draught of air. Colourless crystals of xenon difluor-

ide were observed to condense on the cooled portion of the flask within 3 to 4 hours, the reaction was essentially complete after 4 days. Alternatively, exposure of a mixture of xenon and fluorine to sunlight led to observable formation of crystals within 2 days, the reaction appeared complete after approximately 2 weeks.

The product was pumped out of the reaction vessel through a further thoroughly dried and prefluorinated pyrex vessel held at -22^{o} which allowed passage of excess xenon and traces of impurities such as silicon tetrafluoride but held back the pure sublimed xenon difluoride. Acetonitrile was vacuum distilled onto the xenon difluoride and the mixture was allowed to warm to room temperature when the xenon difluoride dissolved to give a clear colourless solution. The solution was stored under vacuum at -78^{o} and appeared stable indefinitely at this temperature.

^{19}F n.m.r. examination of the solution at $+38^{o}$ showed a singlet at δ = +175.3 p.p.m. with two satellites due to splitting with ^{129}Xe ($S = \frac{1}{2}$, natural abundance = 26.44%); $J_{F-^{129}Xe}$ = 5575 Hz. The spectrum compared quite well with literature values[94,123,124]. The stability of xenon difluoride in acetonitrile solution was examined at room temperature in a plastic capped n.m.r. tube. The concentration of xenon difluoride as monitored by ^{19}F n.m.r. spectroscopy as a function of time is shown in figure [2]. The solution slowly turned brown and traces of solid material were observed in the bottom of the tube after standing 3 weeks.

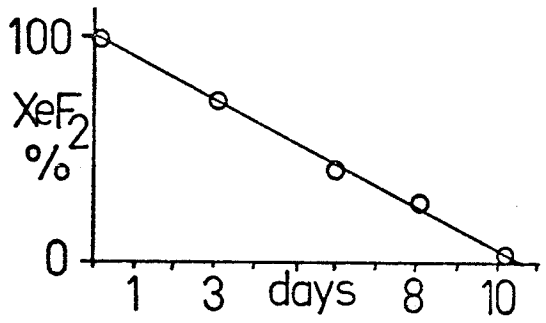


Figure [2]. Stability of Xenon Difluoride in Acetonitrile at ~+20°

After the concentration of xenon difluoride had decreased to zero (10 days) a ^{19}F n.m.r. search was made. No fluorine containing products could be found. The proton n.m.r. spectrum showed, apart from acetonitrile, a weak singlet at -2.4 p.p.m. and several other very weak absorptions in the same region. A solution of hydrogen fluoride in acetonitrile showed a similar singlet at -2.4 p.p.m. and no ^{19}F n.m.r. resonance could be found.

A infra red examination of the decomposed solution showed broad bands above 3000 cm^{-1} but only very weak bands from 1000-1200 cm^{-1}. The rest of the infra red spectrum indicated the bulk of the acetonitrile to be unchanged.

The stability of xenon difluoride in acetonitrile was considerably enhanced if a thoroughly dry, flame sealed, n.m.r. tube was used or if small quantities of cesium fluoride were added to the tube. However, such a procedure was unnecessary since the solutions were always stored at low temperature.

A vapour phase infra red spectrum of xenon difluoride was obtained using the monel cell shown in figure[1]. The doublet band[125] at 552 and 568 cm^{-1} was clearly visible, consistent with previous work; no bands were found corresponding to XeF_4, XeF_6 or $XeOF_4$.

A final check on the purity of the xenon difluoride was made by mass spectrometry. Attempts to obtain mass spectra from crystalline xenon difluoride were unsuccessful, presumably due its relatively high volatility (hence rapid pumping away) or its reactivity in the solid state towards the mass spectrometer materials. However good mass spectra were obtained by injecting solutions of xenon difluoride in acetonitrile into the mass spectrometer as a "liquid" sample. Apart from peaks due to acetonitrile, $XeF_2^{\cdot+}$, XeF^+, $Xe^{\cdot+}$ and Xe^{++} were all visible; they are tabulated below. Xenon containing fragments are readily identifiable by their characteristic isotope pattern.

m/e	Relative Intensity	Assignment
166-174 Xe pattern	7	XeF_2
147-155 Xe pattern	10	XeF
128-136 Xe pattern	100	Xe
64-68 Xe pattern	20	Xe

All the reactions described in the following sections involving

xenon difluoride/acetonitrile solutions were either carried out using freshly prepared solutions or solutions stored at -78°. The concentrations were conveniently determined by allowing a known aliquot to react with mercury and weighing the xenon produced. The molarities determined by this method were estimated to be accurate to ±5%.

Reaction of Trimethylchlorosilane with Xenon Difluoride

Trimethylchlorosilane (80 mg, 0.74 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.15 mmoles XeF_2) at -10°. As the solution was allowed to warm to +38° in the sample probe of the n.m.r. spectrometer the solution turned light brown and a gas was given off. Examination of the ^{19}F n.m.r. spectrum revealed that all the xenon difluoride reacted within 3 minutes. An n.m.r. search revealed a dectet at +156.1 p.p.m., J_{F-H} = 7.5 Hz, consistent with the formation of trimethylfluorosilane. The chemical shift compared well with tabulated values.[96,72,126] The yield was estimated to be 100% based on xenon difluoride starting material. The proton spectrum revealed a doublet at -0.26 p.p.m., J_{H-F} = 7.5 Hz, and excess trimethylchlorosilane.

The pale brown colour of the solution was discharged upon addition of olefins such as styrene or cyclohexene. Peaks appeared in the ^1H n.m.r. spectrum consistent with chlorination of the olefins.

The reaction was repeated on a larger scale to improve the

estimation of the yield of trimethylfluorosilane. Trimethylchlorosilane (1.0 g, 9.2 mmoles) was added to a solution of xenon difluoride in acetonitrile (3.5 ml, 4.1 mmoles XeF_2) at -20^{o}. The reaction flask was kept cooled by an ice bath as the reaction proceeded to completion. Volatile fractions were separated, xenon was identified by mass spectrometry, chlorine by its bleaching action on litmus paper and precipitation of silver chloride from aqueous silver nitrate. The trimethylfluorosilane was separated out after several careful distillations on the vacuum line, the yield was 0.72 g, 7.9 mmoles, i.e. 96% based on XeF_2.

An improved method was sought for the detection of chlorine produced during the reaction. It was found that ultra violet spectroscopy was a convenient method of monitoring the production of chlorine. A solution of chlorine (~50 mg in 1 ml) in acetonitrile showed a strong band at 315-320 nm.[127]

The reaction of xenon difluoride with trimethylchlorosilane was studied as follows. A divided u.v. cell was used with two 4.375 mm path length compartments. The teflon cell cap was drilled (0.5 mm) to allow escape of xenon during the course of the reaction. The two reactants were introduced to the compartments and reaction was initiated by quickly inverting the cell. The reaction was moderated by prior cooling of the cell in an ice bath. Sweeps of appropriate regions of the u.v. spectrum were taken every 20-30 seconds.

Two runs were made with a 2:1 and a 20:1 $(CH_3)_3SiCl/XeF_2$ mole

ratio. The results of these experiments will be discussed later. In a separate experiment using ^{19}F n.m.r. spectroscopy it was found that a large excess of trimethylchlorosilane had no deleterious effect on the yield of trimethylfluorosilane, the ^{1}H spectrum indicated some production of chloromethyldimethylchlorosilane (see later).

Kinetics of the Reaction of Xenon Difluoride with Trimethylchlorosilane

Any proposed reaction scheme for the interaction of xenon difluoride with organosilicon chlorides must be consistent with experimentally derivable kinetics. The reaction with trimethylchlorosilane was chosen for study.

The technique outlined below was used to determine the order of the reaction with respect to trimethylchlorosilane and xenon difluoride.

As mentioned previously the xenon difluoride central ^{19}F resonance was a convenient method of following the reactions described in this thesis. The order with respect to xenon difluoride could be determined by having a fixed large excess of chlorosilane and varying the xenon difluoride concentration to see if a pseudo-first order rate plot could be obtained. Similarly, by using a large excess of xenon difluoride and varying the concentration of chlorosilane, it would be possible to obtain the order of the reaction with respect to that reagent. However, immediate experimental difficulties arise, a large excess of xenon difluoride is not possible since the solubility in

acetonitrile is limited. Very small quantities of chlorosilane could not be used because only very small changes in xenon difluoride ^{19}F integration would occur leading to large random errors. A large excess of chlorosilane is feasible but the range over which the xenon difluoride concentration could be varied is limited; in addition, in the presence of a large excess of chlorosilane, the chlorosilane is becoming the solvent rather than acetonitrile, with unknown effects on the reaction rate.

For the reasons outlined above the following technique was used. If a reaction is first order in reagent A and first order in reagent B and the overall stoichiometry is,

$$A + 2B \longrightarrow \text{products}$$

it is possible to show* that:

$$kt = \frac{1}{(B_o - 2A_o)} \cdot \ln \frac{A_o B}{B_o A}$$

where B_o = initial concentration of B

B = concentration of B after time t

A_o = initial concentration of A

A = concentration of A after time t

This then is a good test for the reaction:

* See Appendix I.

$$XeF_2 + 2(CH_3)_3SiCl \longrightarrow Cl_2 + Xe + 2(CH_3)_3SiF$$

where $XeF_2 \equiv A$

and $(CH_3)_3SiCl \equiv B$

If there is no specific interest in the rate constant k then the term $\frac{1}{(B_o - 2A_o)}$ may be gathered up so:

$$C \cdot t = \ln \frac{A_o B}{B_o A}$$

$\left(\frac{1}{B_o - 2A_o} \text{ is a constant for any given experiment.} \right)$

Similarly it is not necessary to work with A and B in terms of moles per litre. The concentration of xenon difluoride, A, can be represented by the peak area of the central resonance in the ^{19}F n.m.r. spectrum of XeF_2. This is perfectly satisfactory for determining A_o and values of A during the reaction, but what of the concentration of chlorosilane, B ?

The following method of assigning a value for B was used. After the reaction had gone to completion the ratio of the initial chlorosilane concentration to final fluorosilane concentration was determined by careful and repeated integration of the ^1H n.m.r. spectrum.

$$\frac{[(CH_3)_3SiF]_{final}}{[(CH_3)_3SiCl]_{initial}} = \Gamma$$

$$\left(\text{using } [(CH_3)_3SiCl]_{initial} = [(CH_3)_3SiF]_{final} + [(CH_3)_3SiCl]_{final}\right)$$

Γ is a number without units, i.e. it is not important to know $[(CH_3)_3SiF]$ or $[(CH_3)_3SiCl]$ in moles/litre.

Now:

$$[(CH_3)_3SiF]_{final} = 2[XeF_2]_{initial}$$

But $[XeF_2]$ is represented by a number A_o, therefore $[(CH_3)_3SiCl]_{initial}$ may be represented by a number $= \frac{2 \cdot A_o}{\Gamma}$,

$$\text{i.e.} \quad B_o = \frac{2 \cdot A_o}{\Gamma}$$

That is, knowing Γ and A_o, it is possible to assign a number, B_o, directly proportioned to the initial concentration of chlorosilane. Similarly, during the reaction at time t,

$$B = B_o - 2(A_o - A)$$

Hence knowing A, B_o and A_o one may calculate a number for B which is directly proportional to the concentration of chlorosilane at time t.

The trimethylchlorosilane was added using a dry syringe to a

solution of xenon difluoride at -5^{o} in an n.m.r. tube, shaken, and quickly inserted into the n.m.r. probe at 0^{o}. An integration of the XeF_2 resonance was immediately taken before significant reaction occurred. Integrations were then taken at one (or two) minute intervals as the reaction proceeded.

Figures [3] and [4] show two experiments both run at 0^{o} in the probe of the n.m.r. spectrometer. Run I had an Γ value of 0.50 while Run II had an Γ value of 0.75. Plots of $\ln \frac{A_o B}{B_o A}$ versus time showed straight lines through the origin, within experimental error. This confirms that the reaction of xenon difluoride with trimethylchlorosilane is first order with respect to both the reactants. The decay of XeF_2 central resonance is also shown in figures [3] and [4].

Of added interest is that, during the course of these smooth reactions carried out in the dark at 0^{o} in the n.m.r. probe, significant yields of chloromethyldimethylfluorosilane and chloromethyldimethylchlorosilane were given. The chloromethyl derivatives were readily recognised in the ^{1}H spectrum by the characteristic downfield shift of the methylene protons on the CH_2Cl group (-2.98 p.p.m. for $\underline{CH}_2Cl(CH_3)_2SiF$, -3.06 p.p.m. for $\underline{CH}_2Cl(CH_3)_2SiCl$). The yields never exceeded ~5% but were taken into account in the calculation of Γ. Reactions run at room temperature showed little or no chloromethylsilane derivatives.

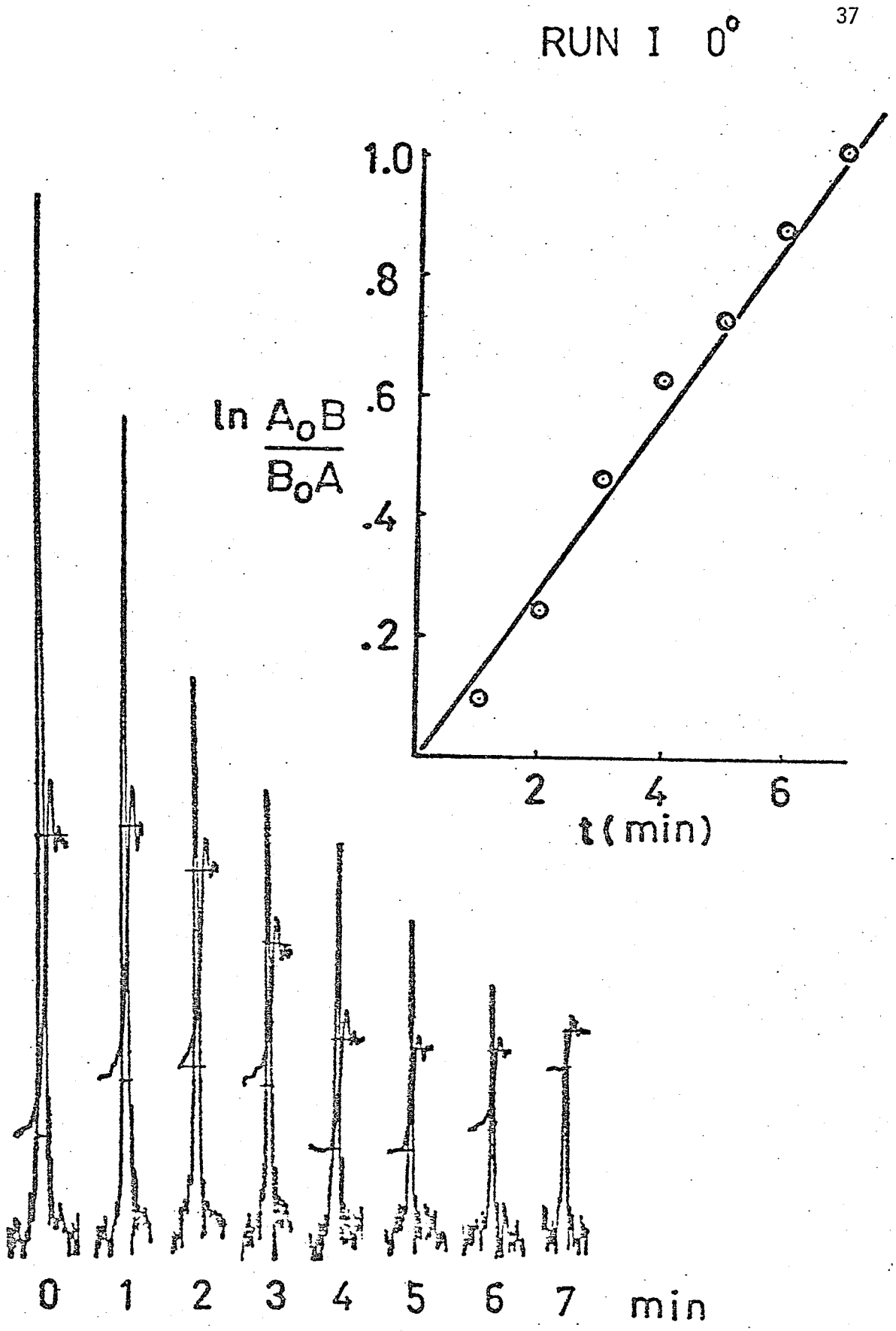


Figure [3]. Reaction of XeF_2 with Trimethylchlorosilane, Kinetic Study

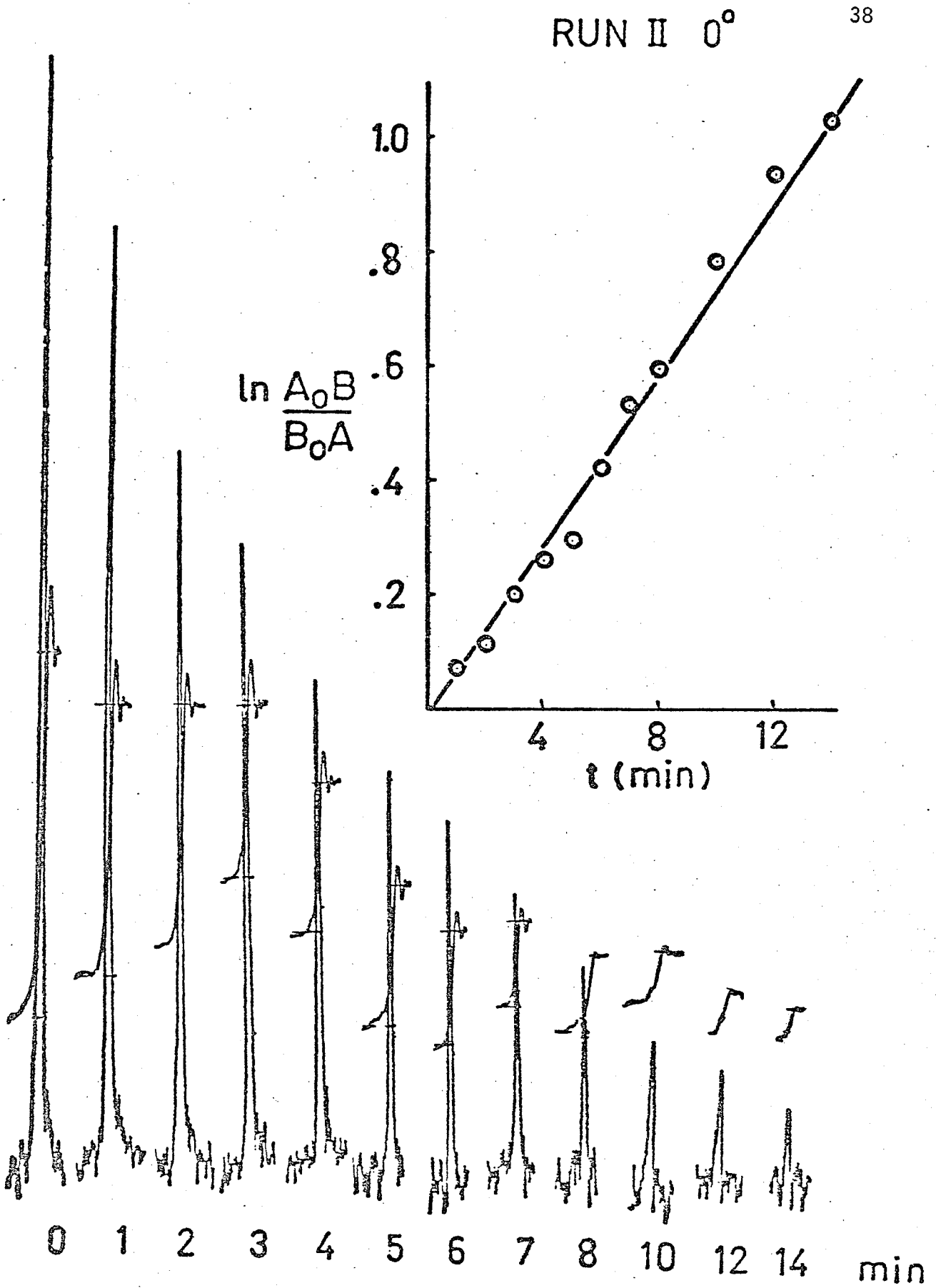


Figure [4]. Reaction of XeF_2 with Trimethylchlorosilane, Kinetic Study

Reaction of Dimethyldichlorosilane with Xenon Difluoride

Dimethyldichlorosilane (16 mg, 0.13 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.15 mmoles XeF_2) at -10^o. As the mixture was allowed to warm to $+38^o$ in the sample probe of the n.m.r. spectrometer the solution turned light brown and a gas was evolved. Examination of the ^{19}F n.m.r. spectrum revealed that the reaction was complete within 4 minutes. An n.m.r. search revealed a septet at +130.4 p.p.m., J_{F-H} = 6.5 Hz, consistent with the formation of dimethyldifluorosilane. The chemical shift compared well with tabulated values.[126,72,96] The yield was approximately 70% based on xenon difluoride starting material. The proton spectrum revealed a triplet at -0.37 p.p.m., J_{H-F} = 6.5 Hz.

A second product present in approximately 30% yield was observed in the ^{19}F n.m.r. spectrum at +138.2 p.p.m. The signal appeared to be a quartet of triplets and was assigned to the compound chloromethylmethyldifluorosilane $(CH_2Cl)CH_3SiF_2$. (This was confirmed in the following experiment, see figure [5]). The proton spectrum revealed a poorly resolved triplet at -0.54 p.p.m., $(CH_2Cl)\underline{CH}_3SiF_2$, and a barely resolved triplet downfield at -2.9 p.p.m., $(\underline{CH}_2Cl)CH_3SiF_2$.

Using excess of dimethyldichlorosilane led to little change in the dimethyldifluorosilane yield although a third product appeared in the ^{19}F n.m.r. spectrum at +136.4 p.p.m. The yield was always low (<5%) and, because it was a septet, was assigned to dimethylchlorofluorosilane, $(CH_3)_2SiClF$.

Chlorination of Dimethyldifluorosilane

A. Since no data are available in the literature on the nuclear magnetic resonance spectra of chloromethylfluorosilanes, it was decided to chlorinate an authentic sample of dimethyldifluorosilane to produce chloromethylmethyldifluorosilane. A direct comparison of the ^{19}F n.m.r. spectrum could then be made with the compound produced in the previous experiment.

Into a pyrex tube at -196° was condensed dimethyldifluorosilane (1.97 g, 20.5 mmoles) and chlorine (1.12 g, 15.8 mmoles). The volume of the pyrex vessel was such that a pressure of approximately 3-4 atmospheres of chlorine would develop when warmed to room temperature.

No reaction occurred in the dark, however on exposure to sunlight the greenish colour of the chlorine was slowly discharged. Some tarry products collected on the sides of the tube over a period of two days and the reaction was assumed complete after three days. The products were pumped out on the vacuum line and condensed under vacuum into an n.m.r. tube at -196° and flamed sealed.

^{19}F n.m.r. examination showed unreacted dimethyldifluorosilane and a variety of other products. Of highest yield was a multiplet at +138 p.p.m. assigned to $(CH_2Cl)CH_3SiF_2$. The excess dimethyldifluorosilane was carefully removed on the vacuum line and the residue was dissolved in acetonitrile. The spectrum at +138.2 p.p.m. was identical to that assigned to $(CH_2Cl)CH_3SiF_2$ in the previous experiment. Figure [5] shows a comparison of the two spectra and a first order interpre-

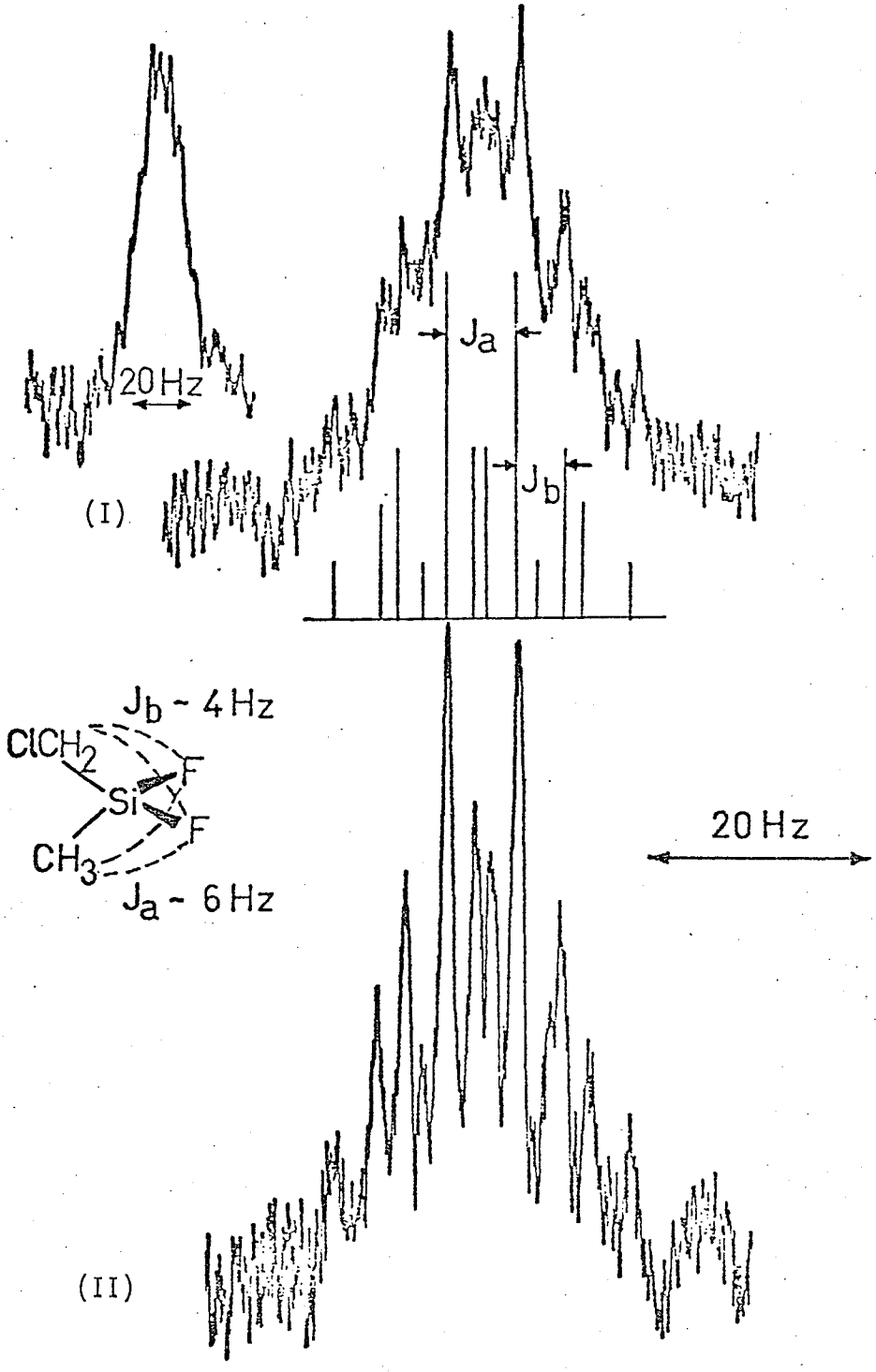


Figure [5]. ^{19}F n.m.r. Spectrum of $(CH_2Cl)CH_3SiF_2$

(I) From $XeF_2 + (CH_3)_2SiCl_2$

(II) From $(CH_3)_2SiF_2 + Cl_2$

tation as a quartet of triplets with coupling constants as indicated.

The proton spectrum revealed a triplet at -0.56 p.p.m. and a triplet at -2.91 p.p.m. with an intensity ratio of 3:2.

Other products identifiable by ^{19}F and ^{1}H n.m.r. were $(CCl_3)CH_3SiF_2$, $(CCl_2H)CH_3SiF_2$ and, surprisingly, some $(CH_3)_2SiFCl$.

B. Into a solution of dimethyldifluorosilane (0.05 g, 0.52 mmoles) in acetonitrile (0.2 ml) was bubbled dry chlorine (estimated to be ~0.5 mmoles). The chlorine dissolved and the solution turned pale brown, examination by u.v. spectroscopy showed the characteristic band due to chlorine at 315 nm. The reaction of chlorine with dimethyldifluorosilane was quite slow and appeared to be light catalysed. On standing for 3 days a small quantity of $(CH_2Cl)CH_3SiF_2$ was produced along with a variety of other products.

Reaction of Triethylchlorosilane with Xenon Difluoride

Triethylchlorosilane (43 mg, 0.29 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.12 mmoles XeF_2) at -10^{o}. As the mixture was allowed to warm to $+38^{o}$ in the sample probe of the n.m.r. spectrometer the solution turned pale brown and a gas was evolved. Examination of the ^{19}F n.m.r. spectrum revealed that all the xenon difluoride had reacted within 9 minutes. An n.m.r. search revealed a multiplet at +175 p.p.m. consistent with formation of triethylfluorosilane. The chemical

shift compares well with tabulated values[96,130]. The yield decreased quite rapidly if the solution was allowed to stand for any length of time, however the initial yield appeared to be ~90% based on xenon difluoride starting material.

The ^{1}H n.m.r. spectrum showed an A_2B_3X pattern in close agreement to that reported by Schmidbaur[130]. A very small amount of excess triethylchlorosilane was also present which has an A_2B_3 spectrum.

Reaction of Dimethylphenylchlorosilane with Xenon Difluoride

Dimethylphenylchlorosilane (49 mg, 0.29 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.12 mmoles XeF_2) at -10^{o}. As the mixture was allowed to warm to $+38^{o}$ in the sample probe of the n.m.r. spectrometer the solution turned very pale brown and a gas was evolved. Examination of the ^{19}F n.m.r. revealed that the reaction was complete after 6 minutes. An n.m.r. search revealed a septet at +159.4 p.p.m., J_{F-H} = 7.5 Hz, consistent with the formation of dimethylphenylfluorosilane. The yield was 50% based on xenon difluoride starting material. The ^{1}H n.m.r. spectrum showed a doublet at -0.5 p.p.m., J_{H-F}= 7.5 Hz, and peaks in the phenyl region.

There was a further unresolved multiplet in the ^{19}F n.m.r. spectrum at +164 p.p.m. corresponding to approximately 25-30% yield. In addition the proton spectrum contained a doublet at -0.67 p.p.m., J_{H-F}= 7 Hz, and a second doublet at -3.28 p.p.m., J_{H-F}= 6.5 Hz. The spectrum is assigned to $(CH_2Cl)CH_3SiF(C_6H_5)$, the low field doublet

in the proton spectrum is assigned to the CH_2Cl- group.

Reaction of Methylphenylchlorosilane with Xenon Difluoride

A. Methylphenylchlorosilane (25 mg, 0.16 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.15 mmoles XeF_2) at -10^{o}. As the mixture was allowed to warm to $+38^{o}$ in the sample probe of the n.m.r. spectrometer a gas was evolved, however the solution stayed almost colourless. Examination of the ^{19}F n.m.r. spectrum revealed that all the xenon difluoride was consumed within 3 minutes. An n.m.r. search revealed a quartet at +136.0 p.p.m., $J_{F-Si-CH_3}$ = 6 Hz; the yield was close to 100% based on xenon difluoride starting material. The ^{1}H n.m.r. spectrum showed a triplet at -0.7 p.p.m., J_{H-F} = 6 Hz and phenyl peaks. The n.m.r. spectra are entirely consistent with the formation of methylphenyldifluorosilane; only an ambiguous reference could be found in the literature to the n.m.r. spectrum of this compound however.[131] A broad singlet at -4.0 p.p.m. in the proton spectrum may be attributed to hydrogen chloride.

B. The reaction was repeated using a 6:1 molar excess of methylphenylchlorosilane. The yield of methylphenyldifluorosilane decreased to approximately 30%, however a second product was now found in the ^{19}F n.m.r. spectrum at +170.8 p.p.m. consisting of a doublet of quartets, J_{F-Si-H} = 58 Hz and $J_{F-Si-CH_3}$ = 8 Hz, consistent with the formation of phenylmethylfluorosilane, $(C_6H_5)CH_3SiF(H)$; the

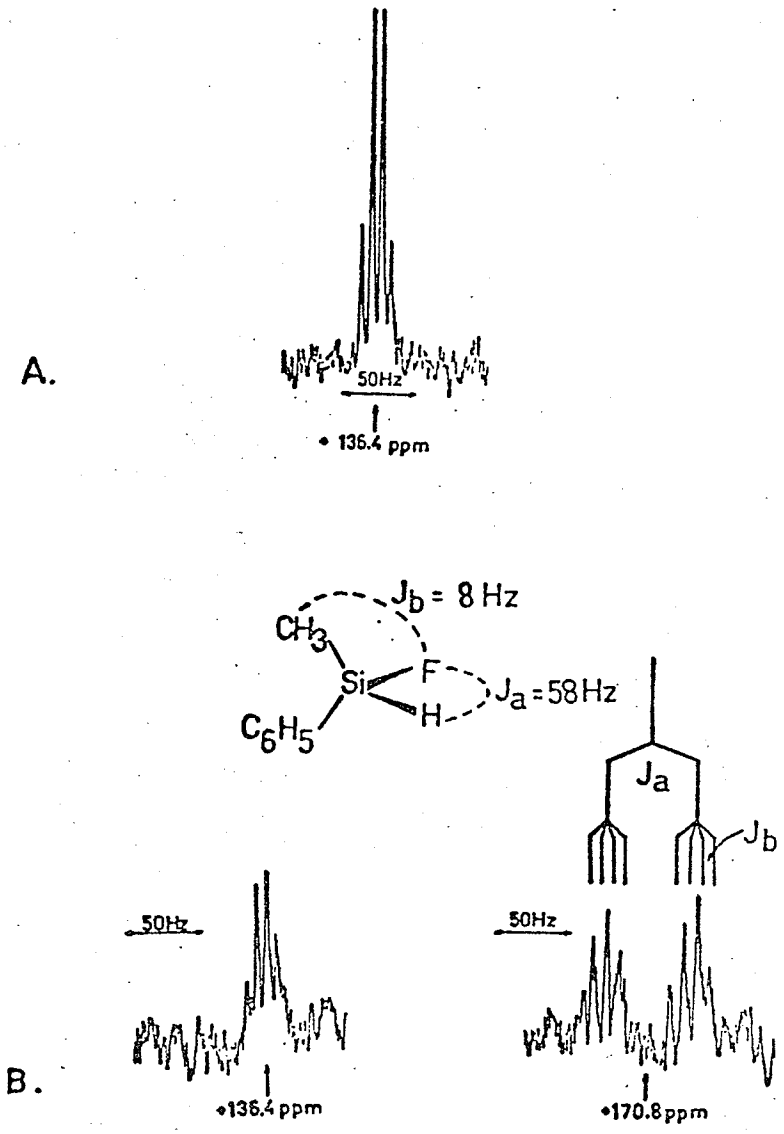


Figure [6]. Products from the Reaction of $(C_6H_5)CH_3Si(H)Cl$ with XeF_2

A. 1:1 molar ratio of reactants

B. 6:1 molar excess of $(C_6H_5)CH_3Si(H)Cl$

yield was approximately 60%. The ^{19}F n.m.r. of experiments A and B are shown in figure [6]. The proton spectrum was unhelpful in experiment B since the CH_3-Si region was now a triplet overlaid by a doublet of doublets and the Si-H region, if resolvable, would be a doublet of quartets. The product was not present in sufficient concentration to detect the proton spectrum, particularly in the Si-H region. Attempts to concentrate the phenylmethylfluorosilane failed due to the very small quantities available.

Reaction of Triphenylchlorosilane with Xenon Difluoride

Triphenylchlorosilane (105 mg, 0.36 mmoles) dissolved in acetonitrile (approx. 0.4 ml) was added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.12 mmoles XeF_2) at -10^o. As the mixture was allowed to warm to $+38^o$ in the sample probe of the n.m.r. spectrometer the solution stayed nearly colourless but a gas was given off. Examination of the ^{19}F n.m.r. spectrum revealed that the reaction was complete after 15 minutes. The products were not simple, an n.m.r. search revealed two singlets, +169.7 p.p.m. (50-60% yield based on XeF_2) and +140 p.p.m. (30% yield). The singlet at +169.7 p.p.m. may have been due to silicon tetrafluoride and that at +140 p.p.m. to phenyltrifluorosilane. The shifts compare reasonably well with values reported elsewhere[72,60]. However,it should be added that examination of the gas phase infra red spectrum of the vapours in equilibrium with the solution failed to reveal any silicon tetrafluoride. The solution

was unstable and the concentrations of the two species decreased quite rapidly with time.

Reaction of Triphenylchloromethane with Xenon Difluoride

Xenon difluoride solution (0.5 ml containing 0.16 mmoles XeF_2) was added to powdered triphenylchloromethane (90 mg, 0.32 mmoles) at room temperature. A rapid reaction did not take place although the solution slowly turned pale green. The triphenylchloromethane appeared to be almost insoluble in acetonitrile. All the xenon difluoride was consumed within 2 days but no products could be positively identified; the reaction was not investigated further. In addition it is noted here that trichlorofluoromethane used as an n.m.r. reference did not react with xenon difluoride under any of the experimental conditions described. Indeed, solutions of xenon difluoride in CH_3CN/$CFCl_3$ mixtures appeared as stable as in acetonitrile itself.

Reaction of Triphenylsilane with Xenon Difluoride

Triphenylsilane (60 mg, 0.25 mmoles) was dissolved in acetonitrile (approx. 0.2 ml) and added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.12 mmoles XeF_2). The reaction could be monitored in the usual way (^{19}F n.m.r. spectroscopy); alternatively attack of xenon difluoride on the Si-H bond could be monitored by observing the Si-H resonance in the proton spectrum at -5.52 p.p.m. A rapid reaction did not take

place, the xenon difluoride concentration being virtually unchanged after 1 hour. Only approximately half the xenon difluoride had reacted after 2 days with no readily definable products. The reaction was not studied further.

As a comparison in reactivity a small quantity of dry chlorine was bubbled into a solution of triphenylsilane in acetonitrile. A vigorous exothermic reaction occurred and the ^{1}H n.m.r. spectrum revealed loss of the Si-H resonance. Similary methylphenylchlorosilane reacted vigorously with chlorine at 0^{o} to give excellent yields of methylphenyldichlorosilane.

Reaction of Trimethylsilane with Xenon Difluoride

Trimethylsilane (30 mg, 0.41 mmoles) was condensed onto a sample of xenon difluoride in acetonitrile (0.3 ml containing 0.12 mmoles XeF_2) at -196^{o}; the n.m.r. tube was flame sealed and allowed to warm to room temperature. Examination of the ^{19}F n.m.r. spectrum revealed little initial reaction, however approximately 30% of the xenon difluoride had reacted after 1 hour, 70% after 4 hours and 100% after 24 hours. A ^{19}F n.m.r. search revealed trimethylfluorosilane as the only detectable product in approximately 75% yield based on xenon difluoride starting material. The proton spectrum showed only unreacted trimethylsilane (doublet and a dectet) and trimethylfluorosilane (doublet J_{H-F}= 7.5 Hz).

Again, as a comparison in reactivity, chlorine was bubbled

into a solution of trimethylsilane in acetonitrile at 0^{o}. A violent uncontrollable reaction occurred, the reaction was not pursued any further.

Reaction of Allyldimethylchlorosilane with Xenon Difluoride

Allyldimethylchlorosilane (19 mg, 0.14 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.15 mmoles XeF_2) at -10^{o}. As the mixture was allowed to warm to $+38^{o}$ in the sample probe of the n.m.r. spectrometer a gas was evolved, the solution became very faintly yellowish coloured. Examination of the ^{19}F n.m.r. spectrum showed all the xenon difluoride had reacted within 6 minutes. An n.m.r. search revealed dimethyldifluorosilane as the only fluorine containing product; the yield was close to 100% based on xenon difluoride starting material.

An examination of the proton spectrum showed the characteristic triplet for the dimethyldifluorosilane. However, a careful examination of the region from -3 to -7 p.p.m. showed that the allyl group, A_2BX_2, spectrum had been preserved. Allylchloride, $CH_2{=}CH{-}CH_2Cl$, was identified by comparison with an authentic sample, the broadened doublet of the $-CH_2Cl$ group being very characteristic (δ = -4.1 p.p.m., $J_{\underline{CH}_2Cl\text{-}\underline{CH}=}$ = 7 Hz). The yield was difficult to estimate but was at least 60%. Attempts at concentration of the allylchloride failed; although removal of dimethyldifluorosilane was straightforward the separation from acetonitrile was not possible due to the small amounts involved.

However mass spectrometry of the acetonitrile solution showed M^+ for CH_2=CH-CH_2Cl.

Reaction of Allyltrimethylsilane with Xenon Difluoride

Allyltrimethylsilane (23 mg, 0.20 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.12 mmoles XeF_2). Examination of the ^{19}F n.m.r. spectrum revealed that a rapid reaction was not taking place, the xenon difluoride concentration being virtually unchanged after 1 hour. After 3-4 days the xenon difluoride had all reacted and trimethylfluorosilane was the only detectable product although in low yield. The rate of the reaction and the yield of trimethylfluorosilane appeared to be somewhat variable over the several reactions tried; the reaction did also appear to be light sensitive. The destiny of the allyl group was not determined, the proton n.m.r. spectrum indicated several products but separation was found not to be possible on the vacuum line; removal of the solvent and volatile products left traces of an oily material.

Reaction of Allyldimethylchlorosilane with Chlorine

Dry chlorine was bubbled into a 10% solution of allyldimethylchlorosilane in acetonitrile at 0^o. Examination of the products revealed that cleavage of the allyl group was the predominant process to give allylchloride and dimethyldichlorosilane.

Reaction of Dimethyldiethoxysilane with Xenon Difluoride

Dimethyldiethoxysilane (27 mg, 0.18 mmoles) was added to a solution of xenon difuoride in acetonitrile (0.3 ml containing 0.15 mmoles XeF_2). Examination of the ^{19}F n.m.r. spectrum revealed that a rapid reaction was not taking place, the xenon difluoride concentration being virtually unchanged after 1 hour. However all the xenon difluoride had reacted after 4 days, the ^{19}F n.m.r. spectrum showing that dimethyldifluorosilane had been produced, surprisingly at close to 100% yield. The proton spectrum revealed the characteristic triplet of dimethyldifluorosilane along with a new ethyl group (A_2X_3) spectrum. This product was found to be ethanol by addition of a few drops of the pure alcohol to the mixture and re-examining the spectrum.

Reaction of Hexaphenyldisilane with Xenon Difluoride

Hexaphenyldisilane (100 mg, 0.19 mmoles) was added in powdered form to a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.15 mmoles XeF_2). The mixture was mechanically shaken for 3 days at room temperature; the concentration of xenon difluoride decreased slowly but no new products were found, very little of the hexaphenyldisilane appeared to have dissolved in the solvent.

Reaction of Hexachlorodisilane with Xenon Difluoride

Hexachlorodisilane (60 mg, 0.22 mmoles) reacted violently with xenon difluoride solution even when added at -20^{o}. A dark brown mass was left after the reaction subsided, the reaction was not investigated further.

Reaction of Trimethylgermanium bromide with Xenon Difluoride

Trimethylgermanium bromide (79 mg, 0.40 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.40 ml containing 0.25 mmoles XeF_2). The reaction appeared to be complete after 10 min, the solution turned the characteristic reddish brown colour of bromine. The colouration could be discharged by the addition of olefins. Examination of the ^{19}F n.m.r. spectrum revealed trimethylgermanium fluoride in quantitative yield (+186.5 p.p.m., J_{F-H}= 7 Hz, dectet). The proton spectrum revealed a doublet at -0.6 p.p.m., J_{H-F}= 7 Hz. The spectral data are very similar to those reported by Kay.[120] Mass spectrometry was used to confirm the presence of $(CH_3)_3GeF$.

Reaction of Hexamethyldisilazane with Xenon Difluoride

Hexamethyldisilazane (32 mg, 0.20 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.15 mmoles XeF_2). Examination of the ^{19}F n.m.r. spectrum showed that the xenon difluoride reacted slowly to completion over a

period of 25 minutes. During this time the solution turned light brown and a pale brown solid separated out from the mixture. A ^{19}F n.m.r. search showed that trimethylfluorosilane was produced in close to quantitative yield based on xenon difluoride starting material. The solid material was separated from the solution, washed with cold acetonitrile and pumped on for 3 hours at 25^{o} to remove any volatile materials present. The yield of solid material was low ($\sim$1 mg). An infra red spectrum of the material showed broad bands in the N-H region, a band in the N=N region[132] at 1404 cm^{-1} and a broad strong band at 740 cm^{-1}. In addition there was a weak band at 1255 cm^{-1} and a weak sharp band at 482 cm^{-1}. There were no bands in the C-F stretching region. The solid did not have a sharp melting point, on heating the sample decomposition occurred leaving a dark mass.

The reaction was repeated using increased quantities of starting materials; hexamethyldisilazane (0.52 g, 3.3 mmoles) was condensed onto a solution of xenon difluoride in acetonitrile (8 ml containing 3.2 mmoles XeF_2) at -196^{o}. A vacuum gauge was attached to the vessel to monitor the course of the reaction. The reactants were allowed to warm to room temperature and mixed by shaking. The reaction appeared complete after 30 minutes and a brown precipitate was once again formed. The volatile materials were separated from the solution; the pressure recorded in a known volume corresponded to slightly greater than 100% yield of xenon and trimethylfluorosilane. Cooling the volatile materials

to -105° condensed out the fluorosilane, the yield of which appeared to be approximately 95%; however even at -196° there was still a small residual pressure in the system. A gas phase infra red spectrum showed no absorptions.

A ^{1}H n.m.r. spectrum of the remaining acetonitrile solution was unrevealing, no peaks of detectable amplitude could be found apart from a singlet in the trimethylsilyl region attributable probably to the slight excess of hexamethyldisilazane. The solid was separated by pumping off the solvent and excess hexamethyldisilazane. The crude product was pumped on for 1 day at +25° to ensure complete removal of volatile materials. The oily solid was washed with cold acetonitrile; a proton n.m.r. spectrum of a concentrate of the washings showed a small singlet at -1.9 p.p.m. and an even smaller singlet at -2.7 p.p.m. Removing acetonitrile from the washings gave an oily dark brown residue having broad bands in the N-H stretching region of the infra red spectrum.

The pale brown solid remaining after the washings was found to be insoluble in common organic solvents. It was, however, found to be partially soluble in acetone and very soluble in water without any apparent reaction. A proton n.m.r. spectrum in water showed a broad singlet or multiplet at -2.6 p.p.m. No ^{19}F resonances were observed, however the solution was extremely dilute. The yield of brown solid was low (~0.03 g) and only the most economical techniques could be used to gain information as to its nature. The infra red spectrum was almost identical to that mentioned previously. A mass

spectrum provided some insight however; m/e values up to 750 were observable and a fragmentation pattern from 700 downwards was clearly discernible. No evidence was found for fluorine containing species in the mass spectrum although there was slight evidence for Si-O-Si low mass fragments (glassware or H_2O traces?).

An elemental analysis of the brown solid proved confusing; the analysis was C 7.55%, H 5.55%, N 22.56%, F 30.30%. There was insufficient sample for silicon analysis, the balance was assumed to be silicon and/or oxygen (34.37%).

Reaction of N,N-dimethylaminotrimethylsilane with Xenon Difluoride

A. Reactions in Acetonitrile

Typically N,N-dimethylaminotrimethylsilane (49 mg, 0.42 mmoles) was condensed onto a solution of xenon difluoride in acetonitrile (0.30 ml containing 0.20 mmoles XeF_2) at -196^{o} in a presilylated tube. As the reactants warmed to above -20^{o} a brisk reaction occurred, complete within 1-2 minutes. The reaction was highly exothermic, the colour of the resulting solution being dependant on careful cooling of the mixture during the reaction. Overheating resulted in very dark solutions and large quantities of oily intractable materials. Pale brown solutions could be obtained by maintaining the solution at -15^{o} during the reaction.

Examination of the ^{19}F n.m.r. spectrum revealed trimethylfluorosilane as the only detectable fluorine containing product,

the yield was close to quantitative. The proton spectrum showed, in the Si-$\underline{CH}_3$ region, the doublet due to trimethylfluorosilane, a singlet due to slight excess of N,N-dimethylaminotrimethylsilane and a second smallsinglet attributable to hexamethyldisiloxane. The yield of hexamethyldisiloxane was variable and was reduced considerably by using a presilylated tube and a presilylated vacuum manifold for manipulations of N,N-dimethylaminotrimethylsilane.

In the N-$\underline{CH}_3$ region (-1.25 to -3.25 p.p.m.) there appeared to be a variety of products, some twelve singlets in this region indicated a complex reaction. The yields varied from reaction to reaction (depending on the reaction temperature etc.) and some of the products appeared to be unstable. The singlet due to$(CH_3)_3SiN(\underline{CH}_3)_2$ at -2.46 p.p.m. was readily identifiable as was the singlet at -2.36 p.p.m. due to $(\underline{CH}_3)_2NH$. The dimethylamine was produced in quite high yield, constituting 20-30% of the available $(CH_3)_2N$- groups.

Despite the obvious complexity of the reaction it was decided to undertake a search for the hoped-for product, tetramethylhydrazine $(CH_3)_2NN(CH_3)_2$. Indeed the mixture contained a singlet at a suitable chemical shift when compared with an authentic sample (kindly supplied by Dr.P.Jones). Unfortunately the sample was destroyed in a laboratory fire before further confirmation could be made.

Trimethylfluorosilane, dimethylamine and some acetonitrile could be removed from the mixture of products without much difficulty. However attempts to remove the bulk of the acetonitrile or to effectively separate any of the other products proved fruitless,

some products being obviously of the same order of volatility as acetonitrile. A mass spectrum of the bulk material failed to show M^+ for tetramethylhydrazine, however a mass spectrum could not be found in the literature so the expected intensity of M^+ was not known. Fortunately a source of tetramethyltetrazine ($(CH_3)_2NNNN(CH_3)_2$) was available; pyrolysis of the tetrazine in the vapour reservoir of the mass spectrometer (200^o, 2 hours) produced tetramethylhydrazine[133]. The essential features of the mass spectrum are reproduced below.

m/e	Relative Intensity	Assignment
88	20	M^+
73	20	$M^+ - CH_3$
58	15	$M^+ - 2CH_3$
45	50	H_4CN_2 or H_7C_2N
44	100	$N(CH_3)_2$
43	40	H_2CN_2 or H_5C_2N
42	90	HCN_2 or H_4C_2N

Vapour phase chromatography combined with mass spectrometry was utilised in an attempt to elucidate the course of the reaction of N,N-dimethylaminotrimethylsilane with xenon difluoride in acetonitrile.

Two types of column were used, 8% FFAP on chromosorb 45 and untreated chromosorb 103. The FFAP column was excellent for organometallic, particularly organosilicon, derivatives but elution times for organo-nitrogen compounds were long and the peak shapes were badly distorted. In particular N-H containing compounds were very poorly eluted, temperature programming being necessary to remove dimethylamine from the column. In contrast the chromosorb 103 column was considerably better for nitrogen containing compounds but the organosilicon derivatives were badly resolved, hexamethyldisiloxane in particular being very badly tailed.

Some 22 compounds were detected by flame ionisation on the FFAP column and a similar number (but not necessarily the same compounds) on the chromosorb 103 column. Unfortunately most of the compounds were far too dilute for detection by mass spectrometry. Separate experiments indicated that 1-5% wt/vol concentrations were required to obtain good mass spectra under the conditions employed.

Temperature programming was found to be necessary for both columns; unfortunately considerable column bleeding occurred with the FFAP column above ~160^{o} which added a considerable background to the mass spectra. The chromosorb 103 was found to have a higher thermal stability and temperatures of 200^{o} could be used with this column.

A number of investigations by gas chromatography and mass spectrometry were made & the results will be discussed later. The procedure was not as productive as might have been hoped, however, and in none of the experiments was tetramethylhydrazine indicated as a product.

In all the reactions of N,N-dimethylaminotrimethylsilane with xenon difluoride in acetonitrile there was always an involatile oil remaining if the mixture of products was pumped on, even indefinitely.

B. Reactions without a solvent

N,N-dimethylaminotrimethylsilane (0.35 g, 3.0 mmoles) was condensed onto solid xenon difluoride (0.28 g, 1.65 mmoles) at -196° in a presilylated tube attached to a pressure gauge. The mixture was allowed to warm very slowly using a series of cold baths; the xenon difluoride appeared to dissolve in the N,N-dimethylaminotrimethylsilane at -35° without apparent reaction. At -22° (CCl_4 bath) a reaction, followed by monitoring the pressure in the tube, began to occur. If the rate began to increase rapidly the tube was recooled to -196° and the warming process commenced once more. When the reaction was complete the products, except for the xenon, were condensed back into an n.m.r. tube at -105° and the tube was flame sealed.

Examination of the ^{19}F and ^{1}H n.m.r. spectra indicated an 86% yield of trimethylfluorosilane based on the N,N-dimethylaminotrimethylsilane starting material. The yield was later confirmed

by separation of the trimethylfluorosilane by trap to trap distillation and weighing. There were other singlets in the Si-$\underline{CH}_3$ region contributing to about 10% yield although no other fluorine containing products were detectable in the ^{19}F n.m.r. spectrum.

Other materials from the reaction included dimethylamine (17% yield from vapour pressure measurements in a known volume after careful separation from trimethylfluorosilane by trap to trap distillation) and products corresponding to a variety of singlets in the ^{1}H n.m.r. spectrum from -2.00 to -3.00 p.p.m. One of these was formed in quite large quantities (-2.21 p.p.m., singlet, approximately 20% yield) and may have been due to tetramethylhydrazine (-2.22 p.p.m. from independant n.m.r. spectrum of an authentic sample). Unfortunately mass spectrometric facilities were not immediately available to examine for tetramethylhydrazine.

Instead an attempt was made to synthesise the methyl iodide salt of tetramethylhydrazine, pentamethylhydrazonium iodide; the melting point of this derivative has been reported in the literature.[134] The mixture of products, after removal of dimethylamine and trimethylfluorosilane, was treated with an appropriate quantity of methyl iodide. A dark yellow solid was observed to form. Recrystallisation was attempted from ethanol and a melting point of the pale yellow crystals was taken (192-198^{o}), repeating the recrystallisation improved the melting point to 207-211^{o} however there was insufficient sample to carry out further recrystallisations. The melting point of the pure derivative is reported as 222-223^{o} (186-188^{o} for the

crude product).[134]

There was also an involatile oil produced during the course of the reaction of xenon difluoride with N,N-dimethylaminotrimethylsilane. The yield was not high (~0.04 g). An analysis gave C 33.07%, H 9.17%, N 19.17%, F 38.91%.

The reaction in the absence of a solvent appeared to be quite promising especially if the material in 25% yield could be confirmed as tetramethylhydrazine. Unfortunately another sample was never prepared for mass spectroscopic or any other studies. A reaction was attempted using an identical apparatus and cold baths; approximately 2 to 3 minutes after the onset of the reaction the tube sufferred a sharp detonation. Another reaction using a wide tube and slightly larger quantities of N,N-dimethylaminotrimethylsilane sufferred a similar fate, the detonation left only a white powder and a trace of oily material to be examined. Similarly a mixture of reactants sealed in a tube was allowed to stand at -35^{o} for 10 hours without apparent reaction. On warming the xenon difluoride was again observed to dissolve at around -30^{o}, the rate of warming was maintained at around 4^{o} hr^{-1}. At -25^{o} a white solid seemed to precipitate out of the solution followed shortly after by an extremely loud detonation sufficient to completely destroy the 2 litre wide-necked dewar flask in which the sample was suspended.

The reaction without a solvent was abandoned in view of the danger and cost in terms of chemicals and equipment. Two other detonations occurred while working with this system and should

be mentioned here. The reaction was attempted in $CFCl_3$ in which the xenon difluoride is insoluble. A detonation occurred at approximately -15^{o} shortly after the formation of a white precipitate in the solvent. A similar detonation occurred when a saturated solution of xenon difluoride in acetonitrile was used.

C. Reaction in a Flow System

Attempts to r e a c t xenon difluoride with N,N-dimethylaminotrimethylsilane using a flow system were not productive. Dry nitrogen was passed over xenon difluoride crystals and then into a reactor, similarly dry nitrogen was passed over N,N-dimethylaminotrimethylsilane and then into the reactor. Despite using an entirely presilylated system the products were found to be hexamethyldisiloxane, trimethylfluorosilane, dimethylamine, a trace of oily material and a white solid identified as $(CH_3)_2NH_2^+ F^-$. The mass balance was poor. Attempts at a vapour phase reaction in a static system were similarly unsuccessful; there was a higher yield of brown oily deposit and some reduction in hexamethyldisiloxane yield.

D. Electron Spin Resonance Experiments

An electron spin resonance study was undertaken to see if intermediate free radicals could be detected during the reaction of xenon difluoride with N,N-dimethylaminotrimethylsilane. A flow system was found to be experimentally unfeasible since the xenon gas produced interfered badly with the mixing and smooth flowing of the reactants dissolved in

acetonitrile. A reaction in the absence of a solvent was considered far too dangerous, instead an attempt was made to rapidly quench a reaction in progress in acetonitrile.

N,N-dimethylaminotrimethylsilane (25 mg, 0.21 mmoles) was allowed to react with a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.10 mmoles XeF_2) at -10^{o} in a silica tube. When a vigorous reaction was observed to be occurring the solution was rapidly cooled to -196^{o} and an e.s.r. spectrum taken. A very poorly resolved but nevertheless repeatable spectrum was obtained showing a 28 gauss splitting in agreement with that reported for the dimethylamino radical.[135] If the reaction was allowed to go to completion no signal was observed, both the starting materials were checked to be free of spurious e.s.r. signals. The best spectrum obtained had a signal to noise ratio of around 2:1 and all the lines were not resolved; the assignment can only be regarded as tentative.

Reaction of N,N-Diethylaminotrimethylsilane with Xenon Difluoride

This reaction was repeated many times in baked out glassware, silylated glassware, teflon tubes, a monel reactor and in a polypropylene container, all essentially giving identical results.

Typically N,N-diethylaminotrimethylsilane (49 mg, 0.34 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.5 ml containing 0.16 mmoles XeF_2) at -10^{o}. A brisk reaction occurred, complete within 1 to 2 minutes, and a brown solution resulted.

Examination of the ^{19}F n.m.r. spectrum showed trimethylfluorosilane as the only detectable fluorine containing product in 90-100% yield. The proton n.m.r. spectrum showed the doublet due to trimethylfluorosilane, a trace of hexamethyldisiloxane (present in the starting material), and a new ethyl group, A_2X_3, spectrum ($\delta_{CH_2-CH_3}$ = -2.78 p.p.m., J_{H-H} = 7.5 Hz; $\delta_{CH_2-CH_3}$ = -1.22 p.p.m., J_{H-H} = 7.5 Hz). This material was shown to be diethylamine by infra red and n.m.r. spectroscopy in comparison with an authentic sample. The yield was variable but was ~80% of the available diethylamino groups. The only other product was an intractable oily residue that remained after pumping on the products for 14 hours at room temperature. In an e.s.r. experiment similar to that described previously no free radicals could be observed.

Reaction of N,N-Diisopropylaminotrimethylsilane with Xenon Difluoride

Again the products and yields from this reaction proved invariant despite changes in materials used for reaction vessels etc.

N,N-diisopropylaminotrimethylsilane (74 mg, 0.42 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.4 ml containing 0.20 mmoles XeF_2) at -10^{o}. On warming the sample to $+38^{o}$ in the sample probe of the n.m.r. spectrometer the solution turned dark brown and a gas was evolved. Examination of the ^{19}F n.m.r. spectrum showed that all the xenon difluoride had reacted within 5 minutes. An n.m.r. search revealed trimethylfluorosilane

as the only detectable fluorine containing product in close to quantitative yield. The proton n.m.r. spectrum showed trimethylfluorosilane, a trace of hexamethyldisiloxane and a new isopropyl, AX_6, spectrum ($\delta_{-C\underline{H}(CH_3)_2}$ = -2.92 p.p.m., J_{H-H} = 6.5 Hz; $\delta_{-CH(C\underline{H}_3)_2}$ = -1.00 p.p.m., J_{H-H} = 6.5 Hz). This material was shown to be diisopropylamine by comparison with an authentic sample; the yield was 80-90%. The only other product was an involatile oil.

E.s.r. experiments proved to be misleading, an excellent multi-line spectrum was observed even at room temperature. However this spectrum was also observed in a sample of unreacted N,N-diisopropylaminotrimethylsilane and was attributed to a trace of diisopropylnitroxide, $((CH_3)_2CH)_2NO^{\cdot}$, in the starting material.[136]

Reaction of Tert-butylthiotrimethylsilane with Xenon Difluoride

A. Reaction in Acetonitrile

Xenon difluoride (0.14 g, 0.83 mmoles) was carefully weighed into an n.m.r. tube; acetonitrile was added (0.3 ml) and a saturated solution was formed. The solution was cooled to -196° and tert-butylthiotrimethylsilane (0.28 g, 1.73 mmoles) was quickly added, the tube was pumped out at -196° and flame sealed. Upon plunging the tube into an ice/salt bath at -7° a reaction occurred, complete within 7-9 minutes, resulting in a pale yellow solution.

Examination of the ^{19}F n.m.r. spectrum showed trimethylfluorosilane as the only detectable fluorine containing product. The proton spectrum

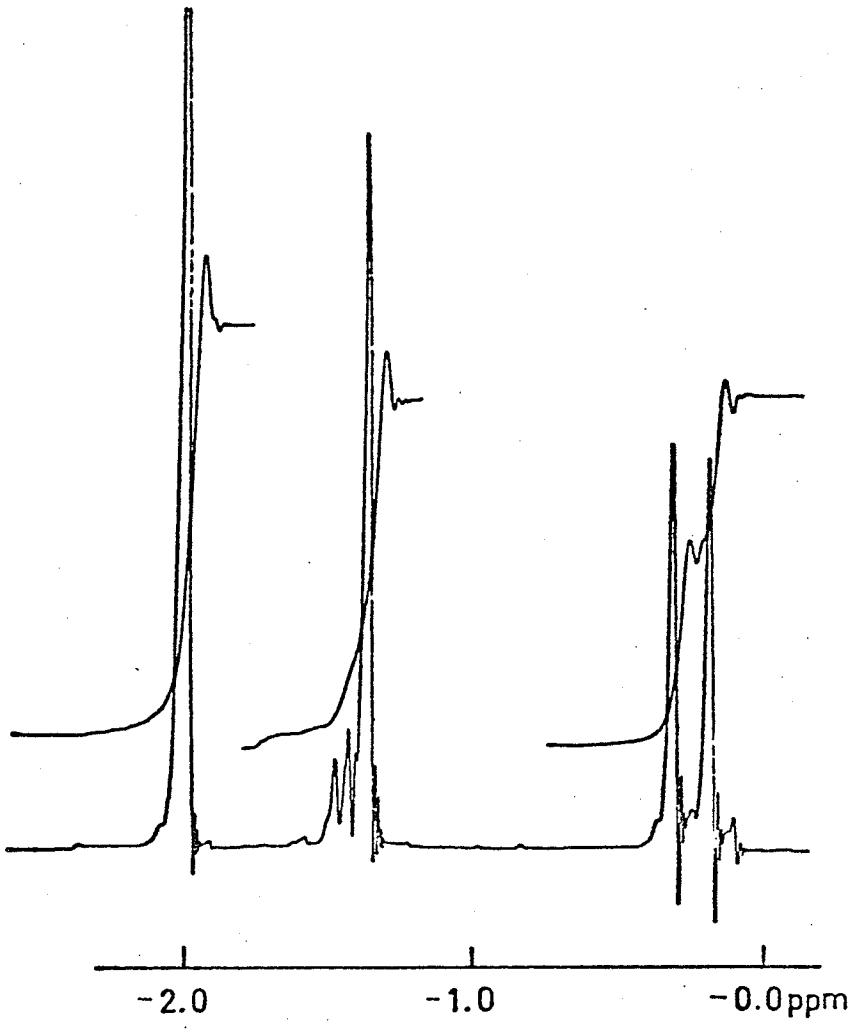


Figure [7]. Reaction of XeF_2 with $(CH_3)_3CSSi(CH_3)_3$, ^1H n.m.r. Spectrum

showed a very clean reaction; the spectrum is reproduced in figure [7]. Apart from the solvent acetonitrile there were three singlets in the tert-butyl region, the tabulated chemical shifts and approximate yields are given below.

Chemical Shift	Approx. Yield
-1.36 p.p.m.	85%
-1.43 p.p.m.	7%
-1.48 p.p.m.	7%

The tube was opened at -196° and the solution pumped on gently at -10° to remove xenon and trimethylfluorosilane, the yields were 100%. Pumping gently on the solution at room temperature removed the acetonitrile and the singlet at -1.48 p.p.m., identified as tert-butylthiol by comparison with an authentic sample.

The remaining materials were examined by mass spectrometry, very strong fragments due to di-tert-butyldisulphide (M^+= 178) were found, the spectrum was identical to that of an authentic sample, as indeed was the n.m.r. spectrum in acetonitrile (δ = 1.36 p.p.m.). Also present in the mass spectrum was a peak assignable to the compound $(CH_3)_3CSSSC(CH_3)_3$, (M^+= 210). This was also found as an impurity in the authentic di-tert-butyldisulphide as was a very small peak at -1.43 p.p.m. in the proton spectrum in acetonitrile. The third product is therefore assumed to be this compound; this assignment is strongly supported by the reaction carried out in the absence of a solvent, described below.

B. Reaction without a Solvent

The apparatus consisted of an n.m.r. tube attached via a glass sinter to a U-tube which in turn was attached to the pressure gauge on the monel vacuum line. The glassware was silylated and baked out thoroughly.

Xenon difluoride (0.14 g, 0.83 mmoles) was weighed into the U-tube and cooled to -196°, tert-butylthiotrimethylsilane (0.25 g, 1.54 mmoles) was quickly added and the system was pumped out rapidly with the reactants maintained at -196°. The reaction was monitored by observing the pressure change in the system. The mixture was allowed to warm slowly towards room temperature and at approximately -30° a rapid reaction began to take place. The reaction could not be moderated successfully by cooling and was complete within 10 seconds, the final temperature of the mixture was ~+60°.

The products were separated into those readily volatile at room temperature and a yellow viscous oil and solid remaining in the U-tube. Material volatile at -100° was found to be xenon by mass spectrometry, the yield was 100%. The other volatile products were condensed into a second n.m.r. tube on another part of the vacuum system and examined by ^{19}F and ^{1}H n.m.r. spectroscopy.

The ^{19}F n.m.r. spectrum revealed trimethylfluorosilane as the major product but a second dectet at +131.4 p.p.m., J_{F-H}= 20 Hz,

was also observed, this was attributed to tert-butyl fluoride; the spectral data compares well with literature values.[137] The ratio of fluorosilane to tert-butyl fluoride was found to be approximately 6:1; the yield of fluorosilane was close to quantitative based on tert-butylthiotrimethylsilane starting material. The proton spectrum of the volatile materials showed a doublet due to trimethylfluorosilane and a second doublet at -1.40 p.p.m., J_{H-F}= 20 Hz, due to tert-butyl fluoride. Traces of other materials, not readily identifiable, were also present in the $-C(CH_3)_3$ region.

The mixture of yellow oil and solid remaining in the U-tube was dissolved in chloroform as far as possible and filtered through the sinter into the n.m.r. tube. The n.m.r. tube was flame sealed at -196°. A yellow solid (0.012 g) remaining on the sinter was examined by mass spectrometry and found to be S_8. A ^{19}F n.m.r. search of the oil in chloroform showed no signals. A proton spectrum revealed a large number of singlets in the $-C(CH_3)_3$ region. Di-tert-butyldisulphide was present in 10-15% yield identified by comparison with an authentic sample. The chloroform was removed carefully under vacuum and the yellow oil was investigated by mass spectrometry.

When the yellow oil was injected as a liquid sample only $(CH_3)_3CSSC(CH_3)_3$ and $(CH_3)_3CSSSC(CH_3)_3$ could be found, no evidence was found for $(CH_3)_3CC(CH_3)_3$ or $(CH_3)_3CSC(CH_3)_3$. However when the oil was introduced using the solid sample technique additional information was obtained. At +40° only $(CH_3)_3CSSC(CH_3)_3$ and $(CH_3)_3CSSSC(CH_3)_3$ were observed, however as the sample warmed from

+80° to +200° the following fragments were identified, (all fragments showing the correct $S^{32}S^{34}$ ratio).

t-BuSSt-Bu
t-BuSSSt-Bu
t-BuSSSSt-Bu
t-BuSSSSSt-Bu
t-BuSSSSSSt-Bu
t-BuSSSSSSSt-Bu

↑ increasing intensity in the mass spectrum.

On standing for 2-3 weeks the yellow oil precipitated sulphur and the yields of $(CH_3)_3CSSC(CH_3)_3$ and $(CH_3)_3CSSSC(CH_3)_3$ increased.

Reaction of Phenyldichlorophosphine with Xenon Difluoride

Phenyldichlorophosphine (12 mg, 0.07 mmoles) was condensed under vacuum onto a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.15 mmoles XeF_2) at -196°. The tube was flame sealed and allowed to warm slowly; a vigorous reaction occurred necessitating moderation by maintaining the temperature at 0°. The reaction appeared complete within 1 minute at this temperature. A ^{19}F n.m.r. search of the resulting brown solution revealed a doublet at +54.5 p.p.m., J_{F-P}= 972 Hz. The spectrum is entirely consistent with the formation of phenyltetrafluorophosphorane.[60] The yield was 100% based on xenon difluoride starting material;

repeating the reaction using an excess (0.15 mmoles) of phenyldichlorophosphine gave the same product in the same yield.

Reaction of Diphenylchlorophosphine with Xenon Difluoride

Diphenylchlorophosphine (22 mg, 0.10 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.15 mmoles XeF_2) at -10^{o}. As the mixture warmed to $+38^{o}$ in the sample probe of the n.m.r. spectrometer the solution turned light brown and a gas was evolved. Examination of the ^{19}F n.m.r. spectrum indicated the reaction was complete within 4 minutes. An n.m.r. search revealed a doublet of doublets at +34.3 p.p.m., J_{Fa-Fe}= 39.5 Hz, J_{Fa-P}= 830 Hz and a doublet of triplets at +79.5 p.p.m., J_{Fe-Fa}= 39.5 Hz, J_{Fe-P}= 915 Hz. The spectrum is shown in figure [8]. The spectrum is entirely consistent with the formation of diphenyltrifluorophosphorane[60]; the yield was close to 100% based on xenon difluoride starting material.

Reaction of Triphenylphosphine with Xenon Difluoride

Triphenylphosphine (52 mg, 0.20 mmoles) was dissolved in acetonitrile (0.3ml) and then added to a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.12 mmoles XeF_2) at -10^{o}. As the solution warmed to $+38^{o}$ in the sample probe of the n.m.r. spectrometer a gas was evolved and a white solid precipitated out. Examination of the ^{19}F n.m.r. spectrum indicated that the reaction

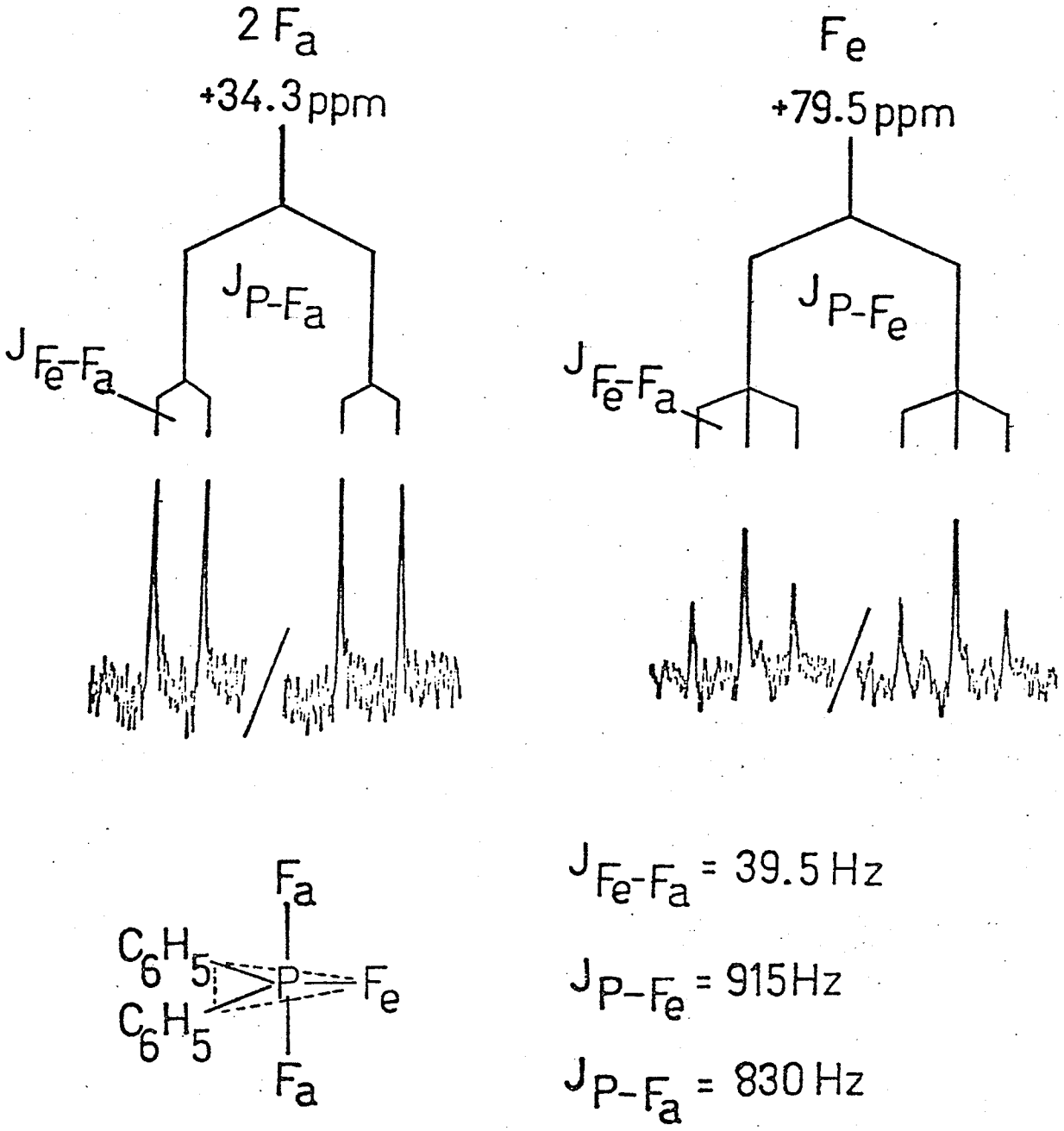


Figure [8]. ^{19}F n.m.r. Spectrum of Diphenyltrifluorophosphorane; Product from the Reaction of XeF_2 with $(C_6H_5)_2PCl$

was complete within 4 minutes. An n.m.r. search revealed no fluorine containing products were present in solution. The mixture was centrifuged and the precipitate was washed with cold acetonitrile and dried under vacuum, the weight was 35 mg. Chloroform (0.9 ml) was added and the precipitate dissolved to give a clear solution. A ^{19}F n.m.r. search revealed a doublet at +40.0 p.p.m., J_{F-P}= 714 Hz, entirely consistent with the formation of triphenyldifluorophosphorane.[60] The yield was 94% by weight, i.e. close to quantitative, based on xenon difluoride starting material.

Reaction of Iodine with Xenon Difluoride

A few crystals of pure iodine were dissolved in a solution of xenon difluoride in acetonitrile (0.4 ml containing 0.12 mmoles XeF_2). The colour of the iodine was only slowly discharged over a period of >24 hours at +20°.

Similarly a few crystals of iodine were dissolved in a second sample (0.35 ml containing 0.11 mmoles XeF_2) but this time carefully dried trimethylfluorosilane was bubbled into the solution until approximately 0.1 molar. The iodine colour was rapidly replaced by a dark milky brown colouration which in turn faded to give a colourless solution. The total reaction took 3-5 minutes to go to completion.

In separate experiments it was shown that trimethylfluorosilane does not react with xenon difluoride or with iodine.

Reaction of Methyl Iodide with Xenon Difluoride

Methyl iodide (0.16 g, 1.12 mmoles) was added to a solution of xenon difluoride in acetonitrile (0.4 ml containing 0.20 mmoles XeF_2) at $+20^{o}$. An examination of the ^{19}F n.m.r. spectrum revealed that a rapid reaction was not taking place; approximately 75% of the xenon difluoride had reacted after 100 minutes. The proton spectrum showed, during the same period, a well defined triplet growing in intensity downfield from methyl iodide (δ= -4.23 p.p.m., $J_{H-F?}$= 7 Hz, $\delta_{\frac{1}{2}}$= 2-3 Hz). The triplet reached maximum intensity after approximately 60 minutes, after 100 minutes decomposition products around -2.5 to -3.5 p.p.m. were observed and the intensity of the triplet began to decrease; decomposition was complete within a few hours. The triplet can reasonably be assigned to methyldifluoroiodine(III). A ^{19}F n.m.r. search failed to detect a suitable resonance for this compound, the concentration was very low making detection of the expected quartet unlikely. Attempts at separation of the products on the vacuum line failed, decomposition occurred rapidly when the solution was pumped on. A mass spectrum of the solution showed a fragment assignable to CH_3IF^+ but M^+ could not definitely be assigned.

The use of trimethylfluorosilane as a catalyst was tried; the rate of production of the triplet in the proton spectrum was indeed enhanced, maximum intensity being reached after 30 minutes. Unfortunately the rate of decomposition was also somewhat faster so that overall there was little gain.

Reaction of Hexafluoroacetone with Xenon Difluoride

A. In Acetonitrile Solution

Hexafluoroacetone (100 mg, 0.60 mmoles) was condensed onto a solution of xenon difluoride in acetonitrile (0.3 ml containing 0.15 mmoles XeF_2) at -196°; the n.m.r. tube was flame sealed and allowed to warm to room temperature. An examination of the ^{19}F n.m.r. spectrum showed that a rapid reaction was not taking place. After standing 3 weeks at room temperature all the xenon difluoride had been consumed; an examination of the solution by ^{19}F n.m.r. spectroscopy revealed excess hexafluoroacetone, a doublet at +82.8 p.p.m., J_{F-F}= 2 Hz, and a broad septet at +125.8 p.p.m., J_{F-F}= 2 Hz. The doublet and septet were present in a 6:1 ratio and are assigned to the alcohol $(CF_3)_2CF(OH)$. The spectrum is shown in figure [9]. The two components are not at the same spectrum amplitude. No evidence for any xenon containing species was found during the course of the reaction.

B. In the Absence of a Solvent

Hexafluoroacetone (0.2 g, 1.2 mmoles) was condensed onto xenon difluoride (25 mg, 0.15 mmoles) at -196°. The n.m.r. tube was flame sealed and very carefully warmed to room temperature. The xenon difluoride crystals were insoluble in hexafluoroacetone and little or no reaction was observed. The tube was shaken at room temperature for several days during which time the crystals

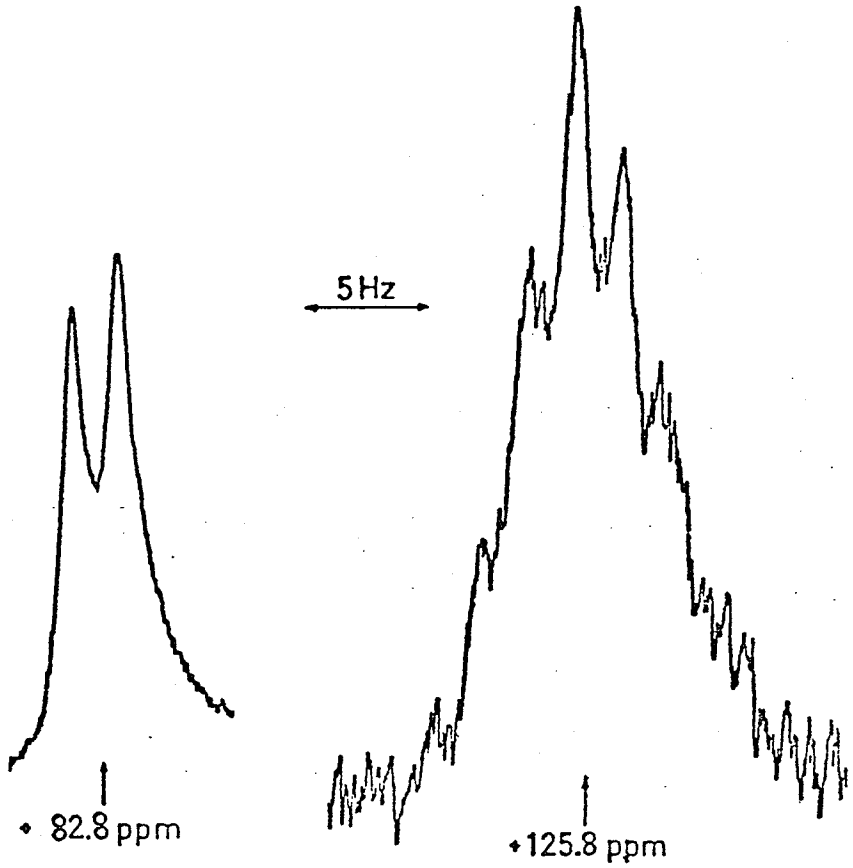


Figure [9]. ^{19}F n.m.r. Spectrum of the Product from the Reaction of XeF_2 with Hexafluoroacetone

of xenon difluoride slowly disappeared. An examination of the solution by ^{19}F n.m.r. spectroscopy after 5 days showed no detectable products other than excess hexafluoroacetone. No evidence was found for any xenon containing species or any fluorinated products such as $(CF_3)_2CF(OF)$.

C. Vapour Phase Reaction in the Presence of Cesium Fluoride Catalyst

Hexafluoroacetone (0.6 g, 3.6 mmoles) was condensed at -196^{o} onto a mixture of xenon difluoride (0.6 g, 3.6 mmoles) and cesium fluoride (0.2 g) in a baked out pyrex U-tube attached to the monel vacuum line. The hexafluoroacetone was allowed to warm slowly towards room temperature and to vapourise into the vacuum system. The consumption of xenon difluoride was monitored by the pressure gauge. After 4 days only ~15% of the xenon difluoride had reacted and only ~30% had reacted after 1 week. The products were condensed into an n.m.r. tube. Examination by ^{19}F n.m.r. spectroscopy revealed only hexafluoroacetone and a small trace of hexafluoroacetone hydrate.

Reaction of Disodium Perfluoropinacolate with Xenon Difluoride

The sodium perfluoroalkoxide was synthesised by the reaction of sodium with hexafluoroacetone in tetrahydrofuran. Details of the experimental technique may be found elsewhere.[138] The resultant solution of $[OC(CF_3)_2C(CF_3)_2O]^{2-}\cdot 2Na^{+}$ in tetrahydrofuran is unsuitable for direct reaction with xenon difluoride since separate experiments indicated that solutions of xenon difluoride in tetrahydrofuran were very unstable. Pumping on the alkoxide solution left a brown sticky solid which still contained some tetrahydrofuran solvated to the salt. However it was found that upon addition of acetonitrile the tetrahydrofuran could be removed by pumping on the solution.

Several treatments with acetonitrile were necessary to remove all the tetrahydrofuran.

A typical experiment with xenon difluoride is as follows; xenon difluoride (60 mg, 0.35 mmoles) was condensed onto a solution of $[OC(CF_3)_2C(CF_3)_2O]^{2-}\cdot 2Na^+$ in acetonitrile (0.5 ml containing 0.32 mmoles) at -196°. The reaction was monitored by pressure change. As the mixture was allowed to warm to -20° the brown solution turned rapidly yellow to greenish yellow and finally colourless, in addition a white precipitate was formed. Gas phase infra red spectroscopy indicated the major products to be hexafluoroacetone and perfluoropinacol $[HOC(CF_3)_2C(CF_3)_2OH]$. The volatile materials were condensed into an n.m.r. tube and examined by ^{19}F n.m.r. spectroscopy. Hexafluoroacetone was the major product along with a considerable amount of perfluoropinacol and a trace of hexafluoroacetone hydrate. The materials were identified by comparison with authentic samples.

The white precipitate left in the U-tube was washed with acetonitrile then dissolved out in water and recovered as a white microcrystalline material. A powder pattern X-ray spectrum positively identified the solid as sodium fluoride. Very faint lines in the spectrum indicated that the powder also contained ~5% Na_2SiF_6.

The reaction with xenon difluoride was repeated several times and the following observations were made:

(i) The solution turned from brown to colourless <u>without</u> precipitation of the white solid but <u>with</u> some evolution of xenon.

(ii) Further evolution of xenon coincided with the formation of sodium fluoride.

(iii) In one experiment a transient white solid was formed with pale plate-like crystals after some sodium fluoride had precipitated. The solid appeared to decompose rapidly even when the solution was quickly recooled.

Reaction of xenon difluoride with laboratory perfluoropinacol proved fruitless. Perfluoropinacol was quite resistant to attack by xenon difluoride, the only noticeable product being a small quantity of hexafluoroacetone.

CHAPTER 3

REACTIONS OF XENON DIFLUORIDE - DISCUSSION

3.1 REACTIONS WITH ORGANOSILICON COMPOUNDS

Xenon difluoride dissolved in acetonitrile proved to be an extremely versatile fluorinating agent towards many organosilicon compounds containing suitable functional groups. Xenon difluoride is an attractive fluorinating agent for several reasons although if the xenon gas produced during the reactions is not recycled the high cost of the starting materials may be prohibitive. One small disadvantage to the use of xenon difluoride in acetonitrile is its instability in this solvent. This was investigated by ^{19}F n.m.r. spectroscopy and was found to be similar to that reported by other workers[123]. Thus an approximately 0.5 molar solution decomposed over a period of 10 days, the decay of the xenon difluoride appearing to be linear.

An infra red examination of the decomposed solution showed broad bands in N-H stretching region but only weak bands in the CF stretching region. No resonances could be found in a ^{19}F n.m.r. search; dilute solutions of hydrogen fluoride in acetonitrile similarly showed no ^{19}F n.m.r. resonance, presumably due to exchange mechanisms occurring involving acetonitrile/HF complexes. The results are consistent with decomposition of xenon difluoride in acetonitrile

to give hydrogen fluoride and brown polymeric materials.

However, solutions freshly prepared (or stored at -78°) reacted readily and cleanly with organosilicon chlorides. Fluorosilane products were readily identified by their characteristic ^{1}H and ^{19}F n.m.r. spectra. Yields in most cases were determined by n.m.r. integration and can only be regarded as approximate. However a mass balance was obtained for $(CH_3)_3Si-$ and F- in the reaction of trimethylchlorosilane with xenon difluoride. The reaction had a 2:1 stoichiometry.

$$2\ (CH_3)_3SiCl + XeF_2 \longrightarrow 2\ (CH_3)_3SiF + Xe + Cl_2$$

The stoichiometry was confirmed by weighing the trimethylfluorosilane produced. Xenon was readily identified by its characteristic mass spectrum and chlorine was identified by reaction with styrene and its characteristic absorption at 315 nm in the u.v. spectrum in acetonitrile solution as found by other workers.[127]

Other simple chlorosilanes were observed to react by analogous 2:1 or 1:1 stoichiometries.

$$2\ (C_6H_5)(CH_3)_2SiCl + XeF_2 \longrightarrow 2\ (C_6H_5)(CH_3)_2SiF + Xe + Cl_2$$

$$(CH_3)_2SiCl_2 + XeF_2 \longrightarrow (CH_3)_2SiF_2 + Xe + Cl_2$$

$$2\ (C_2H_5)_3SiCl + XeF_2 \longrightarrow 2\ (C_2H_5)_3SiF + Xe + Cl_2$$

On the other hand many bifunctional organosilicon chlorides were found to undergo more complex reactions,

$$C_6H_5(CH_3)SiCl(H) + XeF_2 \longrightarrow C_6H_5(CH_3)SiF_2 + Xe + HCl$$

$$(CH_2{=}CH\text{-}CH_2)(CH_3)_2SiCl + XeF_2 \longrightarrow (CH_3)_2SiF_2 + Xe + CH_2{=}CH\text{-}CH_2Cl$$

these will be discussed later.

The reaction of xenon difluoride with trimethylchlorosilane was investigated in some detail. Experiments were performed to determine the order with respect to xenon difluoride and chlorosilane for this reaction at 0^o in acetonitrile solution. Two separate experiments showed that the reaction was first order with respect to both materials. It is possible therefore to write a rate expression for the reaction as follows:

$$\text{Rate} = k\left[(CH_3)_3SiCl\right]\left[XeF_2\right]$$

This strongly implies, but cannot of course prove, that the reaction is of the following type:

$$XeF_2 + (CH_3)_3SiCl \xrightarrow{\text{slow}} \left[\text{intermediates}\right]$$

$$\left[\text{intermediates}\right] + (CH_3)_3SiCl \xrightarrow{\text{fast}} 2(CH_3)_3SiF + Xe + Cl_2$$

As has been pointed out in the general introduction the reactivity of silicon compounds is often explained by the ability of silicon to expand its coordination number from four (tetrahedral) to five (trigonal bipyramidal) or six (octahedral). Susceptibility to nucleophilic attack is one of the main facets of organosilicon chemistry; the acceptor properties of these and other group IV compounds have been reviewed by Beattie.[139]

The realisation that organosilicon compounds, particularly organosilicon chlorides, may act as good acceptors via an expansion of coordination number, along with the ability of xenon difluoride to act as a nucleophile by fluoride ion donation, is highly significant and forms the basis for a suggested mechanism supported in part by experimental evidence. It is the proposal of this thesis that organosilicon compounds are sufficiently strong Lewis acids as to initiate reaction with xenon difluoride via an ionisation or ion pair mechanism.

$$XeF_2 + (CH_3)_3SiCl \xrightarrow{\text{slow}} (CH_3)_3\bar{S}i\bar{C}lF....\overset{+}{X}\bar{e}F$$

There is experimental evidence in support of such a process occurring. Iodine was found to be rapidly oxidised by xenon difluoride in acetonitrile in the presence of trimethylfluorosilane. Thus trimethylfluorosilane acts as a catalyst due to its mild acceptor properties; oxidation of iodine was found to be complete within a few minutes. Catalysis of this type has been strongly suggested in the literature as occurring via an ionisation mechanism.[37]

$$XeF_2 + A \longrightarrow XeF^+ + AF^-$$

$$\text{or} \quad 2\ XeF_2 + A \longrightarrow Xe_2F_3^+ + AF^-$$

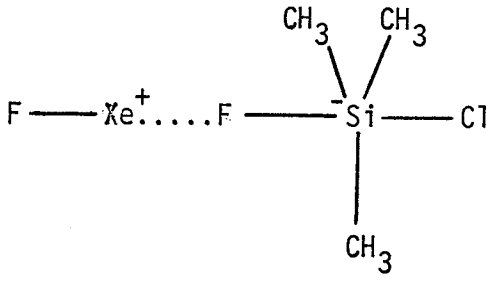
$$XeF^+ + I_2 \longrightarrow IF \rightarrow IF_3 \rightarrow IF_5$$

In the case of trimethylfluorosilane we hence have:

$$XeF_2 + (CH_3)_3SiF \rightleftharpoons (CH_3)_3S\bar{i}F_2....X\overset{+}{e}F$$

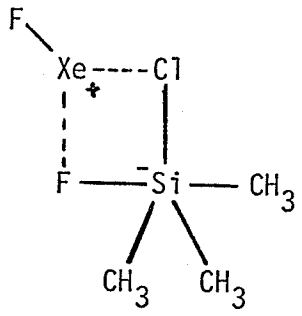
The Lewis acidity of trimethylchlorosilane cannot be much weaker than that of trimethylfluorosilane and a similar interaction would be expected. The resulting species may be fully ionised or exist as an ion pair.

S_N2 - Si



The possibility of flank attack at silicon cannot be ignored[95,97], since four centre intermediates are not unreasonable.

S_Ni - Si



The intermediate may rapidly break down:

$$\longrightarrow (CH_3)_3SiF + Cl^- + {}^+XeF$$

$$\downarrow$$

$$Cl\text{-}Xe\text{-}F$$

Or directly by a four centre mechanism:

$$\longrightarrow (CH_3)_3SiF + Cl\text{-}Xe\text{-}F$$

There is evidence in the literature[140] to suggest that XeClF cannot be synthesised although such intermediates are not unreasonable. It is also reasonable that this species will react rapidly with a second trimethylchlorosilane molecule to yield a stabilised ^+XeCl intermediate.

$$F\text{-}Xe\text{-}Cl + (CH_3)_3SiCl \xrightarrow{\text{fast}} Cl\text{-}Xe^{+}....(CH_3)_3\bar{S}iClF$$

$$\downarrow \text{ fast}$$

$$XeCl_2 + (CH_3)_3SiF$$

The xenon dichloride would be expected to dissociate via a free radical pathway since the bond energy of xenon dichloride must be low.[35]

$$XeCl_2 \longrightarrow Xe + 2Cl\cdot$$

Xenon compounds have been noted to decompose via free radical homolytic cleavage, for example the compound $Xe(OPOF_2)_2$ has been shown to decompose producing $\cdot OPOF_2$ radicals.[141]

Alternatively the intermediate XeClF species may break down before further reaction occurs to give the $\cdot XeF$ radical.

$$Cl\text{-}Xe\text{-}F \longrightarrow \cdot XeF + \cdot Cl$$

or immediate, i.e. during loss of Cl^- from $(CH_3)_3\bar{S}iClF$,

$$Cl^- + {}^{+}XeF \longrightarrow \cdot XeF + \cdot Cl$$

There are arguments against such a proposal. The xenon fluoride radical has been estimated to have a bond energy ~ 20 kcal mole^{-1} and can be regarded as a source of fluorine atoms.[35]

$$\cdot XeF \longrightarrow Xe + \cdot F$$

It is difficult to imagine any convenient facile mechanism for the clean removal of an ·XeF radical produced during the reaction of xenon difluoride with organosilicon chlorides. Attack of methyl groups on silicon would be expected along with cleavage of silicon-carbon bonds; no such occurrences were observed, arguing against the presence of an ·XeF radical.

If there are no hydrocarbons or readily oxidisable materials present intermediate ·XeF radicals have been shown by other workers to disproportionate,[142] e.g.

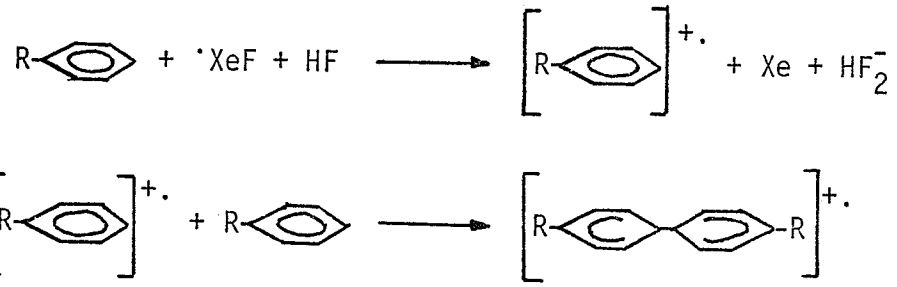
$$FXeOSO_2F \longrightarrow \cdot XeF + \cdot OSO_2F$$

$$2 \cdot XeF \longrightarrow XeF_2 + Xe$$

$$2 \cdot OSO_2F \longrightarrow S_2O_6F_2$$

Also during the course of the hydrogen fluoride catalysed reaction of xenon difluoride with aromatic compounds Shaw and co-workers[42] suggested a mechanism involving production of the ·XeF

radical. This radical is conveniently disposed of by proposing a one electron transfer to form aromatic radical cations in the presence of hydrogen fluoride; similar reactions could not be envisaged with organosilicon compounds.



One might also expect chlorine monofluoride as a product if an intermediate XeClF breaks down before further reaction.

$$Cl\text{-}Xe\text{-}F \longrightarrow Xe + Cl^{\cdot} + F^{\cdot} \longrightarrow ClF$$

No evidence for chlorine monofluoride was found in any of the experiments although it must be added that chlorine monofluoride would not be detected by ^{19}F n.m.r. spectroscopy due to its unusually large chemical shift outside the range of the A56/60 spectrometer.[143] Nevertheless mass spectrometric or u.v. studies did not indicate any species of this type being produced in solution. The near quantitative yields of fluorosilanes also argues against this point.

The mechanism proposed in this thesis does however involve the production of chlorine radicals. What evidence is there for the produc-

tion of such species in solution? It should be pointed out immediately that the effects of chlorine in solution are twofold; one set of effects may be explained by the presence of molecular chlorine and will be discussed later, while other effects may only be reasonably explained by the production of chlorine radicals during the reaction.

During the reaction of xenon difluoride with organosilicon chlorides chlorination of methyl groups was observed in several instances. In particular, the reaction of xenon difluoride with dimethyldichlorosilane produced ~30% yields of chloromethylmethyldifluorosilane, $(CH_2Cl)CH_3SiF_2$. Confirmatory synthesis of this compound by vapour phase chlorination of dimethyldifluorosilane was quite slow and light catalysed. Similarly bubbling of chlorine into a solution of dimethyldifluorosilane in acetonitrile produced little rapid reaction, only small quantities of chlorinated products were given after standing for some time. The reaction of phenylmethyldichlorosilane with xenon difluoride also produced a side product attributed to a chloromethyl derivative. The synthesis of the chloromethyl derivative is supported by the ^1H n.m.r. spectrum and also by the upfield multiplet in the ^{19}F n.m.r. spectrum. The multiplet may have been a quartet of triplets although the resolution was not good enough to allow an unequivocable assignment. However, the spectrum was fairly confidently attributed to chloromethylmethylphenylfluorosilane, $(CH_2Cl)CH_3SiF(C_6H_5)$.

It was carefully noted that chloromethyl derivatives were

always produced during the reaction of xenon difluoride with organosilicon chlorides; after the reactions had gone to completion there was no detectable change in the yield of such derivatives on standing.

Chlorination of alkyl (particularly methyl) groups attached to silicon has long been acknowledged to be a free radical process. The reaction may be initiated by irradiation or by peroxides.[95]

$$\text{e.g.} \quad (CH_3)_4Si + Cl_2 \xrightarrow{h\nu} (CH_3)_3SiCH_2Cl \qquad 144$$

$$(CH_3)_3SiCl + SO_2Cl_2 \xrightarrow{(C_6H_5COO)_2} CH_2Cl(CH_3)_2SiCl \qquad 145$$

Attack of acetonitrile by molecular or atomic chlorine would not be expected and was not observed. Temperatures of $\sim 400^{o}$ have been recorded as necessary for the vapour phase reaction of chlorine with acetonitrile.[146]

Additional evidence for chlorine radicals comes from two further experiments. Solutions of chlorine in acetonitrile have been reported in the literature as absorbing strongly at 315-320 nm.[127] Figure [10] demonstrates how the xenon difluoride reactions could be monitored by ultra violet spectroscopy. A 20:1 molar excess of trimethylchlorosilane suppresses production of chlorine. A band at 360 nm was detected and this is attributed to hydrogen chloride; this was checked by bubbling anhydrous hydrogen chloride into acetonitrile in a u.v. cell. Examination of the u.v. spectra in figure [10] shows that hydrogen chloride is produced during the reaction and molecular chlorine is not an

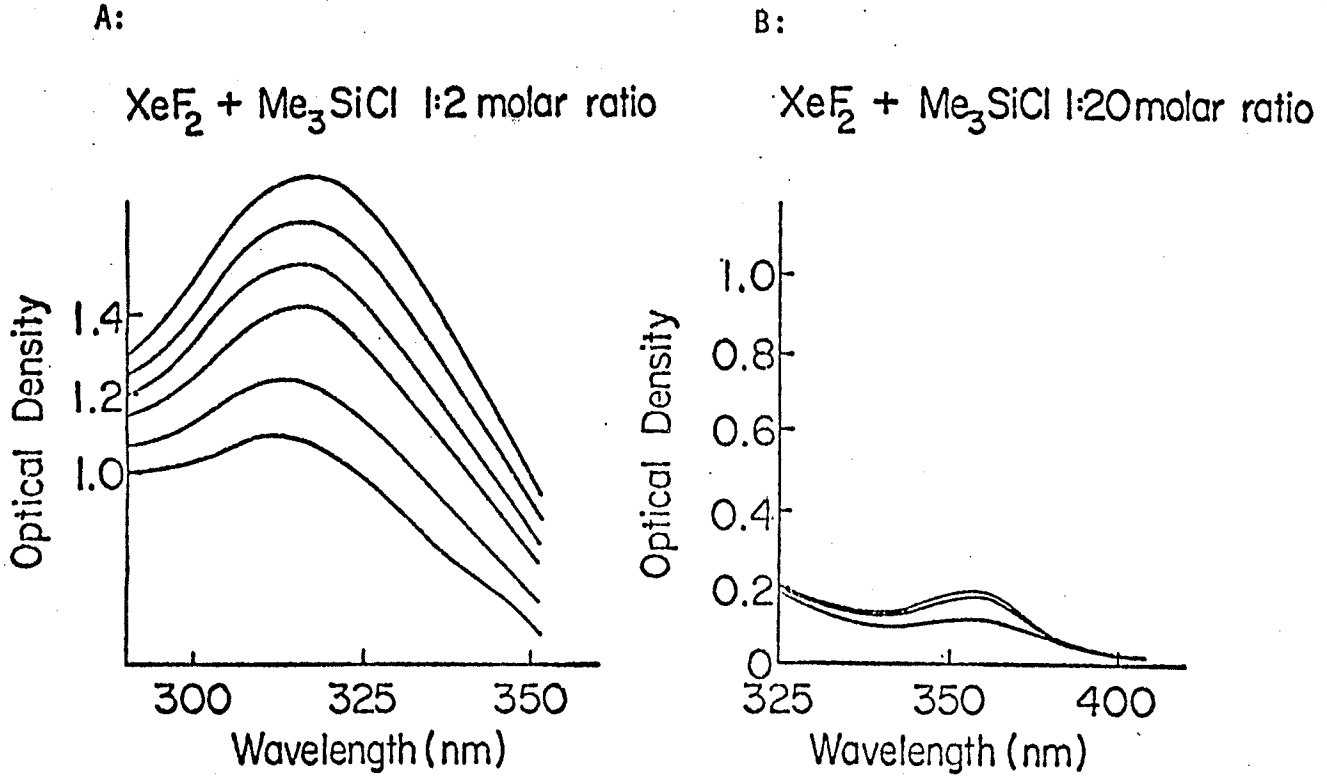


Figure [10]. Reaction of XeF_2 with $(CH_3)_3SiCl$ in Acetonitrile, U.V. Spectroscopic Studies

A. 1 ml XeF_2 solution (0.33 mmoles) + 1 ml $(CH_3)_3SiCl$ solution (0.68 mmoles)

B. 1 ml XeF_2 solution (0.17 mmoles) + 1 ml $(CH_3)_3SiCl$ solution (3.4 mmoles)

intermediate. Presumably a competition reaction is occurring:

$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2 \qquad \ldots\ldots 1$$

$$Cl^{\cdot} + (CH_3)_3SiCl \longrightarrow \text{chloromethyl derivatives} \qquad \ldots\ldots 2$$

If the concentration of trimethylchlorosilane is sufficiently high, reaction 2 predominates and production of molecular chlorine is largely suppressed. Additional evidence for chlorine radicals is provided by the experiments used to determine the kinetic orders with respect to xenon difluoride and trimethylchlorosilane. Whereas under normal conditions ($+38^{o}$) little or no chloromethyldimethylfluorosilane, $CH_2Cl(CH_3)_2SiF$, is found, reactions run at 0^{o} in the dark produced significant yields of the chloromethyl derivative. Presumably at $+38^{o}$ the steady state concentration of atomic chlorine, $[Cl^{\cdot}]$, is greater than at 0^{o} and, since the rate of formation of molecular chlorine $\propto [Cl^{\cdot}]^2$, nearly all the chlorine dimerises to Cl_2 and little chlorination of methyl groups occurs. On the other hand at 0^{o} the steady state concentration of chlorine radicals would be lower (indeed intermediates such as $XeCl_2$ or XeClF would be more stable) and there is opportunity for chlorination to occur before dimerisation takes place. The rate of free radical chlorination of methyl groups attached to silicon should be relatively temperature independant.

The reaction mechanism proposed cannot be unequivocal , there

are several other less likely possibilities. For example, catalysis by traces of acids:

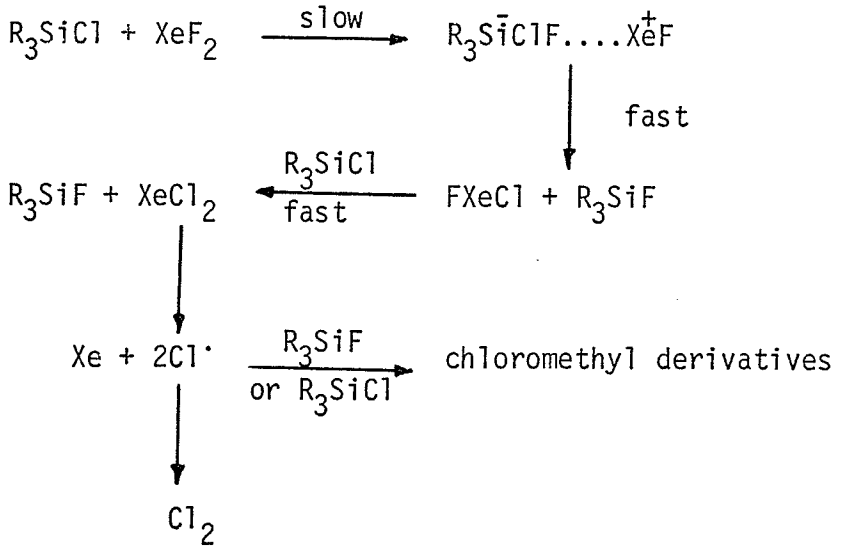
$$2\ HCl\ (trace) + XeF_2 \longrightarrow Xe + 2Cl^{\cdot} + HF$$

$$HF + (CH_3)_3SiCl \longrightarrow HCl + (CH_3)_3SiF$$
$$\downarrow \quad + XeF_2 \text{ etc.}$$

The derived rate expression would argue against, but not disprove, such mechanisms. The reaction of xenon difluoride with hydrogen chloride in high concentration has been studied and would seem to be comparatively slow.[140,43] Some unpublished work by this laboratory on the preparation of fluorosilanes by treatment of chlorosilanes with hydrogen fluoride would indicate the second reaction is also quite slow compared with the observed rates of reaction of xenon difluoride with organosilicon chlorides. Effects of impurities cannot be entirely ruled out however. The participation of species such as $Xe_2F_3^+$ or $Xe_2F_2Cl^+$ cannot be speculated on, neither can disproportionation reactions such as:

$$FXeCl + FXeCl \longrightarrow Xe + 2Cl^{\cdot} + XeF_2$$

It is not possible from the experimental evidence available to rule out such species or reactions. In summary, the proposed reaction scheme is:



It is worthwhile at this stage to discuss the reasoning behind the ability of xenon difluoride to donate fluoride ions so readily. It has been shown that nearly all the reactions of xenon difluoride described in the literature occur via an initial ionisation or polarisation of the xenon difluoride.

From calorimetric studies[147] the best estimate of the total bond energy of xenon difluoride is 64 kcal $mole^{-1}$. Its kinetic stability is attributed at least partially to the observation by a number of workers that the first bond dissociation energy is considerably larger than the second although quantitative estimates disagree as to the exact energies required.[35] Many studies and calculations have been made describing the bonding in xenon difluoride and other xenon compounds. The most popular from stereochemical considerations is the electron pair repulsion theory[148] while three centre molecular

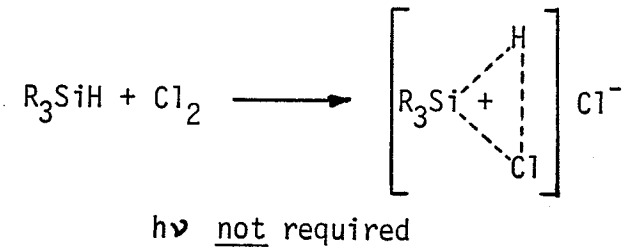
orbital theory has been applied extensively to gain a better understanding of the electronic nature of the bonding.[149] Xenon difluoride may best be looked upon as a resonance hybrid thus:

$$\left.\begin{array}{l} F - Xe^{+} \quad F^{-} \\ F^{-} \quad Xe - F \\ F^{-} \quad Xe^{++} \quad F^{-} \end{array}\right\} \text{ approximates to } F^{-\frac{1}{2}} - Xe^{+} - F^{-\frac{1}{2}}$$

The bonding has been described as semi-ionic or highly polarised. The calculations appearing in the literature have differed mainly on the extent of contribution of electrons from suitable orbitals on xenon to the bonding. The XeF^{+} species (isoelectronic with IF) may be treated as having a full two electron bond and consequently be expected to have a much higher bond energy than one bond in XeF_2 (32 kcal $mole^{-1}$). The best estimate of the bond energy of XeF^{+} is 48 kcal $mole^{-1}$ from thermodynamic data.[35] The consequence of the above statements is that xenon difluoride readily donates fluoride ions to suitable acceptors, examples were given in the general introduction. It has also been suggested by Bartlett that a variety of species, XeL^{+}, should be capable of existence even if XeL_2 is thermodynamically unstable.[35] A species XeL^{+} would be expected to have ~75% of the <u>total</u> bond energy of XeL_2. Thus the $XeCl^{+}$ species may well be thermodynamically stable.

Whereas silicon-chlorine (and silicon-nitrogen & silicon-sulphur) bonds appear to react readily with xenon difluoride other bonds are surprisingly stable. Xenon difluoride has no direct rapid reaction with silicon hydrides, alkoxides, allyls or with disilanes. The lack of reactivity may reflect the poor leaving ability of these groups. Reactions of phenyl derivatives, for example phenylmethylchlorosilane or, particularly, triphenylchlorosilane, gave lower yields of desired materials; this may be due to some cleavage of silicon-carbon bonds or attack on the aromatic system. For example, chlorine is known in some instances to substitute onto aromatic rings attached to silicon[95] or, more often, to cause cleavage.[150] Acids are also known to cleave silicon-carbon(aryl) bonds.[151,152] In addition the reaction of xenon difluoride with aromatic systems in the presence of acid catalysts has been described previously.

Trimethylsilane was found to be remarkably stable towards xenon difluoride compared with trimethylchlorosilane. Halogens on the other hand react vigorously with silicon hydrides. The reaction has been rationalised by Sommer as an example of electrophilic attack at silicon via a three centre positively charged intermediate.[97]



Clearly the inertness of xenon difluoride towards silicon hydrides is no longer surprising since xenon difluoride is not capable of a similar electrophilic attack. The slow reaction with trimethylsilane to give trimethylfluorosilane may be attributed to a more complex mechanism.

$$(CH_3)_3SiH + XeF_2 \xrightarrow[\text{slow}]{CH_3CN} \text{trace of HF}$$

$$(CH_3)_3SiH + HF \longrightarrow (CH_3)_3SiF + H_2$$

$$H_2 + XeF_2 \longrightarrow 2HF + Xe$$

$$\downarrow + (CH_3)_3SiH$$

etc.

Acids are known to react with silicon hydrides to produce hydrogen[153,154] while the reaction of hydrogen with xenon difluoride is also well known.[155]

If chlorine was also attached to silicon the observed reaction was quite different. For example, phenylmethylchlorosilane was observed to react with xenon difluoride to give high yields of phenylmethyldifluorosilane. The reaction is probably multistep.

$$2\ C_6H_5(CH_3)SiHCl + XeF_2 \longrightarrow 2\ C_6H_5(CH_3)SiHF + Cl_2 + Xe$$

$$C_6H_5(CH_3)SiHF + Cl_2 \longrightarrow C_6H_5(CH_3)SiClF + HCl$$

$$2\ C_6H_5(CH_3)SiClF + XeF_2 \longrightarrow 2\ C_6H_5(CH_3)SiF_2 + Cl_2 + Xe$$

$$Cl_2 + \text{etc.} \longrightarrow$$

overall:

$$C_6H_5(CH_3)SiHCl + XeF_2 \longrightarrow C_6H_5(CH_3)SiF_2 + Xe + HCl$$

It is unnecessary to invoke chlorine radicals to explain these reactions since, as has been pointed out, electrophilic attack of silicon hydrides by chlorine is not light catalysed.

The above multi-step mechanism is strongly supported by the reaction of a 6:1 excess of phenylmethylchlorosilane with xenon difluoride. The intermediate phenylmethylfluorosilane, $C_6H_5(CH_3)Si(H)F$, was identified by its very characteristic doublet of quartets in the ^{19}F n.m.r. spectrum, the yield was 60%. The large excess of phenylmethylchlorosilane would tend to absorb the available chlorine. The only other product was phenylmethyldifluorosilane, formed in 30% yield. No phenylmethylchlorofluorosilane was observed, presumably this species must be considerably more reactive towards xenon difluoride

than phenylmethylchlorosilane. This is consistent since it would be a much stronger Lewis acid.

Allyltrimethylsilane did not react readily with xenon difluoride; like silicon hydrides allyl groups attached to silicon are known to be more susceptible to electrophilic rather than nucleophilic attack.[156,157] After 4 days only low yields of trimethylfluorosilane were given. The reaction may be explained by the production of hydrogen fluoride in solution and resultant cleavage of the silicon-carbon (allyl) bond.

$$XeF_2 \xrightarrow[CH_3CN,\ \text{etc.}]{\text{slow},\ CH_2=CH-CH_2-Si(CH_3)_3} HF + \text{other products}$$

$$HF + CH_2=CH-CH_2-Si(CH_3)_3 \longrightarrow CH_2=CH-CH_3 + (CH_3)_3SiF$$

Allyldimethylchlorosilane, on the other hand, was found to react rapidly with xenon difluoride, again presumably by a multi-step reaction.

$$2\ CH_2=CH-CH_2-Si(CH_3)_3 + XeF_2 \longrightarrow 2\ CH_2=CH-CH_2-Si(CH_3)_2F + Cl_2 + Xe$$

$$CH_2=CH-CH_2-Si(CH_3)_2F + Cl_2 \longrightarrow CH_2=CH-CH_2Cl + (CH_3)_2SiClF$$

$$2\ (CH_3)_2SiClF + XeF_2 \longrightarrow 2\ (CH_3)_2SiF_2 + Cl_2 + Xe$$

$$\downarrow \text{etc.}$$

overall:

$$CH_2=CH-CH_2-Si(CH_3)_2Cl + XeF_2 \longrightarrow (CH_3)_2SiF_2 + CH_2=CH-CH_2Cl$$

The cleavage of an allyl group by chlorine was surprising since chlorine has been reported as adding to allyl groups attached to silicon.[158,159]

Bromine, on the other hand, has been reported as causing cleavage giving allylbromide and bromosilanes.[158] However a control reaction in which chlorine was added to a solution of allyldimethylchlorosilane in acetonitrile was observed here as giving high yields of cleavage products. Presumably chlorine is a more powerful electrophile in a polar solvent such as acetonitrile and its electrophilic reactions resemble those of bromine in non-polar solvents.

Diethoxydimethylsilane was quite unreactive towards xenon difluoride, ethanol and dimethyldifluorosilane being the products on standing 4 days. Reaction schemes involving xenon intermediates could be postulated:

$$XeF_2 + (C_2H_5O)_2Si(CH_3)_2 \longrightarrow (CH_3)_2SiF_2 + C_2H_5OXeOC_2H_5$$

$$C_2H_5OXeOC_2H_5 \longrightarrow Xe + 2\ {}^{\cdot}OC_2H_5$$

$${}^{\cdot}OC_2H_5 \xrightarrow{\text{H abstraction}} C_2H_5OH$$

Much more likely however are decomposition side reactions to give hydrogen fluoride which would readily cleave ethoxy-silicon bonds.

$$XeF_2 \xrightarrow[(CH_3)_2Si(OC_2H_5)_2]{CH_3CN,\ etc.} HF$$

$$2\ HF + (C_2H_5O)_2Si(CH_3)_2 \longrightarrow 2\ C_2H_5OH + (CH_3)_2SiF_2$$

Despite the large amount of experimental work reported on the reaction of xenon difluoride with silicon-nitrogen compounds, few firm conclusions can be made. Certainly the yield of trimethylfluorosilane in each case was close to quantitative but the reactions involving the nitrogen containing groupings are far from fully understood.

$$XeF_2 + 2(CH_3)_3SiNR_2 \longrightarrow 2(CH_3)_3SiF + Xe + ?$$

N,N-dimethylaminotrimethylsilane gave a large number of products on reaction with xenon difluoride in acetonitrile. The nature of these products was investigated by combined gas chromatography/mass spectrometry. The procedure was not as unequivocal as had been hoped for and, of the many compounds detected by flame ionisation, full or partial mass spectra could be obtained for only relatively few. The results are summarised in tables [1] & [2] and some speculative assignments are listed.

Column. 8% FFAP on chromosorb 45, 4', glass, carrier gas helium, temperature programmed from 50-160^{o} at 8^{o} min^{-1} then isothermal at 160^{o}. Compounds listed in order of elution.

Mass Spectra of Chromatograph Peaks.	Assignment.
129,131,132,134,136	Xe
92,77,73	$(CH_3)_3SiF$
(162), 147,131,117,103	$(CH_3)_3SiOSi(CH_3)_3$ (trace)
41,40,39	CH_3CN
84, 83, 58, 44, 42	$(CH_3)_2NCH_2CN$?
123, 82	? ?
87, 44, 42	$(CH_3)_2N$- containing ?
45,44,43	$(CH_3)_2NH$

Table [1]. Combined GC/MS of Products from the Reaction of XeF_2 with $(CH_3)_2NSi(CH_3)_3$ in Acetonitrile, FFAP Column

Column. Chromosorb 103, 4', glass, carrier gas helium, temperature programmed from 70-200° at 6° min^{-1} then isothermal at 200°. Compounds listed in order of elution.

Mass Spectra of Chromatograph Peaks.		Assignment.
	129,131,132,134,136	Xe
	45 ,44,43	$(CH_3)_2NH$
one broad peak	41 ,40,39	CH_3CN
	92 ,77,73	$(CH_3)_3SiF$
	(162),147 ,131,117,103	$(CH_3)_3SiOSi(CH_3)_3$
	73,59,44,42	$(CH_3)_3N-N=NH$??
	84,83,58,44,42	$(CH_3)_2N-CH_2CN$?
	102,(59),58,(57),42,44	$(CH_3)_2N-CH_2-N(CH_3)_2$??
	58,44,42	$CH_3-N=N-CH_3$?
	75,42,44,45	? ?

Table [2]. Combined GC/MS of Products from the Reaction of XeF_2 with $(CH_3)_2NSi(CH_3)_3$ in Acetonitrile, Chromosorb 103 Column

The reaction of N,N-dimethylaminotrimethylsilane with xenon difluoride in acetonitrile is obviously very complex although yields of trimethylfluorosilane were always found to be high and yields of dimethylamine were also significantly high. The detection of twenty or more compounds from this reaction makes the problem of a simple interpretation almost impossible. A mass spectrum of the bulk material failed to show M^+ for tetramethylhydrazine, the expected product from dimerisation of dimethylamino radicals. In addition, none of the gas chromatographic peaks could be attributed to this compound. However there seems to be good evidence for several species containing $(CH_3)_2N$- groups and a fairly intense mass spectrum consistent with $(CH_3)_2NCH_2CN$ was found.

Some reasonable evidence for the production of dimethylamino radicals was obtained from the e.s.r. studies, the spectra were similar to those reported by Jones[135,160] although signal to noise ratio was poor. In view of the somewhat tentative assignment the e.s.r. results will not be discussed further.

It seems pointless to enter into a very extensive discussion of such an obviously complex reaction. A reaction scheme as shown below could account for much of the experimental observations.

$$(CH_3)_3SiN(CH_3)_2 + XeF_2 \longrightarrow (CH_3)_3SiF + {}^{\cdot}N(CH_3)_2 + {}^{\cdot}XeF$$

$${}^{\cdot}N(CH_3)_2 + CH_3CN \longrightarrow HN(CH_3)_2 + {}^{\cdot}CH_2CN$$

$$\cdot CH_2CN + \cdot N(CH_3)_2 \longrightarrow (CH_3)_2NCH_2CN$$

$$\cdot XeF + H\text{-}\overset{|}{\underset{|}{C}}\text{-} \longrightarrow \cdot\overset{|}{\underset{|}{C}}\text{-} + HF + Xe$$

$$HF + (CH_3)_3SiN(CH_3)_2 \longrightarrow (CH_3)_3SiF + (CH_3)_2NH$$

$$\cdot CH_2CN + \cdot\overset{|}{\underset{|}{C}}\text{-} + \cdot XeF \longrightarrow \text{polymers}$$

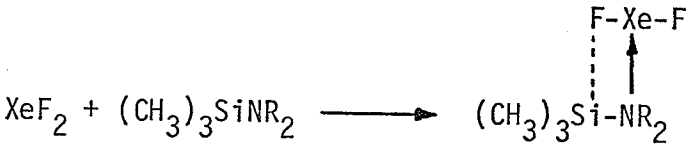
There is some evidence in the literature to suggest that dimethylamino radicals are not particularly powerful hydrogen abstractors[161], on the other hand dimethylamino radicals have been found to disproportionate in the gas phase to give hydrogen.[162]

$$2\ (CH_3)_2N\cdot \longrightarrow 2\ CH_3N{=}CH_2 + H_2$$

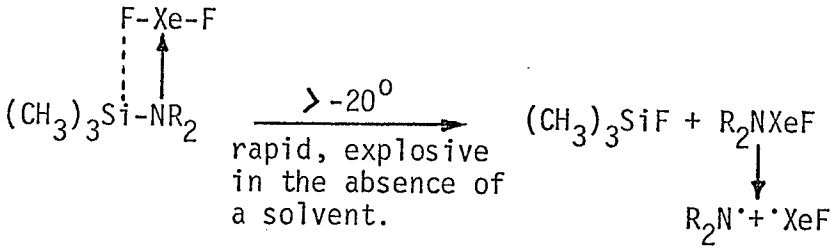
The photolysis of trimethylamine[163] is assumed to occur via a dimethylamino radical intermediate and the products were hydrogen, ethane, methane and polymer. The polymer was produced from $CH_3N{=}CH_2$.

In the one successful reaction of N,N-dimethylaminotrimethylsilane with xenon difluoride in the absence of a solvent there may have been some tetramethylhydrazine produced but positive confirmation was not possible (whether the singlet observed at -2.21 p.p.m. was in fact tetramethylhydrazine remains unanswered). As covered extensively in the experimental section these reactions are susceptible to deton-

ation in the absence of a solvent. It is very interesting to note that small quantities of a white solid were usually observed just prior to detonation. The possibility of adduct formation cannot be overlooked; it seems likely that during the reaction of xenon difluoride with silicon-nitrogen compounds an intermediate complex may form at low temperatures.



Formation of such a complex may be an inhibitor to a smooth reaction, the complex could break down in a highly exothermic manner.



It is interesting to note that the oily material separated from the one successful reaction in the absence of a solvent showed a high fluorine content (38.91%) although a slight excess of xenon difluoride had been used. Nevertheless the C:N:H ratio was close to that of $\left[(CH_3)_2\overline{N}\right]_n$; the oil may well be a polymeric species containing $(CH_3)_2N^+ F^-$ moieties.

In support of the suggestion of adduct formation it should be mentioned that xenon difluoride has been shown by other workers to complex with 2,2'-bipyridine although no definite compounds could be separated out from the solution.[164] Other reactive fluorides are known to form adducts with amines and silicon-nitrogen compounds prior to substitution. For example, phosphorus pentafluoride forms adducts with amines before substitution reactions occur[165] while boron trifluoride forms adducts with silicon-nitrogen compounds which are stable at low temperature but decompose to give fluorosilanes at room temperature.[166]

$$(CH_3)_3SiNHR + BF_3 \xrightarrow{0^o} (CH_3)_3\overset{BF_3}{\overset{\uparrow}{S}}iNHR$$

$$(CH_3)_3\overset{BF_3}{\overset{\uparrow}{S}}iNHR \xrightarrow{20^o} (CH_3)_3SiF + BF_2NHR$$

The donor power of nitrogen attached to silicon has been investigated by Paul and co-workers[167] who showed that nitrogen attached to silicon is sufficiently nucleophilic to complex with, for example, tin tetrachloride.

The possibility of the formation of xenon-nitrogen compounds has been discussed in the literature. The spectrum of the transient XeN moiety has been observed[168] and several theoretical studies have been made.[169—171] It has been suggested that XeN^+ salts may be stable. Nevertheless attempts by Kay to produce xenon-nitrogen compounds proved unsuccessful.[120]

Using the highly electronegative hexafluoroacetone-imine group attempts were made to react xenon difluoride with a number of metal-imine derivatives. The parent imine was the only product in each case despite changes in solvent and reaction vessel materials.

$$2\ (CH_3)_3M\text{-}N{=}C(CF_3)_2 + XeF_2 \longrightarrow 2\ (CH_3)_3MF + 2\ H\text{-}N{=}C(CF_3)_2 + Xe$$

Similarly reactions studied in the work reported here between N,N-diethylaminotrimethylsilane and N,N-diisopropylaminotrimethylsilane and xenon difluoride in acetonitrile resulted in high yields of parent amines. The most obvious method of production would be by hydrogen abstraction reactions of the dialkylamino radicals from the solvent, $(CH_3)_3Si$ groups, walls of the vessel, etc.

There are many references in the literature[172] concerning the study and reactions of dialkylamino radicals that may partially support such a mechanism. In many cases the studies are in the gas phase or by matrix isolation techniques and it would be dangerous to draw parallels between such studies and reactions carried out in acetonitrile at, or close to, room temperature. It seems reasonable, however, that production of dialkylamino radicals and some xenon fluoride radicals could explain the observed ~80% yields of amines, close to quantitative yields of fluorosilanes, and small quantities of oily polymeric materials. The possibility of such oils containing traces of $NR_4^+F^-$ species or $2NR_4^+SiF_6^{2-}$ species (from the glass, etc.) cannot be ignored.

The reaction of xenon difluoride with hexamethyldisilazane was interesting. The yield of fluorosilane was once again high and the solid material that separated out from the acetonitrile solution appeared to be polymeric. Its water solubility, infra red spectrum, elemental analysis and mass spectrum may well indicate a polymeric species with a backbone of acetonitrile and NH units, with the possibility of some fluoride or fluorosilicate salts present. Indeed the bands observed in the i.r. spectrum at 780 and 482 cm^{-1} are entirely consistent with the presence of hexafluorosilicate anions[173]. The silicate may well be from the glassware; the yield is, of course, low. Such a species could well be explained by reactions of intermediate $^{\cdot}XeF$, $^{\cdot}NHSi(CH_3)_3$ or $\dot{:}NH$ moieties with the solvent or reaction vessel. In this reaction there is also the possibility of attack of the N-H bond by xenon difluoride, ammonium fluoride salts are likely to result from such reactions. Intermediate acid fluoride salts would cleave silicon-nitrogen bonds to increase the yields of trimethylfluorosilane. The uncondensable gas found in the reaction was assumed to be nitrogen. The yield was very low, corresponding to only ~5% of the available nitrogen from the silazane.

The reaction of xenon difluoride with tert-butylthiotrimethylsilane in acetonitrile proved to be exceptionally smooth and clean, di-tert-butyldisulphide being produced in high yield. The reaction is not easy to rationalise from the preceeding discussion, any xenon-sulphur intermediate must have an extremely low bond energy. It is surprising how analogous the reaction is to that of silicon-

chlorides with xenon difluoride. However it is well worth noting that the "ionic bond energy" (as defined in Eaborn's[95] book p. 91) of the silicon-sulphur bond is almost exactly the same as that of the silicon-chlorine bond. Indeed, the ionic bond energies of various listed silicon-element bonds follow exactly the same trends as to their reactivities towards nucleophiles, this may be of considerable and overriding importance when discussing the reactions with xenon difluoride. One would predict from the numerical values presented by Eaborn that silicon-carbon, silicon-hydrogen and silicon-oxygen bonds might well be stable towards xenon difluoride whereas silicon-sulphur, silicon-chlorine and silicon-bromine bonds would not (trimethylgermanium bromide reacted readily with xenon difluoride to give bromine and trimethylgermanium fluoride).

Thus the observed reaction of tert-butylthiotrimethylsilane with xenon difluoride in acetonitrile was:

$$2\ (CH_3)_3SiSC(CH_3)_3 + XeF_2 \longrightarrow 2\ (CH_3)_3SiF + (CH_3)_3CSSC(CH_3)_3 + Xe$$

The reaction of tert-butylthiotrimethylsilane with xenon difluoride in the absence of a solvent was more complex, most probably due to the rapidity of the reaction and inadequate cooling of the reactants. The existence of species such as $(CH_3)_3CS_7C(CH_3)_3$, confirmed by mass spectrometry, is quite good evidence for intermediate tert-butylthio radicals adding to sulphur being produced in situ. Although the exact

nature of the oily sulphur containing product was not confirmed the large number of singlets in the proton n.m.r. spectrum would seem to correspond to a number of "polysulphides", $(CH_3)_3CS_nC(CH_3)$ n=2-7, found in the mass spectrum. It is not possible of course to distinguish positively if all the listed ions in the mass spectrum were legitimate compounds or were fragments from S_6 or S_7 derivatives.

The production of tert-butyl fluoride in low yield may well be the result of free radical processes involving sulphur-carbon bond cleavage. Such processes have been reported in the literature;[174,175] tri- and tetra-sulphides were noted as products in such reactions. A suggested reaction scheme that would account for the experimental observations on the reaction of xenon difluoride with tert-butylthio-trimethylsilane in the absence of a solvent is as follows:

$$XeF_2 + 2\ (CH_3)_3SiSC(CH_3)_3 \longrightarrow 2\ (CH_3)_3SiF + 2\ (CH_3)_3CS\cdot$$

$$2\ (CH_3)_3CS\cdot \longrightarrow (CH_3)_3CSSC(CH_3)_3$$

$$(CH_3)_3C\cdot + S \xrightarrow{(CH_3)_3CS\cdot} (CH_3)_3CS_nC(CH_3)_3$$

$$(CH_3)_3C\cdot \xrightarrow{XeF_2} (CH_3)_3CF$$

To conclude this section of the discussion it is useful to compare the fluorinating ability of xenon difluoride with the myriad

of other techniques that have been used for the preparation of fluorosilanes. There are two general methods; the treatment of silicon tetrafluoride with Grignard or organolithium reagents and the reaction of organosilicon compounds containing suitable functional groups with fluorinating agents. Some examples are listed below:

$$SiF_4 + o\text{-}CH_3C_6H_4MgBr \longrightarrow (o\text{-}CH_3C_6H_4)_2SiF_2 + 2MgBrF \quad [176]$$

$$SiF_4 + 2C_{10}H_7Li \longrightarrow (C_{10}H_7)_2SiF_2 + 2LiF \quad [177]$$

$$(CH_3)_3SiCl + SF_4 \longrightarrow (CH_3)_3SiF + SF_3Cl \text{ etc.} \quad [178]$$

$$(C_2H_5)_3SiCl + HF/H_2O/C_2H_5OH \longrightarrow (C_2H_5)_3SiF + HCl \quad [179]$$

$$R_3SiOH \text{ or } R_3SiCl + MF \longrightarrow R_3SiF \quad , M = Na, NH_4, B, Sb \quad [180]$$

$$RSiH_3 + PF_5 \longrightarrow RSiH_{3-n}F_n + nHPF_4 \quad [181]$$

$$CH_3OSiH_3 + PF_5 \longrightarrow SiH_3F + CH_3OPF_4 \quad [182]$$

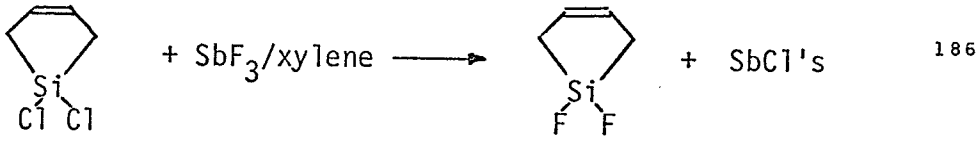
$$(CH_3)_3SiOCH_3 + IF_5 \longrightarrow (CH_3)_3SiF + IF_4OCH_3 \quad [183]$$

$$(CH_3)_3SiNR_2 + TeF_6 \longrightarrow (CH_3)_3SiF + TeF_5NR_2 \quad [184]$$

$$(CH_3)_3SiNR_2 + SF_4 \longrightarrow (CH_3)_3SiF + SF_3NR_2 \quad [87\ 88]$$

$$R_3SiH + NH_4F/NH_4HF_2 \longrightarrow R_3SiF + H_2 \quad [153]$$

$$(CH_3)_2Si(OCH_3)_2 + 2WF_6 \longrightarrow (CH_3)_2SiF_2 + 2WF_5OCH_3 \quad [185]$$



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$$((C_2H_5)_3Si)_2O + 2NH_4F + H_2SO_4 \longrightarrow 2(C_2H_5)_3SiF + (NH_4)_2SO_4 + H_2O$$

Many of these methods of synthesis have been reviewed by Eaborn.[95] The reactions described above have been used as convenient synthetic routes to fluorosilanes or as routes to other novel compounds (e.g. WF_5OCH_3, SF_3NR_2). Only in a very few instances have the mechanisms of the reactions been discussed in any detail, presumably, it would seem, due to lack of experimental evidence for intermediates.

3.2 REACTIONS WITH PHOSPHORUS III COMPOUNDS

No reports have appeared in the literature on the use of xenon difluoride as an oxidative fluorinator of phosphorus III compounds; the reactions reported in this thesis represent facile syntheses of fluorophosphoranes. The experiments carried out with phenyldichloro-, diphenylchloro- and triphenylphosphine indicated the following reactions were occurring:

$$C_6H_5PCl_2 + 2\ XeF_2 \longrightarrow C_6H_5PF_4 + Xe + Cl_2$$

$$2\ (C_6H_5)_2PCl + 3\ XeF_2 \longrightarrow 2\ (C_6H_5)_2PF_3 + 3\ Xe + Cl_2$$

$$(C_6H_5)_3P + XeF_2 \longrightarrow (C_6H_5)_3PF_2 + Xe$$

The products were readily identified by their characteristic ^{19}F n.m.r. spectra. The spectrum of phenyltetrafluorophosphorane was a doublet due to rapid intramolecular exchange of axial and equatorial fluorine environments while the spectrum of triphenyldifluorophosphorane was a doublet since both fluorines are in equivalent axial environments. On the other hand the spectrum of diphenyltrifluorophosphorane was observed as a doublet of triplets and a doublet of doublets; it represents a good example of non-equivalence of axial and equatorial sites on a trigonal bipyramidal molecule observable under conditions of very slow intramolecular exchange.

It is possible that during the reactions of the chlorophosphines with xenon difluoride the oxidation step was the result of chlorine produced in situ.

$$C_6H_5PCl_2 + XeF_2 \longrightarrow C_6H_5PF_2 + Cl_2 + Xe$$

$$C_6H_5PF_2 + Cl_2 \longrightarrow C_6H_5PF_2Cl_2$$

$$C_6H_5PF_2Cl_2 + XeF_2 \longrightarrow C_6H_5PF_4 + Cl_2 + Xe$$

However,since triphenylphosphine was also observed to be rapidly oxidised by xenon difluoride the postulation of such a mechanism is not necessary, an oxidative addition followed by a substitution reaction is more likely.

$$C_6H_5PCl_2 + XeF_2 \longrightarrow C_6H_5PCl_2F_2 + Xe$$

$$C_6H_5PCl_2F_2 + XeF_2 \longrightarrow C_6H_5PF_4 + Cl_2 + Xe$$

Phosphorus III compounds are in general very readily oxidised to phosphorus V compounds. Many trialkylphosphines are unstable in air and are converted to phosphine oxides.

$$R_3P \xrightarrow{[O]} R_3P{=}O$$

This ease of oxidation has been reported on extensively in the literature for the synthesis of fluorophosphoranes from suitable phosphines.

e.g.

$$3\ RPCl_2 + 3\ SbF_5 \longrightarrow 3\ RPF_4 + SbF_3 + 2\ SbCl_3 \quad [188]$$

$$3\ R_2PCl + 3\ MF_3 \longrightarrow 3\ R_2PF_3 + 2\ M + MCl_3 \quad M{=}As \text{ or } Sb \quad [188]$$

$$RPCl_2 \xrightarrow{Cl_2} RPCl_4 \xrightarrow{SbF_3} RPF_4 \quad [189]$$

$$2\ R_3P + SF_4 \longrightarrow 2\ R_3PF_2 + S \quad [190,77]$$

$$2\ ((CH_3)_2N)_3P + SF_4 \longrightarrow 2\ ((CH_3)_2N)_3PF_2 + S \quad [191]$$

Phosphorus V derivatives or fluorophosphoranes themselves may also

be used as convenient starting materials.

$$R_3P{=}O + SF_4 \longrightarrow R_3PF_2 + SOF_2 \qquad ^{190,77,192}$$

$$2\ R_3P{=}S + SbF_3 \longrightarrow R_3PF_2 + Sb_2S_3 \qquad ^{192}$$

$$PF_5 + 2\ (CH_3)_2NH \xrightarrow{100^{o}} ((CH_3)_2N)_2PF_3 + 2\ HF \qquad ^{193}$$

$$PF_5 + (CH_3)_3SiNR_2 \longrightarrow R_2NPF_4 + (CH_3)_3SiF \qquad ^{193}$$

$$RPF_4 + C_4H_4NSi(CH_3)_3 \longrightarrow C_4H_4NP(R)F_3 + (CH_3)_3SiF \qquad ^{194}$$

Oxidation of R_3P compounds by xenon difluoride may well have an excellent future in synthetic chemistry since the only side product is the very inert xenon gas. This may be particularly useful when the groups, R, are susceptible to attack by the typical residues from other synthetic routes (SbF_3,$SbCl_3$,Sb,S,etc.).

3.3 REACTION WITH METHYL IODIDE

The reaction of xenon difluoride with excess methyl iodide, although not vigorously pursued, gave some indication that methyl-difluoroiodine(III) was formed. The product was found to be unstable and decomposed at a moderate rate at $+20^{o}$. The observed low field triplet in the proton spectrum is assigned to CH_3IF_2 since the conversion from

CH_3I to CH_3IF_2 should cause a downfield shift of the methyl group. The spectrum is not consistent with other possible products such as iododifluoromethane, CHF_2I, since the observed coupling constant is too small; a coupling constant ~70 Hz would be expected for such a molecule.[60] It is unlikely that the observed J value was due to proton-proton coupling since no other multiplets with a similar coupling constant were observed in the proton spectrum.

A list of the coupling constants of "CH_3IF_2", CF_3IF_2 and CF_3IF_4 are given below; it should be immediately added that quantitative comparisons of H-F and F-F coupling constants are not reliable. The data is provided merely as a qualitative observation.

δ_H = -4.23 p.p.m. "CH_3IF_2" J_{H-F} = 7 Hz

CF_3IF_2 J_{F-F} = 8 Hz [195]

CF_3IF_4 J_{F-F} = 18 Hz [195]

(all F's on I are equivalent)

The reaction of xenon difluoride with methyl iodide serves as another demonstration of the enormous potential of xenon difluoride as a source of "clean" fluorine; the main problem in this case was the high kinetic inertness of xenon difluoride towards methyl iodide. Addition of trimethylfluorosilane as a catalyst was not dramatically effective and it is hoped that additional work with boron trifluoride as a catalyst and probably dispensing with the solvent could considerably improve the yield of pure material.

Perfluoroalkyliodine(III) and (V) fluorides have been reported in the literature.[195–197] They have been synthesised by the oxidative fluorination of the corresponding perfluoroalkyliodides.

$$CF_3I + F_2 \xrightarrow[\text{temp.}]{\text{low}} CF_3IF_2 \quad \text{decomposes} > -5^{o} \qquad 196$$

$$R_fI + \begin{matrix} ClF_3 \\ BrF_3 \\ BrF_5 \end{matrix} \longrightarrow R_fIF_2 \text{ or } R_fIF_4 \qquad 197$$

$$CF_3I + ClF_3 \longrightarrow \begin{matrix} CF_3IF_2 & \text{unstable} \\ CF_3IF_4 & \text{slowly decomposes} > 20^{o} \end{matrix} \qquad 195$$

No reports have appeared in the literature of any alkyliodine(III) or (V) fluorides, although a very recent paper describes the preparation of alkoxy derivatives IF_4OCH_3 and $IF_4OC_2H_5$ from the reaction of IF_5 with $(CH_3)_3SiOCH_3$ and $(CH_3)_3SiOC_2H_5$.[183] Clearly the reactions listed above would not be applicable to the attempted synthesis of, say, CH_3IF_4 since fluorine or chlorine trifluoride would vigorously attack C-H bonds. If the existence of CH_3IF_2 can indeed be fully proven then its stability must be noted as surprising in comparison with CF_3IF_2.

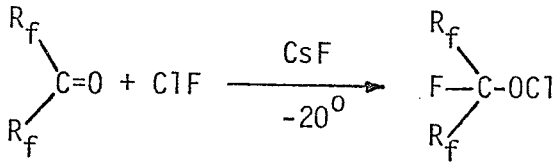
3.4 REACTION WITH HEXAFLUOROACETONE

No reaction could be detected between xenon difluoride and hexafluoroacetone either in the presence or absence of solvent, or in

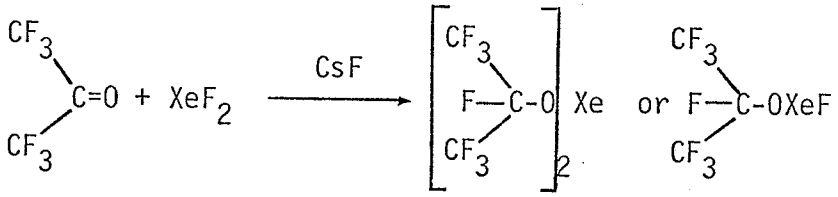
the presence or absence of cesium fluoride catalyst. The alcohol $(CF_3)_2CFOH$ was the only product identified from the reaction carried out in acetonitrile and may be simply rationalised as the product of hydrogen fluoride addition to hexafluoroacetone, the hydrogen fluoride being produced by decomposition of xenon difluoride in acetonitrile.

The lack of reactivity may be due to the kinetic inertness of xenon difluoride or more likely be due to the instability of the product which might well decompose back to the starting materials. This mode of decomposition is at least partially observed for analogous hypochlorites.[199]

Chlorine monofluoride has been shown to add smoothly to hexafluoroacetone and similar perfluoroketones, particularly in the presence of metal fluoride catalysts, to give high yields of hypochlorites.[198–200]



Since the charge distribution in chlorine monofluoride is generally acknowledged to be Cl^+-F^- it was considered that a similar reaction with xenon difluoride might occur to give novel perfluoroesters.



Some unconfirmed work has appeared in the literature suggesting that xenon esters may be partially stable;[201] the reaction of xenon trioxide with t-butanol has been postulated as occurring via a xenon ester intermediate.

$$XeO_3 + \text{t-BuOH} \longrightarrow \text{t-BuO}XeO_3H, \text{ solvated.}$$

A potentially better way of producing xenon compounds would be the interaction of xenon difluoride with perfluoroalcohols containing no α fluorine. Hypochlorites have been prepared in an analogous manner.[202]

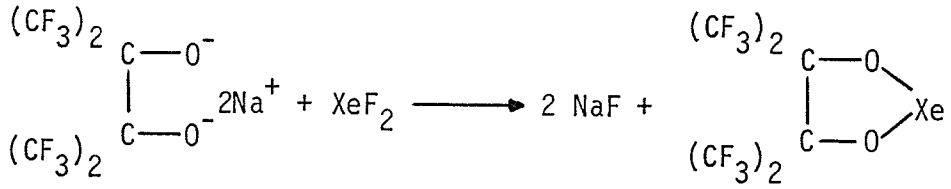
$$2\,(R_f)_3COH + XeF_2 \longrightarrow (R_f)_3COXeOC(R_f)_3 + 2\,HF$$

The only perfluoroalcohol readily available to try such a reaction was perfluoropinacol, a poor choice since it has been shown to be unreactive towards chlorine monofluoride.[202] Similarly no significant reaction was found here on addition of perfluoropinacol to solid xenon difluoride, indeed in an unreported reaction in this laboratory perfluoropinacol proved unreactive towards gaseous fluorine.

3.5 REACTION WITH DISODIUM PERFLUOROPINACOLATE

It was hoped that reaction of xenon difluoride with disodium perfluoropinacolate would give a xenon compound stabilised by the

powerfully electron withdrawing trifluoromethyl groups. Such xenon compounds might be monomeric, "dimeric" xenon bridged, or polymeric.



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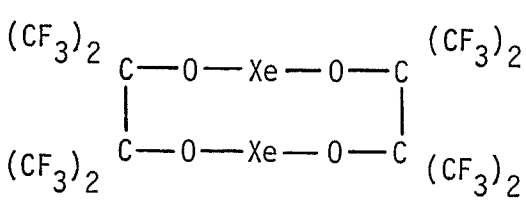

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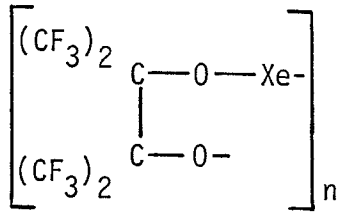
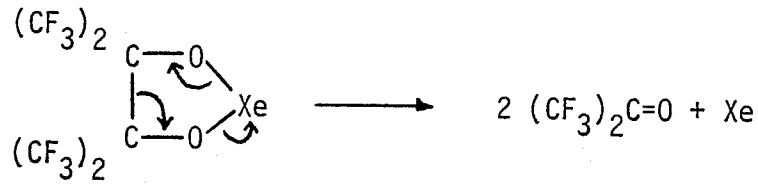
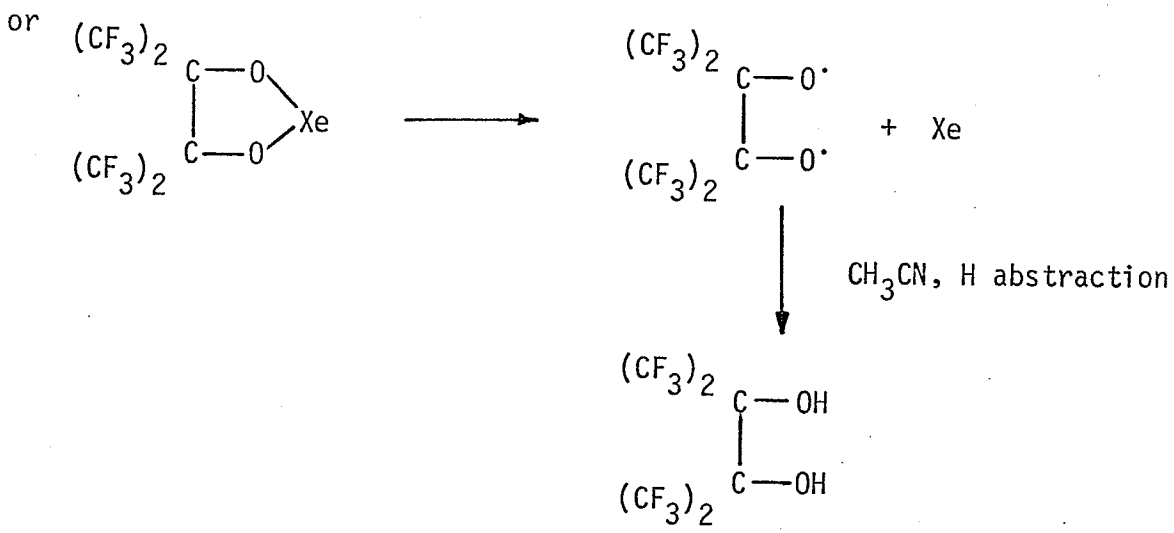


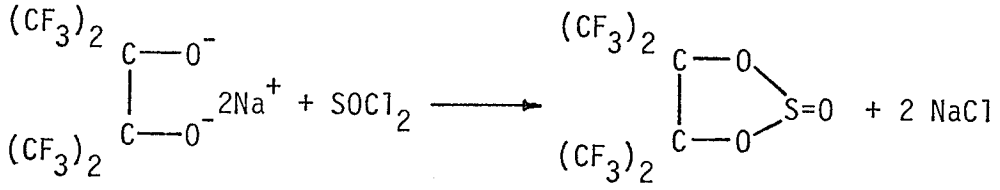
The dimeric or polymeric species are suggested since a non-linear xenon(II) species, by the electron pair repulsion theory, would be expected to be less stable than a similar linear species.

The reactions of xenon difluoride with disodium perfluoropinacolate failed to produce identifiable xenon compounds. However sodium fluoride was formed and the other products, hexafluoroacetone and perfluoropinacol, are consistent with the formation of a xenon containing intermediate.

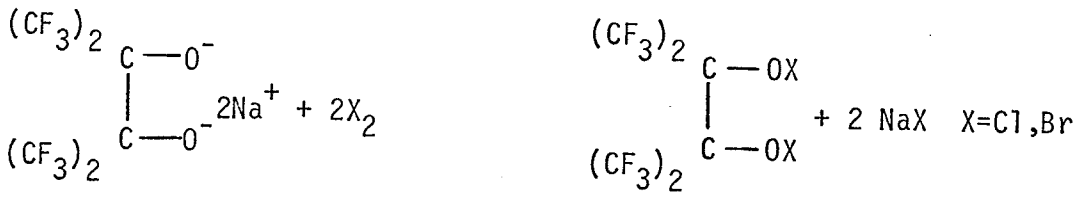




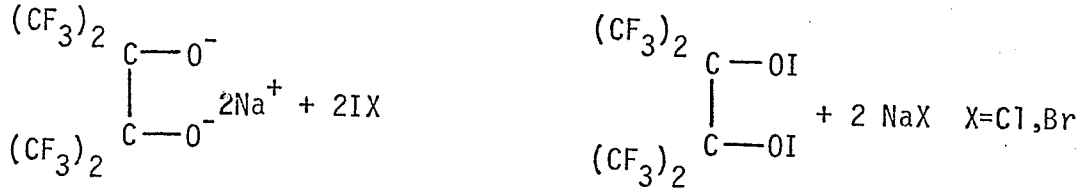
Disodium perfluoropinacolate is an extremely useful precursor for the synthesis of many derivatives containing the $[OC(CF_3)_2C(CF_3)_2O]$ group.[203] For example a cyclic sulphur derivative has been reported from the reaction of disodium perfluoropinacolate with thionyl chloride.



The presence of the strongly electron withdrawing trifluoromethyl groups also enabled unstable hypohalites of perfluoropinacol to be prepared from the reaction of the disodium salt with halides and interhalogen compounds.[204]



or for the hypoiodite,



Perfluoropinacol dihypoiodite in particular shows similar modes of decomposition to those found in the reaction of xenon difluoride with disodium perfluoropinacolate. Iodine and hexafluoroacetone are given, or, in the presence of a suitable hydrogen donor, perfluoropinacol and iodine.[204]

3.6 CONCLUSIONS

The first section of this thesis has described an expansion of the use of xenon difluoride, an inert gas fluoride, as a selective fluorinating agent. In particular it has introduced xenon difluoride to inorganic and organometallic chemistry and has demonstrated the potential usefulness of this simple binary fluoride as a chemical reagent. The experiments described have added to the consensus that inert gas fluorides need not be regarded as crumbling molecules from

which devastatingly exothermic reactions must always occur on contact with less exotic materials. On the contrary xenon difluoride appears to be rather inert when compared with many halogen fluorides for example.

It is surprising that so little work has appeared in the literature on the use of xenon difluoride as a fluorinating agent, particularly towards organometallic compounds. Xenon difluoride is admittedly expensive, indeed the quantities used in this work were kept as low as possible for this very reason, nevertheless conversion of oxidation state by fluorine addition could well succeed with xenon difluoride where other fluorinating agents may fail due to deleterious side reactions. One could not wish for a more inert (?) by-product than gaseous xenon. In large scale operations a recycling of xenon would be entirely feasible.

Finally it is intriguing to this author to suggest that reaction of xenon difluoride with suitable organosilicon derivatives may be a source of future xenon compounds. Who would care to predict, for example, the outcome of the reaction of xenon difluoride with recently synthesised[205] trifluoro(trifluoromethyl)silane, CF_3SiF_3? A xenon-carbon (CF_3) bond may well be stable since the electronegativity of the trifluoromethyl group is quite close to that of fluorine; in addition it is interesting to note that the trifluoromethyl group in CF_3SiF_3 behaves in an analogous manner to chlorine in organosilicon chlorides with respect to ease of nucleophilic displacement.

CHAPTER 4

FLUORINE EXCHANGE STUDIES - EXPERIMENTAL

4.1 GENERAL

This portion of the thesis deals with the study of fluorine exchange in solution by the dynamic n.m.r. method. Since this was, in main part, a study in the effect of traces of water on particular systems it was essential that the utmost precautions be taken at all times to avoid exposure of the materials and solvents to possible sources of moisture contamination. The particular methods used to handle and prepare samples will be given in the experimental sections; however standard vacuum line techniques were used throughout, the entire glass vacuum manifold was presilylated with hexamethyldisilazane or N,N-diethylaminotrimethylsilane (30 min. at 150^{o} then 48 hours at 20^{o}) and thoroughly flamed out under vacuum prior to use. Hexamethyldisilazane was found to be preferable to other common silylating agents such as trimethylchlorosilane or dimethyldichlorosilane since smaller quantities of residues were left on the glassware after the flaming out procedure.

Precautions were taken in the n.m.r. studies of phosphorus pentafluoride since the critical temperature of this material is below room temperature and total vapourisation of the samples occurred on warming to $+20^{o}$. A maximum of 25 atmospheres was considered tolerable

for a flame sealed n.m.r. tube and this corresponds to 0.2 to 0.3 g of phosphorus pentafluoride. N.m.r. tubes while in the spectrometer were maintained at least 20^{o} below a laboratory pretested temperature to avoid sample breakage under pressure while in the probe.

4.2 THE DYNAMIC N.M.R. METHOD

Calculation of Pre-exchange Lifetime, τ, for the Collapse of a Spin-Spin Doublet

The multiplet structure and line shapes of nuclear magnetic resonance spectra can be altered by two fundamentally different types of processes occurring at suitable rates. Intermolecular exchange of nuclei possessing spin as a general rule may lead to collapse of spin-spin multiplets while intramolecular motions such as rotations, ring inversions, etc., may produce coalescence of peaks due to the equilibration of otherwise magnetically non-equivalent nuclei.[60-62] In more complex cases both effects may occur at the same time and density matrix methods are necessary to interpret the resulting line shapes[206]; this will not be discussed further.

The quantitative expressions used to determine characteristic line shapes in nuclear magnetic resonance spectra were originally developed by Bloch[207] from macromolecular considerations of assemblies of spins in a magnetic field; the so-called phenomenological Bloch equations have remained the basis of line shape analysis since that time. For a full description of the Bloch equations and their applications

to n.m.r. line shapes the reader is directed to ref. 58.

Gutowsky, McCall and Slichter modified the original Bloch equations to take into account the effects of relaxation due to chemical exchange.[208] The original theory was modified several times and was finally used to determine the rate of C-N bond rotation in N,N-dimethylformamide using the collapse of the singlets due to the uncoupled, magnetically non-equivalent, methyl groups.[209] The rate of rotation was governed by a lifetime 2τ s. obtainable from analysis of the line shape. (In the literature one may find rates and rate constants related to 2τ or τ, this apparent confusion is only the result of different definitions for τ.)[210]

The lifetime 2τ s. may be related to the rate constants by the following arguments.[211] For an m^{th} order effect in a species I in solution one may write:

$$\frac{-d[I]}{dt} = k[I]^m$$

But 2τ has units of seconds and is a measure of a rate, hence it is intuitively obvious that:

$$\frac{1}{2\tau} = \frac{-1}{[I]} \cdot \frac{d[I]}{dt} \qquad s^{-1}$$

and therefore,

$$\frac{1}{2\tau} = k[I]^{m-1} \qquad s^{-1}$$

for m=1, i.e. for most bond rotations, ring flexing, pseudorotations, etc.

$$\frac{1}{2\tau} = k$$

The observed n.m.r. spectrum is independant of the concentration of species I.

Berger et al.[212] showed that essentially identical expressions to those derived by Gutowsky and co-workers could be used to investigate the spin-spin doublet collapse of the methyl group in N-methylacetamide due to exchange of the proton on the nitrogen atom. There is no difference between the collapse of an uncoupled A B spectrum and the collapse of a spin-spin doublet provided statistical factors are taken into account.[62]

Thus in the exchange of fluorine on trimethylfluorosilane the doublet in the proton spectrum collapses to a singlet; however a fluorine may leave the molecule in either a $+\frac{1}{2}$ or $-\frac{1}{2}$ spin state (since ^{19}F has $S = \frac{1}{2}$) and an incoming fluorine will have a 50% chance of being in the same spin state. No net change will occur unless there is a change in spin state for the system, i.e. only a fluorine replaced by another fluorine of different spin state will be effective in collapsing the

doublet.[210] These effects have been summarised by Ham and Mole,[67] they write a full rate expression as follows:

$$(f_i \tau_i)^{-1} = k[I]^{n-1} F[\text{other species}]$$

f_i = the appropriate statistical factor, = ½ for a ^{19}F exchange.

$F[\text{other species}]$ = dependance of the rate on other species present, a common occurrence for intermolecular exchange.

$\tau_i = 2\tau$, where τ_i is the pre-exchange lifetime for a hypothetical intramolecular exchange (see later).

$I = (CH_3)_3SiF$

In 1958 McConnell[213] simplified the Bloch equations making their use considerably less cumbersome in the prediction of line shapes of n.m.r. spectra. The McConnell formulation of the Bloch equations was used as a basis for the "four-site" computer programme written by B.Goodwin of this department and was used to determine pre-exchange lifetimes of the fluorine on trimethylfluorosilane. The programme was essentially the analysis of an uncoupled four-site A,B,C,D exchange, sites C and D were made non-effective by the insertion of suitable parameters. The input for the programme was:

(i) The separation of A and B (i.e. J for a spin-spin doublet) = 7.50Hz for $(CH_3)_3SiF$.

(ii) A relaxation time T_2^* obtained from the half height width of one component of the doublet of $(CH_3)_3SiF$ in the absence of exchange.

(iii) A τ value corresponding to τ_{AB}.

The data printout gave, for the particular τ value inserted:

(i) Peak separation at intermediate exchange rates.

(ii)Ratio of maximum to minimum peak intensities (i.e. peak to valley ratio).

(iii) Half height widths of partially collapsed doublets.

(iv) Half height widths of the singlet in the region of rapid exchange.

The programme definition for τ_{AB} was such that :

$$k_{\substack{\text{intramolecular} \\ \text{exchange}}} = \frac{1}{2\tau_{AB}} = \frac{1}{2\tau}$$

therefore $$(f_i\tau_i)^{-1} = \frac{1}{\bar{\tau}}$$

therefore $$\frac{1}{\bar{\tau}} = k\left[(CH_3)_3SiF\right]^{m-1} F\left[\text{other species}\right]$$

As will be shown $F\left[\text{other species}\right]$ may be written as $\left[(C_2H_5)_2NH\right]^p \left[H_2O\right]^n$.

$$\frac{1}{\tilde{\tau}} = k\left[(CH_3)_3SiF\right]^{m-1}\left[(C_2H_5)_2NH\right]^{p}\left[H_2O\right]^{n}$$

where $\tilde{\tau} = \tilde{\tau}_{AB}$ in the computer programme.

The determination of $\tilde{\tau}$ values for a simple collapse of the spin-spin doublet of $(CH_3)_3SiF$ is entirely feasible provided the concentration of any other species containing the $(CH_3)_3Si-$ group involved in the exchange is low; this was found in practically all instances (see later). If the concentration of such a species was high, one would be entering the area of simultaneous collapsing and coalescing of a spin-spin doublet and a second magnetically non-equivalent $(CH_3)_3Si-$ group, and a simple treatment would not be adequate.

4.3 INSTRUMENTAL

The instrumental requirements were, in general, as found in section 2.2 except for the following. A Varian temperature controller was used to modify the probe temperatures of the A56/60 n.m.r. instrument from -90^{o} to $+55^{o}$ as required. Actual temperatures were determined by the method of Van Geet[214] using the chemical shift difference between the -OH and $-CH_3$ signals in methanol. Temperatures were judged to be accurate optimistically to $\pm1^{o}$ but more realistically to $\sim\pm2^{o}$.

A few comments concerning the operation of the A56/60 spectrometer are warranted in view of the difficulties encountered. A sweep

width of 1.0 Hz cm^{-1} was necessary to study the collapse of the doublet in trimethylfluorosilane. The exact chemical shifts of the components of the doublet were very sensitive to several factors and precautions had to be taken to ensure instrumentally reproducible spectra. The chemical shifts were very sensitive to both sample and magnet temperatures; samples were allowed to stand at least 5 minutes in the probe to reach a stable temperature. Any deviation from a constant magnet temperature produced significant changes in peak positions; the Varian A56/60 instrument was operated in a non-airconditioned room with a relatively exposed magnet pole and probe area and, despite a water cooled magnet system, shifts of 0.1 Hz min^{-1} were not uncommon when running spectra. During the course of a slow sweep covering the trimethylfluorosilane doublet (15 Hz at 0.1 Hz s^{-1}) shifts of as much as 0.3 Hz were experienced leading to errors in observed peak separations, line widths, etc.

A sample was always maintained at a constant spinning rate while running a spectrum since an unexplained upfield shift of 0.1 to 0.5 Hz could occur by simply increasing the spinning rate; this phenomenon was variable and as far as possible kinetic runs were avoided when this effect was in operation.

Another serious disadvantage of the A56/60 instrument for accurate kinetic studies was the lack of an internal frequency locking mode. The external frequency lock utilised meant a slightly less stable field, an oscilloscope was found particularly useful in judging the "quality"

of the external lock. The best external lock was achieved, as might be expected, under conditions of maximum field homogeneity.

4.4 CHEMICALS

Acetonitrile (M.C.B. Spectroquality) was refluxed over phosphorus pentoxide and stored over fresh phosphorus pentoxide in the vacuum manifold. Diethylamine (Fisher, reagent grade) was redistilled twice and stored over sodium amalgam in the vacuum manifold. Trimethylfluorosilane (P.C.R.) was condensed onto activated molecular sieves and stored in the vacuum manifold at 0^{o}. Activated molecular sieves did not appear to have any serious deleterious effect on trimethylfluorosilane and there was some evidence that ex-cylinder trimethylfluorosilane did contain a trace of moisture. After standing for some time over molecular sieves traces of hexamethyldisiloxane were observed in samples of trimethylfluorosilane condensed directly into n.m.r. tubes. Tetraethylammonium fluoride (P.C.R.) was found to be very deliquescent and was pumped on at $\sim 80^{o}$ for 1 hour before use. Diethylammonium fluoride was obtained by the neutralisation of a methanolic solution of diethylamine with aqueous hydrogen fluoride[72] using a pH meter. The resulting solution was pumped on until a pale brown oil remained, dry methanol was repeatedly added and pumped off and the procedure was repeated with methylene chloride. A crystalline product could not be obtained; the brown, very viscous, oil was finally dried by pumping at 80^{o} for 24 hours.

Methylene chloride (Fisher certified grade) contained 0.02% water and further drying was not attempted. Commercial finely divided silica was washed with methanol before use. Tetra-n-propylammonium hydroxide (Eastman, 10% solution in water) was used as received, as was hydrogen fluoride (Fisher, reagent grade 49%), adequate safety precautions being taken at all times. Methyltrifluorosilane (P.C.R.) was passed over activated molecular sieves prior to use, the n.m.r. spectrum revealed a faint trace of dimethyldifluorosilane. Diphenyldifluorosilane contained a white residue when received and was redistilled prior to use although traces of what seemed to be an identical precipitate soon formed in the distillate.

Phosphorus pentafluoride (P.C.R.) was found to contain a trace of POF_3 but was used without further purification. Diethylether (Fisher anhydrous) was used from a freshly opened can without treatment. Phenyltetrafluorophosphorane was obtained by the reaction of phenyldichlorophosphine (M.C.B.) with antimony trifluoride.[137] A vigorous exothermic reaction occurred and metallic antimony was observed, the product was redistilled into a presilylated glass bulb and stored at -10^{o}. A ^{19}F n.m.r. spectrum of the product compared well with the literature[60] and only a trace of phenyldifluorophosphine oxide was observed. The quantity of the phosphine oxide increased on lengthy storage of the sample.

4.5 EXPERIMENTAL - DETAILS

Hydrolysis of Trimethylfluorosilane Studied by the Dynamic N.M.R. Method

N.m.r. tubes attached to ground glass joints were dried by standing in a muffle furnace at 400° for at least 6 days prior to use; using this technique presilylation of the tubes was found to be unnecessary. Acetonitrile, diethylamine and trimethylfluorosilane were all condensed into the n.m.r. tubes at -196° directly from over their drying agents in the vacuum manifold. The approximate quantities of each material used could be gauged from pressure measurements.

The n.m.r. tubes were flame sealed at -196° and allowed to warm to room temperature, the contents were shaken to ensure complete mixing. The concentrations of the materials were determined by repeated integration of the ^1H n.m.r. spectra; at least five integrations for all three components were taken. The concentrations could be calculated directly from the integrations, neglecting volume changes due to mixing.* The concentrations were estimated to be accurate to ±5-10% when determined by this technique.

The ^1H n.m.r. spectra of such solutions revealed a sharp doublet at -0.3 p.p.m. due to trimethylfluorosilane, a singlet at -2.0 p.p.m. due to acetonitrile, a triplet at -1.0 p.p.m., J_{H-H}= 7 Hz, due to $(C\underline{H}_3CH_2)_2NH$, and a quartet at -2.6 p.p.m., J_{H-H}= 7 Hz, due to $(CH_3C\underline{H}_2)_2NH$. In addition a broad peak ($\delta_{\frac{1}{2}} \sim 5$ Hz) was observed from -1.1 to -0.8 p.p.m. depending on the concentration of diethylamine used,

* See Appendix II

this peak is assigned to $(CH_3CH_2)_2\underline{NH}$; the chemical shifts correspond very closely to those found by Springer and Meek in their study on the hydrogen bonding between diethylamine and acetonitrile.[215]

Water was introduced to the acetonitrile/diethylamine/trimethylfluorosilane mixtures via silicon rubber septum caps after cutting open the n.m.r. tubes. The water was usually introduced as a solution in acetonitrile using a pre-dried 10 μl syringe; 25% vol solutions were often used increasing the volume to be injected by four and correspondingly decreasing the error in injection technique. The solution was shaken well and the n.m.r. spectrum was re-examined. Introduction of traces of water led to sharpening of the N-H peak but more importantly a collapse of the spin-spin doublet due to trimethylfluorosilane was also observed. The amount by which the doublet collapsed was obviously dependant on the concentration of the various species present and a kinetic investigation was undertaken.

The complete n.m.r. spectral data for trimethylfluorosilane before and after addition of water is presented in table [3]. The exchange could be completely halted by syringing in small quantities of silicon-nitrogen compounds and shaking for a few seconds. Thus addition of N,N-diethylaminotrimethylsilane sharpened the doublet due to trimethylfluorosilane; diethylamine and hexamethyldisiloxane were the only observed products.

Exchange on the n.m.r. time scale was also halted by the addition of ~0.1 g of activated molecular sieves. The molecular sieves were particularly effective if added within half an hour

Sample Preparation	^1H spectrum			^{19}F spectrum		
	δ p.p.m.	J_{H-F}(Hz)	$J_{H-^{29}Si}$(Hz)	δ p.p.m.	J_{F-H}(Hz)	$J_{F-^{29}Si}$(Hz)
(a) Degassed 0.5 M solution in acetonitrile containing 0.4 M diethylamine.	-0.28 ±0.01	7.50 ±0.02	7.00 ±0.02	+156.1 ±0.1	7.50 ±0.02	270 ±5
(b) Sample (a) after addition of sufficient water to collapse the proton doublet to a sharp singlet.	-0.28 ±0.01	not observed	7.00 ±0.02	+156.0 ±0.5 very broad	not observed	not observed

Table [3]. N.M.R. Data for Trimethylfluorosilane

after the addition of water.

If a sample containing sufficient water to just collapse the trimethylfluorosilane doublet was allowed to stand the following observations were made:

(i) The observed rate of exchange slowly increased although it remained effectively constant for up to one hour after initial addition of water.

(ii) A small peak due to hexamethyldisiloxane (confirmed by comparison with an authentic sample) was observed after a few hours, the intensity of the peak grew with time.

(iii) After standing >1 week at $+20^{o}$ hexamethyldisiloxane was a major product and the remaining trimethylfluorosilane was present as a sharp singlet. Small quantities of crystalline materials could be obtained by pumping off volatile materials, adding small quantities of methylene chloride, and cooling to -10^{o}. The crystalline material analysed as C 44.0%, H 11.8%, N 12.70%.

It was clearly necessary to run kinetic studies as quickly as possible after addition of water and certainly not after a time lapse of more than 15-20 minutes. The experimental details of the kinetic investigations are as follows:

Determination of Order w.r.t. Trimethylfluorosilane

Eight determinations were made at $+38^{o}$ with a constant water and diethylamine concentration. Constant diethylamine concentrations

were ensured by condensing as close as possible to the same quantities of diethylamine into each tube. Nevertheless some 25% of the samples made up in this manner were rejected that were not within 10% of the mean concentration of diethylamine (0.67 M). Four runs with trimethylfluorosilane concentration ~1.0 M give some idea as to the scatter of points that might be expected in these experiments. A wide range of trimethylfluorosilane concentration from 0.2 to 3.1 M was covered; the experimental results were indirectly confirmed by all the subsequent kinetic runs where $[(CH_3)_3SiF]$ was varied randomly.

Determination of Order w.r.t. Diethylamine

Three separate series of experiments were made at three different water concentrations; the trimethylfluorosilane concentration was varied randomly. The rate of exchange was found to be poorly reproducable beyond ~1.5 M diethylamine concentrations; the samples seemed particularly sensitive to several factors. Good data could be obtained with $[(C_2H_5)_2NH] <$ 1.0-1.5 M however.

Determination of Order w.r.t. Water

Four separate series of experiments were made at four different diethylamine concentrations. Since addition of water and running each spectrum took 5-10 minutes the results are subject to some error since experiments were often completed approximately one hour after the first addition of water. A slight cloudiness was observed in the run where $[(C_2H_5)_2NH]$ = 4.66 M after addition of ~0.04 M H_2O;

production of some hexamethyldisiloxane in this sample was also observed in the n.m.r. spectrum at approximately the same stage of water addition.

Effect of Temperature on Rate of Exchange

Some six runs were made varying diethylamine, trimethylfluorosilane and water concentrations. The temperature dependancy of the exchange was very odd since a rate increase occurred on initial cooling followed by the more normal rate decrease on further cooling. The spectra were reproducible on warming provided the temperature run was not allowed to take $> 1\frac{1}{2}$ hours to complete. Attempts to extend the study to higher temperatures ($>60^{o}$) were not successful since non-reversibility was generally encountered on recooling.

In certain runs a very small, quite broad, peak appeared at low temperature at $\sim$-0.08 p.p.m.; this very small peak seemed to coalesce into the collapsing doublet on warming. This second peak was identified as trimethylsilanol by careful comparison with the spectrum of a authentic sample (prepared by hydrolysis[216] of trimethylchlorosilane). A particularly careful examination was needed since trimethylsilanol when dissolved in acetonitrile showed a surprisingly large chemical shift on cooling to -44^{o}. The small peak due to trimethylsilanol in the exchanging system was never observed at higher ($>-10^{o}$) temperatures.

In addition to the kinetic studies several qualitative studies

were made to clarify the mechanism of exchange. Thus the effect of several sources of fluoride ion on trimethylfluorosilane in acetonitrile was studied.

(i) Addition of ammonium fluoride in quantities of ~ 0.05 g did not cause exchange on the n.m.r. time scale; ammonium fluoride appeared to be partially soluble in acetonitrile. Standing for >2 weeks did not produce any exchange broadening of the trimethylfluorosilane doublet.

(ii) Addition of ~0.2 M aqueous sodium fluoride did not have a marked effect on the trimethylfluorosilane doublet provided less than ~10 μl of the solution was added. However blank runs indicated that similar quantities of water (~ 10 μl, corresponding to ~2.0 M H_2O) produced slight exchange without the presence of F^-.

(iii) Addition of aqueous HF (0.3 ml) to neat trimethylfluorosilane (0.2 ml) in a teflon n.m.r. tube produced no collapse of the trimethylfluorosilane doublet.

(iv) Addition of tetraethylammonium fluoride (0.01 g, 0.067 mmoles) was effective in collapsing the doublet to a broad singlet. The volume of the solution was 0.3 ml, therefore the concentration of tetraethylammonium fluoride (completely soluble in acetonitrile) was approximately 0.22 M. Addition of N,N-diethylaminotrimethylsilane (0.15 mmoles) did not stop the exchange; tetraethylammonium fluoride did not react with silicon nitrogen compounds.

(v) Addition of diethylammoniun fluoride (approx. 0.4 mg) to a solution

of trimethylfluorosilane in acetonitrile (0.4 ml) did not produce any exchange, however addition of 0.01 g was sufficient to collapse the doublet. Addition of N,N-diethylaminotrimethylsilane in excess stopped exchange, the products were trimethylfluorosilane, diethylamine and always a trace of hexamethyldisiloxane. The reaction of diethylammonium fluoride with silicon-nitrogen compounds was also checked in a series of separate experiments. Thus diethylammonium fluoride (19 mg, 0.2 mmoles) reacted smoothly with N,N-diethylaminotrimethylsilane (30 mg, 0.21 mmoles) in acetonitrile (0.3 ml) over a period of 3 minutes to yield trimethylfluorosilane and diethylamine in quantitative yield.

The effect of hydroxide ion sources on the proton n.m.r. spectrum of trimethylfluorosilane in acetonitrile was also studied.

(i) Trimethylfluorosilane and acetonitrile were condensed onto thoroughly dried solid sodium hydroxide in an n.m.r. tube. Very rapid production of hexamethyldisiloxane (or perhaps $(CH_3)_3SiO^- Na^+$) was observed at $+38^o$; the reaction was complete within 3 minutes. Repeating the study at $+10^o$ allowed the reaction to occur smoothly to completion over a period of 10 minutes, a 2:1 excess of trimethylfluorosilane was used in this experiment. No collapse of the trimethylfluorosilane proton n.m.r. doublet was observed during the course of the reaction.

(ii) Since the reaction described in (i) was essentially heterogeneous it was decided to study the addition of aqueous sodium

hydroxide (0.5 M) to trimethylfluorosilane in acetonitrile. No cloudiness was observed on addition of the alkali solution hence the reaction was assumed to be homogeneous. Again at $+38^{o}$ condensation to hexamethyldisiloxane was fairly rapid;however at 0^{o} the condensation was very slow.

Some other general experiments were carried out on the base catalysed exchange of fluorosilanes in acetonitrile. Thus the same type of base catalysed exchange was found with dimethyldifluorosilane and methyltrifluorosilane, the rate appeared to increase with decreasing number of alkyl groups. Triethylamine was also a very effective base for the catalysed exchange while pyridine appeared less effective.

Trimethylfluorosilane was also found to show base catalysed exchange in other solvents although there was some apparent variation in rate. For example the rate in methylene chloride was appreciably slower although water is very nearly insoluble in this solvent.

Five Coordinate Silicon - Exchange Studies

The compounds $\left[(n\text{-}C_3H_7)_4N\right]\left[SiF_4CH_3\right]$ and $\left[(C_2H_5)_4N\right]\left[SiF_3(C_6H_5)_2\right]$ were prepared by the method of Klanberg and Muetterties[72]. Further details will not be given since the experimental technique was almost identical.

The compound $\left[(n\text{-}C_3H_7)_4N\right]\left[SiF_4CH_3\right]$ showed, in methylene chloride solution, equivalent fluorines in the ^{19}F n.m.r. spectrum down to -90^{o} when the solution began to freeze. As found previously[72] coupling

to the methyl group (J_{F-H}= 4.8 Hz) was observed although broadening of both the ^{19}F and $^{1}H(C\underline{H}_3)$ n.m.r. spectra occurred on warming the sample towards room temperature. Addition of a drying agent hexamethyldisilazane did not have a dramatic effect on the spectra; however spectra reported by Klanberg and Muetterties at -58° were found to be easily reproducible at -40° and considerable improvement in the proton spectrum was observed.

The compound $\left[(C_2H_5)_4N\right]\left[SiF_3(C_6H_5)_2\right]$ showed, in methylene chloride solution, two fluorine environments in the n.m.r. spectrum at $<$-50°, the integrations were 2:1 respectively. Considerable sharpening of the peaks occurred on cooling further; addition of hexamethyldisilazane as a drying agent had only a marginal effect on the spectra.

The bulk of the work on five coordinate silicon was carried out on the pentafluorosilicate compound, $\left[(n\text{-}C_3H_7)_4N\right]\left[SiF_5\right]$. The preparation of the pentafluorosilicate compound was interesting in view of the extreme sensitivity of the intermediates to pyrex glass and is reported in some detail.

The basic technique used to synthesise tetra-n-propylammonium pentafluorosilicate was as described by Clark and co-workers[173]. Silica (2.0 g, 33 mmoles), tetra-n-propylammonium hydroxide (0.55 g, 2.7 mmoles as a 10% solution in water), methanol (25 ml) and hydrogen fluoride (excess) were mixed in a polypropylene container. Methanol was repeatedly added to aid the evaporation of water and hydrogen fluoride; the silica dissolved over a period of 6 hours to give a

clear colourless solution. It was found that the solution was very reluctant to evaporate to dryness on its own, too great an excess of hydrogen fluoride presumably had been used. The resulting solution was taken up in methanol (50 ml) and rapidly evaporated to dryness under vacuum in a pyrex flask; the product was dry within 10 minutes. A white solid remained that was recrystallised from hot chloroform/ethyl acetate to give white needle-like crystals, m.p. 244.5-245.5°, yield 0.52 g.

The melting point was sharp and did not correspond to that of the pentafluorosilicate, neither did the infra red spectrum which also indicated that the product was not a hexafluorosilicate derivative.[173] The infra red spectrum did indicate, however, that the product may contain the BF_4^- ion, particularly in view of a strong band at 1050-1095 cm^{-1}.[217] The product was readily soluble in organic solvents and was even sparingly soluble in water without apparent serious decomposition. The ^{19}F n.m.r. spectra in acetonitrile and water are shown in figure [11] and show the compound to be $[(n\text{-}C_3H_7)_4N][BF_4]$. Coupling to the ^{11}B nuclei (81% abundance, $S = \frac{3}{2}$) was clearly visible while the coupling to the ^{10}B nuclei (19% abundance, $S = 3$) was not resolved; the ^{10}B-^{11}B isotope shift was clearly seen in acetonitrile solution but was partially masked in water. The coupling constant ($J_{F-^{11}B}$) was found to be variable with concentration but was ~0.6 Hz in acetonitrile and ~1.3 Hz in water. This is in general agreement with an n.m.r. study by Kuhlmann and Grant.[218] The proton spectrum

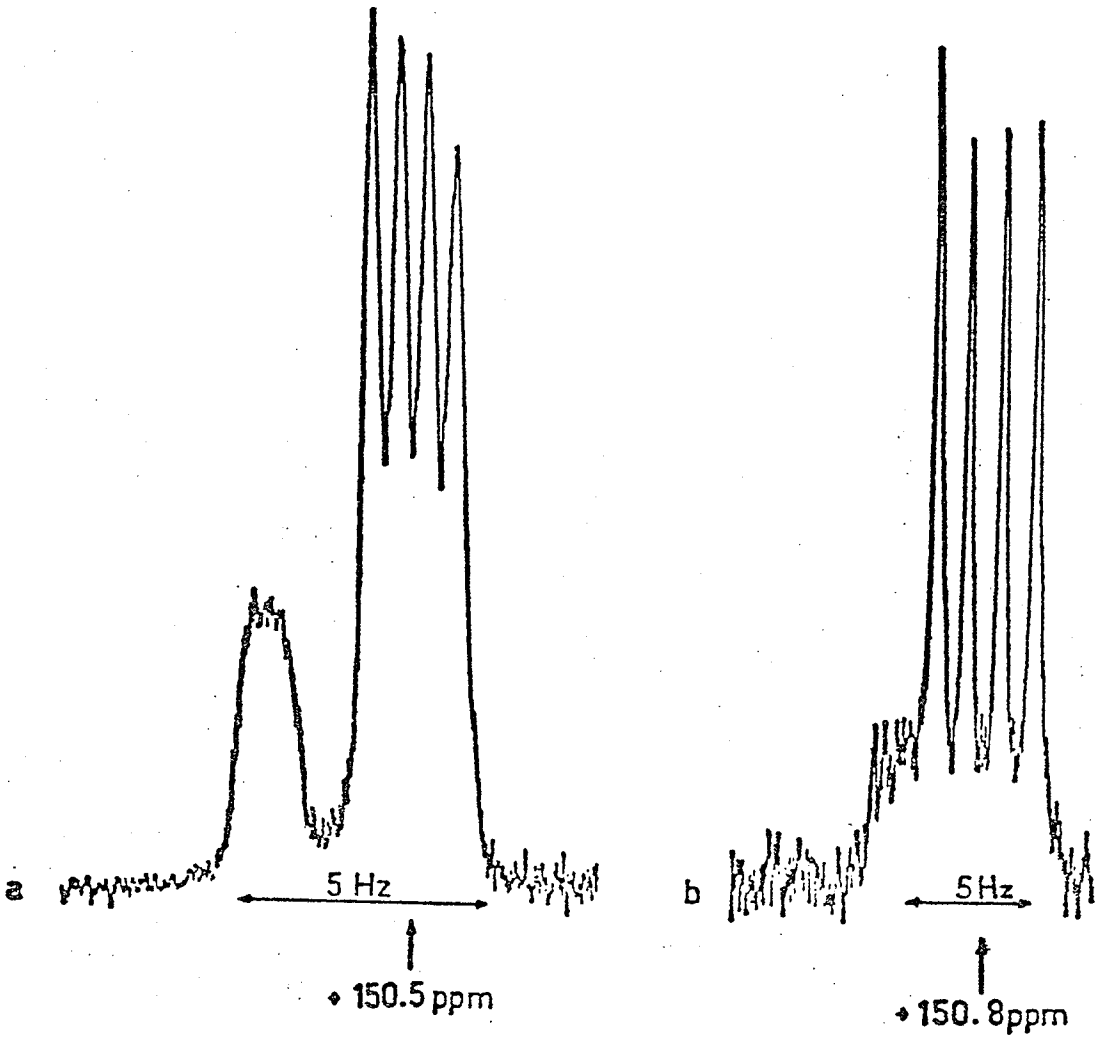


Figure [11]. ^{19}F N.M.R. Spectra of $[(n\text{-}C_3H_7)_4N][BF_4]$

(a) In Acetonitrile

(b) In Water

revealed a characteristic tetra-n-propylammonium spectrum with $\delta_{\underline{CH}_3CH_2CH_2-}$ = -0.9 p.p.m., $\delta_{CH_3\underline{CH}_2CH_2-}$ = -1.6 p.p.m. and $\delta_{CH_3CH_2\underline{CH}_2-}$ = -3.1 p.p.m. There seemed to be considerable ^{14}N-^{1}H interaction due to the high symmetry of the cation.

Repeating the synthesis using all polypropylene equipment except for a very short length of pyrex tubing once again gave the tetrafluoroborate as the major product.

The reaction of the tetrafluoroborate ion with silicon-nitrogen compounds was tried in an attempt to synthesise $BF_3NR_2^-$ derivatives. No reaction occurred between tetra-n-propylammonium tetrafluoroborate and N,N-diethylaminotrimethylsilane even on standing for two weeks.

The pentafluorosilicate salt could only be prepared using a <u>completely</u> pyrex free system. Traces of hydrogen fluoride, methanol and water were removed from the crude product by pumping on the sample in a polypropylene tube attached via a neoprene stopper to a tygon vacuum tube. High yields of crude material, m.p. 203-206°, were obtained and recrystallisation from hot chloroform/ethyl acetate gave small white crystals, m.p. 208-209°, (c.f. m.p. 207.5-208.5° reported by Clark et al.)[173]. Once obtained in this form solutions of the pentafluorosilicate in dry solvents did not appear to attack glass to any noticeable extent, nevertheless crystalline samples were stored under vacuum in a polypropylene tube prior to use. The purity was also checked by infra red spectroscopy; the product, in nujol mull, showed bands at 874 cm^{-1} (vs), 782 cm^{-1} (vs), 480 cm^{-1} (s) and 449 cm^{-1} (s).

The infra red spectrum was identical to that reported by Clark.[173]

The proton n.m.r. spectrum in methylene chloride showed once again the characteristic tetra-n-propylammonium spectrum, $\delta_{\underline{CH}_3CH_2CH_2}$ = -0.95 p.p.m., $\delta_{CH_3\underline{CH}_2CH_2}$ = -1.55 p.p.m. and $\delta_{CH_3CH_2\underline{CH}_2}$ = -3.05 p.p.m. Examination of an approximately 1 molar solution of tetra-n-propylammonium pentafluorosilicate by ^{19}F n.m.r. spectroscopy revealed the characteristic singlet at +136.7 p.p.m.; the chemical shift compares well with the literature.[72] The half height line width at +38° was ~6-7 Hz and no F-^{29}Si coupling was observed, (^{29}Si has an abundance of 4.67%). On cooling the sample essentially the same effects as described by previous workers were found.[72] Thus at -60° ^{29}Si satellites became visible ($J_{F-^{29}Si}$ = 145±5 Hz); the half height width of the central peak at -60° was ~4 Hz; on cooling to -90° no splitting into axial and equatorial fluorine environments took place and the signal, with ^{29}Si satellites, remained sharp.

The effect of adding the drying agent hexamethyldisilazane in trace amounts (5-10 μl) to the solution at -60° was interesting. Considerable improvement in resolution took place, the half height width of the singlet decreased to ~3 Hz and the ^{29}Si satellites became much more pronounced.

The effect of adding hexamethyldisilazane to a solution at +38° was even more startling. Small quantities of hexamethyldisilazane were syringed into the solution through silicon rubber septum caps. The n.m.r. tube was shaken for a few seconds and the spectrum re-

examined under conditions of high gain. A doublet ($J_{F-^{29}Si}$ = 145±5 Hz) appeared as satellites to the considerably sharpened central resonance. Addition of water by the same technique caused broadening of the peak and the satellites disappeared. The high gain spectra were run without spinning of the sample tube, with fast sweep (4 Hz s^{-1}), high band width (4 Hz) and high Rf power. Spectra run under these conditions gave poor resolution but much improved signal to noise and no confusion with spinning side bands could occur.

Spectra showing ^{29}Si side bands could be obtained directly by pretreatment of the methylene chloride solvent with hexamethyldisilazane prior to dissolution of the salt. Tetra-n-propylammonium pentafluorosilicate was recovered unchanged at the end of the experiments; the pentafluorosilicate proved unreactive towards silicon-nitrogen compounds even on standing for some time. The addition of hexamethyldisilazane did produce a very small extra peak at +126 p.p.m., visible at low temperature. The origin of this resonance was not investigated further. Pretreatment of the pentafluorosilicate with hexamethyldisilazane and distilling the methylene chloride off a mixture with hexamethyldisilazane onto the pentafluorosilicate gave spectra identical to those obtained by direct addition of silazane to a methylene chloride solution. Cooling a "dried" solution from $+38^{o}$ to -90^{o} did not alter the spectrum significantly, $F-^{29}Si$ coupling was maintained throughout the whole temperature range.

The interaction of Lewis bases with tetra-n-propylammonium

pentafluorosilicate was studied by ^{19}F n.m.r. spectroscopy. Thus diethylamine (0.083 g, 1.13 mmoles) was added to a solution of $[(n\text{-}C_3H_7)_4N][SiF_5]$ (0.113 g, 0.36 mmoles) in CH_2Cl_2 (0.35 g). A small quantity of hexamethyldisilazane (0.0032 g, 0.02 mmoles) was added to ensure dryness of the system. An immediate downfield shift due to the presence of diethylamine was observed, for example at $+30^o$ the chemical shift was +133.7 p.p.m., a downfield shift of 3.0 p.p.m. from a sample containing no diethylamine. A temperature study was undertaken over the range $+40^o$ to -80^o; the singlet shifted downfield on cooling, reaching ~+126 p.p.m. at -65^o. Cooling from -65^o to -80^o produced no further shifting of the resonance.

Addition of water (0.01 g, 0.56 mmoles) to a typical solution of tetra-n-propylammonium pentafluorosilicate in methylene chloride also produced shifting and broadening of the SiF_5^- resonance. In this case loss of F-^{29}Si coupling was also, of course, observed and side reactions with this quantity of water present were also apparent. The study was not pursued further.

Addition of a large quantity of a weak base such as hexamethyldisilazane produced a downfield shift of the singlet at low temperatures although the effect was much less marked than with diethylamine.

Phosphorus Fluorides - Intramolecular Exchange Studies

The possibility that water acts as a Lewis base towards phosphorus (V) fluorides providing a low energy pathway to intramolecular exchange

was considered, efforts at reducing trace water concentrations are reported.

Phenyltetrafluorophosphorane in methylene chloride solution exhibited a simple doublet, δ = +55.6 p.p.m., J_{F-P} = 960 Hz, consistent with reported values.[60] The doublet was maintained over the range $+45^{o}$ to -95^{o} with little apparent change; treating solutions of phenyltetrafluorophosphorane with hexamethyldisilazane did not have significant effects on the ^{19}F n.m.r. spectrum.

Attempts to pretreat the phenyltetrafluorophosphorane with the silazane and then redistilling the phosphorane directly into the n.m.r. tube also failed to alter the spectrum in any significant manner. Similarly presilylating the n.m.r. tube and thorough drying of the methylene chloride solvent over activated molecular sieves also failed. None of the many experiments tried had any marked effect whatsoever on the simple doublet exhibited by the phenyltetrafluorophosphorane.

Many experiments were also tried with phosphorus pentafluoride in an attempt to "dry" this reactive fluoride. A procedure used by Ibbott[87] for sulphur tetrafluoride, where the fluoride was allowed to react in excess with hexamethyldisilazane followed by condensation of the products (including excess SF_4) into an n.m.r. tube, was tried. Phosphorus pentafluoride appeared very reactive towards hexamethyldisilazane; condensation of the products, mainly excess PF_5 and some $(CH_3)_3SiF$, into an n.m.r. tube gave only a doublet for PF_5 down to -105^{o}.

Phosphorus pentafluoride in $CFCl_3$ solution exhibited a ^{19}F n.m.r. spectrum from -10^o to -90^o consisting of a doublet, δ = +75.5 p.p.m., J_{F-P} = 940 Hz, consistent with literature values[60]. Condensing a small amount of hexamethyldisilazane into such a solution and re-examining the spectrum showed no change in the doublet. Prior "drying" of the PF_5 with cesium fluoride followed by condensation into a presilylated tube also had no effect on the spectrum.

One gas phase n.m.r. study of phosphorus pentafluoride was tried; phosphorus pentafluoride (0.08 g, 0.7 mmoles) was condensed into an n.m.r. tube just "damp" with hexamethyldisilazane. Below -40^o only a doublet was observed, similarly at $+10^o$ only a sharp two line spectrum was observed. At -30^o, close to the vaporisation temperature, a remarkable spectrum was obtained consisting of some sixteen lines. The observed lines would not fit an AB_4X or A_2B_3X system and appeared to be an ABX spectrum overlaid by four A_nX type spectra (i.e. simple doublets where X is phosphorus).

The interaction of phosphorus pentafluoride with the weak base diethylether appears to have been studied only once by ^{19}F n.m.r. spectroscopy[219] and the results were vague; this system was restudied as a model of the interaction of Lewis bases with phosphorus pentafluoride.

Phosphorus pentafluoride (0.15 g, 1.3 mmoles) and diethylether (0.43 g, 5.8 mmoles) were condensed into a presilylated and flamed out n.m.r. tube at -196^o. The tube was flame sealed and allowed to warm to $+20^o$, the contents were shaken to ensure complete mixing of the components. A temperature dependant spectrum was observed on cooling from

-10^{o} to -65^{o}. An AB_4X spectrum was clearly observable at -65^{o} (a trace of POF_3 overlaid the A part) and the spectrum was assignable on a first order basis.

The proton spectrum over the same temperature range was unhelpful, the ethyl group resonances remained broad from -10^{o} to -65^{o} although at -65^{o} a second very broad ethyl group was observable downfield (~1 p.p.m.), this was assigned to diethylether complexed to phosphorus pentafluoride.

CHAPTER 5

FLUORINE EXCHANGE STUDIES - DISCUSSION

5.1 SCOPE OF THE DISCUSSION

The second section of this thesis is a demonstration of how rapid fluorine exchange problems may be misinterpreted mechanistically when all the data pertaining to a particular system not known. Thus commercial diethylamine added to a solution of trimethylfluorosilane in acetonitrile causes collapse of the trimethylfluorosilane doublet; what mechanism can account for this phenomenon? If it is not realised that commercial diethylamine contains a significant concentration of water then mechanisms may be invoked involving diethylamine and trimethylfluorosilane only, conclusions based on such reasoning would be in gross error. This thesis suggests a mechanism which is consistent with all the available data.

An extension of this reasoning is made to a system much more prone to intermolecular exchange. Fluorine exchange in pentafluorosilicates does not require base catalysis; revision and clarification of the mechanism of intermolecular exchange in this species is presented based on an improved understanding of the factors necessary in solution for such an exchange to be observed.

Finally some suggestions will be made concerning intramolecular exchange and how some mechanistic interpretations in the literature may be oversimplifications of a more complex phenomenon.

5.2 TRIMETHYLFLUOROSILANE

Collapse of the doublet of trimethylfluorosilane must be caused by an intermolecular exchange process involving either a silicon-fluorine or a silicon-carbon bond breaking step. The data presented in table [3], chapter 4, proves conclusively that the exchange under examination in this case involves a silicon-fluorine bond breaking step. Even under conditions of fast exchange H-^{29}Si coupling was observed hence a silicon-carbon bond cleavage cannot be occurring. Conversely the ^{19}F n.m.r. spectrum showed loss of F-^{29}Si coupling when exchange was occurring indicating an intermolecular fluorine exchange process.

The above seems reasonable in view of previous work; silicon-carbon bonds are thermodynamically and kinetically quite inert, bond breakage inevitably involves the use of powerful catalysts[67]. No silicon-carbon cleavage reactions have been recorded as occurring at a sufficiently fast rate to be studied by the dynamic n.m.r. method. This is in sharp contrast to other systems such as organo-lithium or organoaluminium compounds where rapid intermolecular exchange of alkyl groups is common.[65,220]

Most of the exchange studies on organo-silicon systems have involved redistribution reactions of halides, pseudohalides, alkoxides etc.[67], i.e. reactions of the type :

$$R_2SiX_2 + R'_2SiY_2 \rightleftharpoons R_2SiXY + R'_2SiXY$$

Even in these cases the reactions are often quite slow and are followed by "classical" n.m.r. kinetics, the formation of new compounds being studied by growth of new peaks in the proton n.m.r. spectrum. For example Moedritzer has studied redistribution equilibria of Cl, Br, I and OC_2H_5 substituents between methylsilicon and methylgermanium moieties.[221,222] The redistribution reactions were not fast however, at least 56 hours at 120° were required to achieve an equilibrium system interpretable by numerous equilibrium constants determined by simple integration of the resulting n.m.r. spectra of the mixtures.

$$(CH_3)_2SiX_2 + (CH_3)_2GeY_2 \xrightarrow[120^{\circ}]{56\ hrs} \text{equilibrated mixtures} \quad [221]$$

$$\text{or} \quad CH_3SiX_3 + CH_3GeY_3 \longrightarrow \text{equilibrated mixtures} \quad [222]$$

$$X \text{ or } Y = Cl, Br, I, OC_2H_5$$

Exchange studies accessible by the dynamic n.m.r. technique are much less common in the literature, however there are certain examples, notably involving silicon-metal bonds, that have been studied. For example tris(trimethylsilyl)thallium undergoes a bimolecular exchange.[223]

$$((CH_3)_3Si)_3Tl \rightleftharpoons$$

bimolecular exchange of $(CH_3)_3Si$ groups giving collapse of H-$^{203/205}$Tl doublets.

Similarly bis(trimethylsilyl)mercury undergoes a bimolecular exchange proposed to occur via an expansion of the coordination around silicon from four to five.[224]

A recent paper[225] describes halide exchange on silicon studied by the dynamic n.m.r. technique.

$$CH_3(CH_2Cl)Si(Cl)N(CH_3)_2 + (C_2H_5)_4N^+Cl^- \rightleftharpoons$$ rapid exchange of Cl on silicon.

The exchange was followed by collapse of the non-equivalent AB spectrum of the CH_2Cl- group which would occur during every S_N2-Si exchange at silicon.

There are no comparable studies in the literature of the type of exchange described in this thesis. Any mechanism proposed for the collapse of the spin-spin doublet of trimethylfluorosilane must be consistent with the observed kinetics and, in particular, consistent with the necessary presence of water for exchange to occur.

A plot of $\frac{1}{\tau}$ (s^{-1}) vs. $[(CH_3)_3SiF]$ (M) at $+38^o$ is shown in figure [12], the concentrations of diethylamine and water for these runs were 0.67 and 0.033 M respectively. Over the wide range of trimethylfluorosilane concentration studied the exchange rate appeared to vary very little. A least squares plot of ln $\frac{1}{\tau}$ vs. ln $[(CH_3)_3SiF]$ gave a slope of 0.05, i.e. $\frac{1}{\tau}$ is zero order in trimethylfluorosilane and hence from the expressions derived previously the overall rate of exchange in solution must be first order with respect to trimethylfluoro-

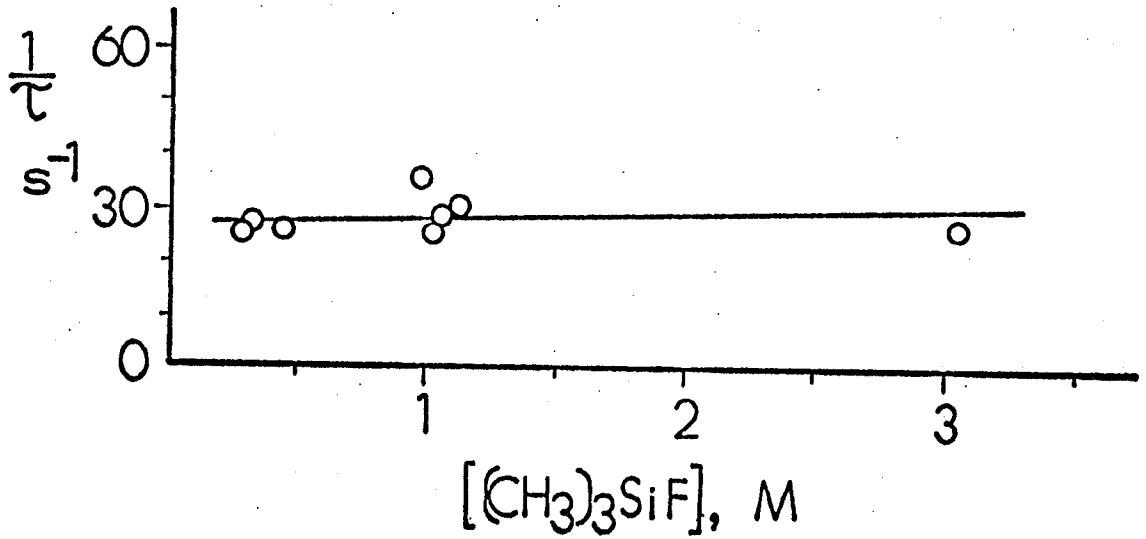
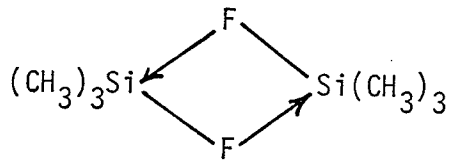


Figure [12]. Trimethylfluorosilane Exchange Study, Plot of $\frac{1}{\tau}$ (s^{-1}) vs. $[(CH_3)_3SiF]$

silane.

$$\text{Rate} \propto \left[(CH_3)_3SiF\right]^1$$

The first order dependancy immediately rules out any bimolecular pathway involving fluorine bridged intermediates, such mechanisms are common in the heavier group V fluorides.[60]



The exchange was base catalysed, plots of $\frac{1}{\tau}$ (s^{-1}) vs. $\left[(C_2H_5)_2NH\right]$ (M) at $+38^{o}$ are shown in figure [13]. Three series of runs were completed at the three different water concentrations shown. Trimethylfluorosilane concentration was not controlled and varied randomly from 0.16 to 0.79 M thus independently confirming the zero order $\frac{1}{\tau}$ dependance. As can be seen from figure [13] the results were generally good up to $\left[(C_2H_5)_2NH\right] \sim 1.5$ M but beyond this concentration reproducibility became difficult. Plots of $\ln \frac{1}{\tau}$ vs. $\ln \left[(C_2H_5)_2NH\right]$ for the three runs shown were least squares fitted over the range $\left[(C_2H_5)_2NH\right]$ $0 \rightarrow 1.6$ M. The results are given in table [4]. As indicated the slope of the natural log plot and hence the order with respect to diethylamine is n.

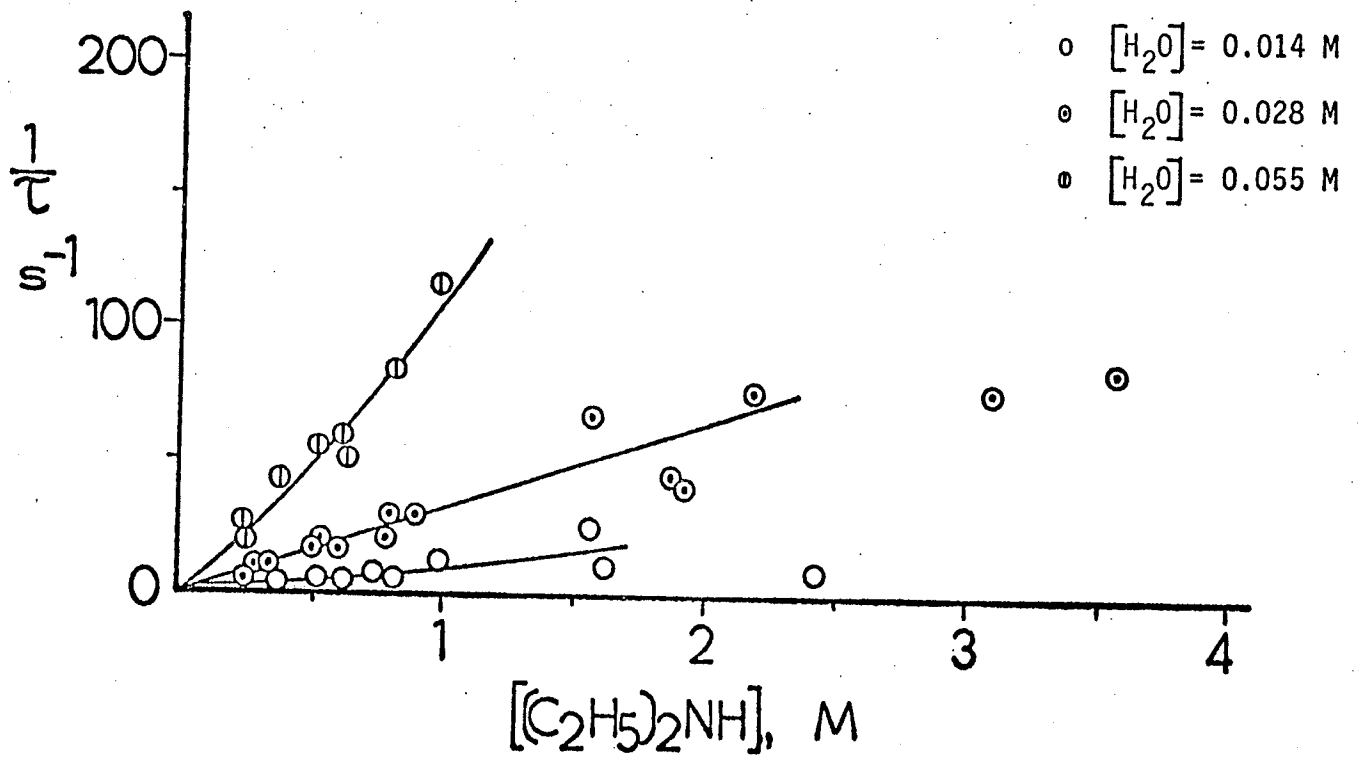


Figure [13]. Trimethylfluorosilane Exchange Study, Plot of $\frac{1}{\tau}(s^{-1})$ vs. $[(C_2H_5)_2NH]$.

$[H_2O]$ (M)	n
0.055	1.07
0.028	1.07
0.014	0.95

Table [4]. Results of Least Squares Fit of $\ln \frac{1}{\tau}$ vs. $\ln [(C_2H_5)_2NH]$, n = Slope.

The rate is therefore first order with respect to $[(C_2H_5)_2NH]$. So far, therefore, we have :

$$\text{Rate of exchange} \propto [(CH_3)_3SiF][(C_2H_5)_2NH]$$

The reasons for the poor reproducability beyond ~1.6 M $[(C_2H_5)_2NH]$ may become clearer later. However it was observed that the rate of hexamethyldisiloxane production was considerably enhanced beyond $[(C_2H_5)_2NH]$ ~2.0 M and the rate determined was quite sensitive to the time the sample was allowed to stand before running the spectrum. Rigid adherance to running spectra exactly five minutes after water addition was not always possible due to frequently encountered magnetic field homogeneity problems that required the necessary corrections

before good spectra could be obtained.

The effect of water concentration on the rate of exchange is shown in figure [14]. Whereas in the previous studies described above, each point on a graph represents a separately made up sample, in this case each line represents one sample with different quantities of water added. This is probably reflected in the lower apparent scatter of the points compared with the plot of $\frac{1}{\tau}$ vs. $[(CH_3)_3SiF]$, for example. The trimethylfluorosilane was varied randomly from 0.49 to 1.18 M for the four samples shown, the diethylamine concentrations for each sample were as listed.

Plots of ln $\frac{1}{\tau}$ vs. ln $[H_2O]$ gave good straight lines with least squares fitted slopes as shown in table [5]. As indicated the slope of the natural log plot and hence the order with respect to water is n.

$[(C_2H_5)_2NH]$ (M)	n
0.24	1.9
0.51	1.7
1.56	1.5
4.66	1.0

Table [5]. Results of Least Squares Fit of ln $\frac{1}{\tau}$ vs. ln $[H_2O]$, n = Slope.

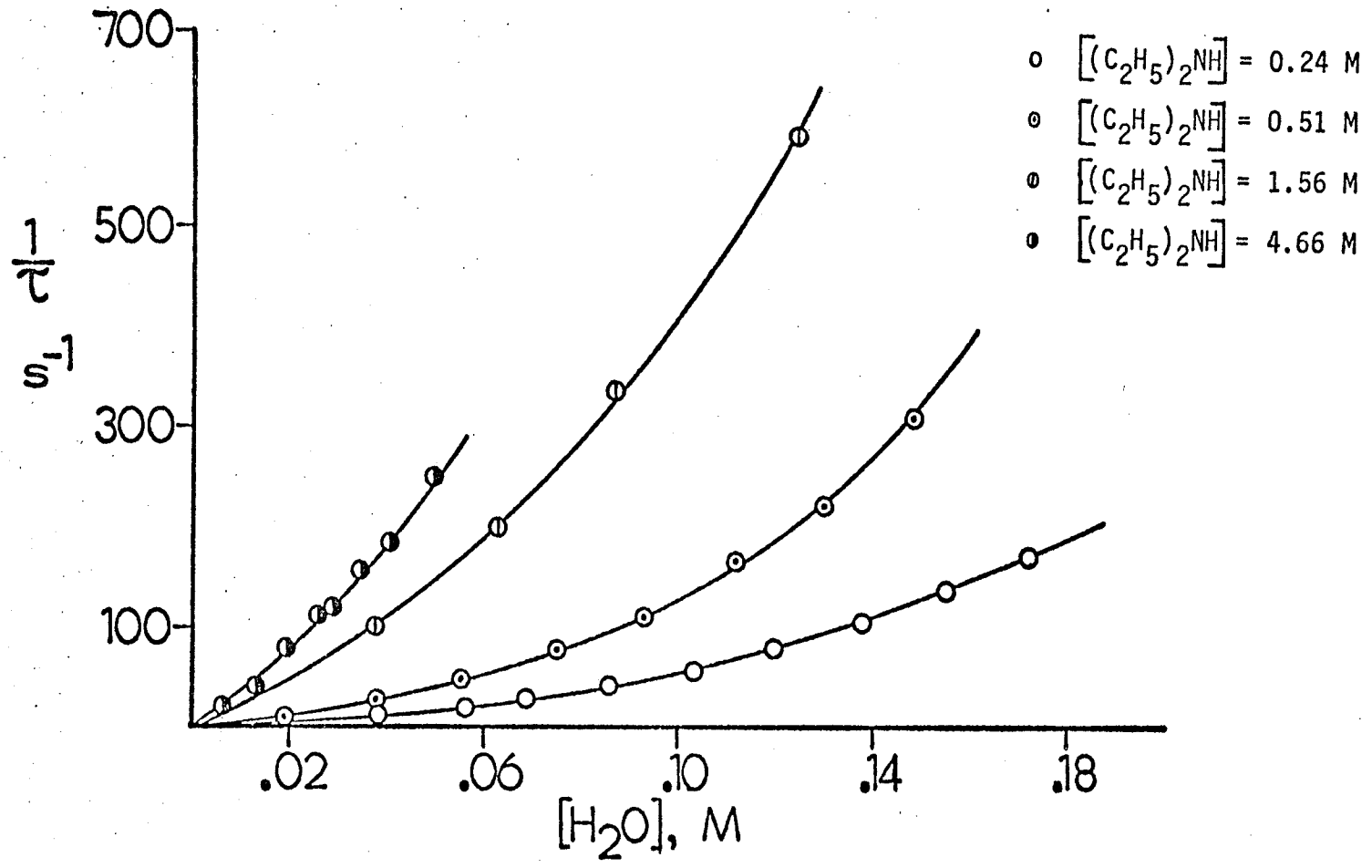


Figure [14]. Trimethylfluorosilane Exchange Study, Plot of $\frac{1}{\tau}$ (s^{-1}) vs. $[H_2O]$

The order with respect to water was clearly dependant on the diethylamine concentration. As a word of precaution however a fifth run, not shown, with $\left[(C_2H_5)_2NH\right]$ also ~0.51 M, gave n = 2.0; the values of n tabulated above are probably only ~±0.2. As an approximation then, the order with respect to water is ~2 for $\left[(C_2H_5)_2NH\right]$ 0 ⟶ 1.0 M and decreases towards 1.0 at higher diethylamine concentrations. This may also explain the effects noted in the plots of $\frac{1}{\tilde{\tau}}$ vs. $\left[(C_2H_5)_2NH\right]$. The overall rate expression at +38° is therefore :

$$R = k_1\left[(CH_3)_3SiF\right]\left[(C_2H_5)_2NH\right]\left[H_2O\right]^n$$

where $n = 1 \rightarrow 2$ depending on $\left[(C_2H_5)_2NH\right]$

and where R = pre-exchange life time of $(CH_3)_3SiF \times \left[(CH_3)_3SiF\right]$

$$= \frac{1}{\tilde{\tau}} \times \left[(CH_3)_3SiF\right].$$

Before continuing the discussion a few points should be made. All the concentrations quoted so far have been on a concentration added basis, but are these the actual concentrations present at equilibrium in solution? To make this clearer let the process of fluorine exchange , without reference to a mechanism, be envisaged as follows:

$$(C_2H_5)_2NH + (CH_3)_3SiF + nH_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{products}$$

The assumption that must be made for the study at $+38^{o}$ is that the concentration of products, [products], is small compared with $[(C_2H_5)_2NH]$, $[(CH_3)_3SiF]$, and $[H_2O]$. This assumption seems valid for $[(C_2H_5)_2NH]$ and $[(CH_3)_3SiF]$, indeed concentration changes for $(CH_3)_3SiF$ would not affect the observed rate in any event. However the water concentration is generally much smaller than the diethylamine or trimethylfluorosilane concentrations in these studies and care must be taken in assuming that the concentration of water added is effectively unchanged after the system has gone to equilibrium.

i.e. $H_2O_{\text{actual}} \simeq H_2O_{\text{added}}$

The quantitative deviation between the added and actual water concentrations will be shown to be small at $+38^{o}$ but significantly large below -10^{o} from the effect of temperature on the observed rate of exchange.

A typical temperature dependant spectrum is shown in figure [15]. The chemical shift indicated is in p.p.m. upfield from acetonitrile, the shift was measured as accurately as possible using ^{13}C satellites of acetonitrile. The chemical shift changed with temperature as shown, an unexchanging dry diethylamine/acetonitrile/trimethylfluorosilane mixture showed exactly the same upfield shift relative to acetonitrile on cooling.

The effects of temperature on the observed pre-exchange lifetimes are summarised in figure [16]. Plots of $\ln \frac{1}{\tau}$ vs. $1000/T(^{o}K)$ for the

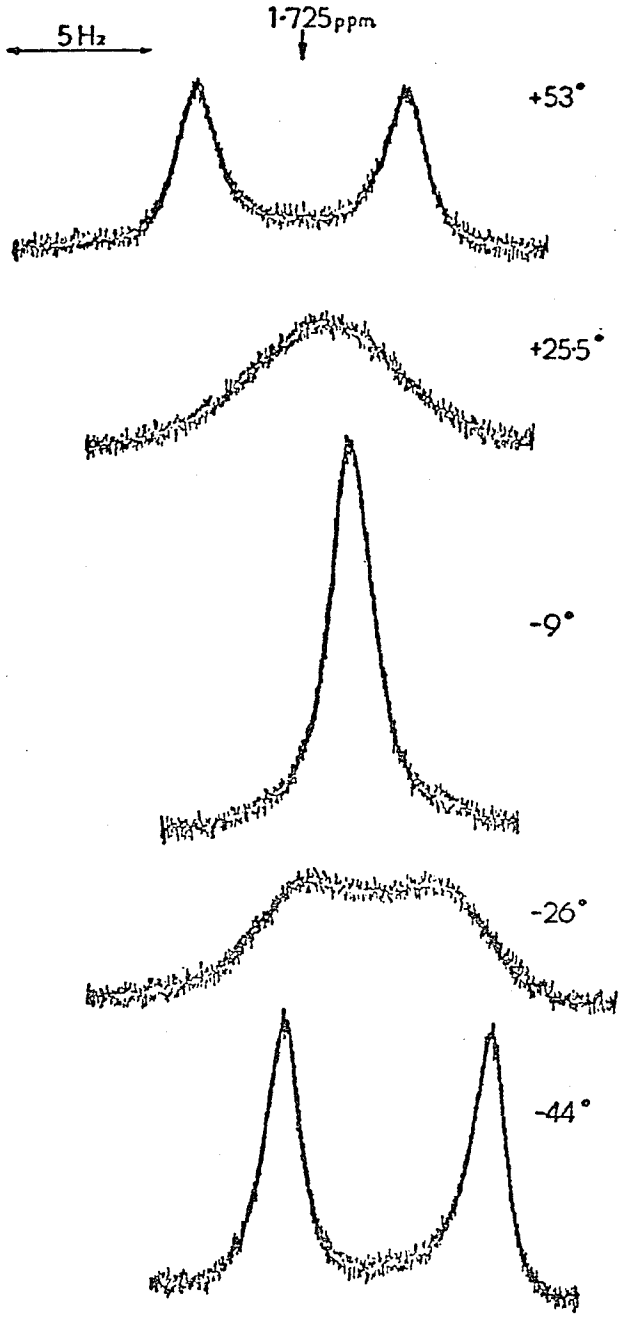


Figure [15]. Temperature Dependant ^{1}H N.M.R. Spectrum of $(CH_3)_3SiF$ in the Presence of Diethylamine and Water (Acetonitrile Solvent)

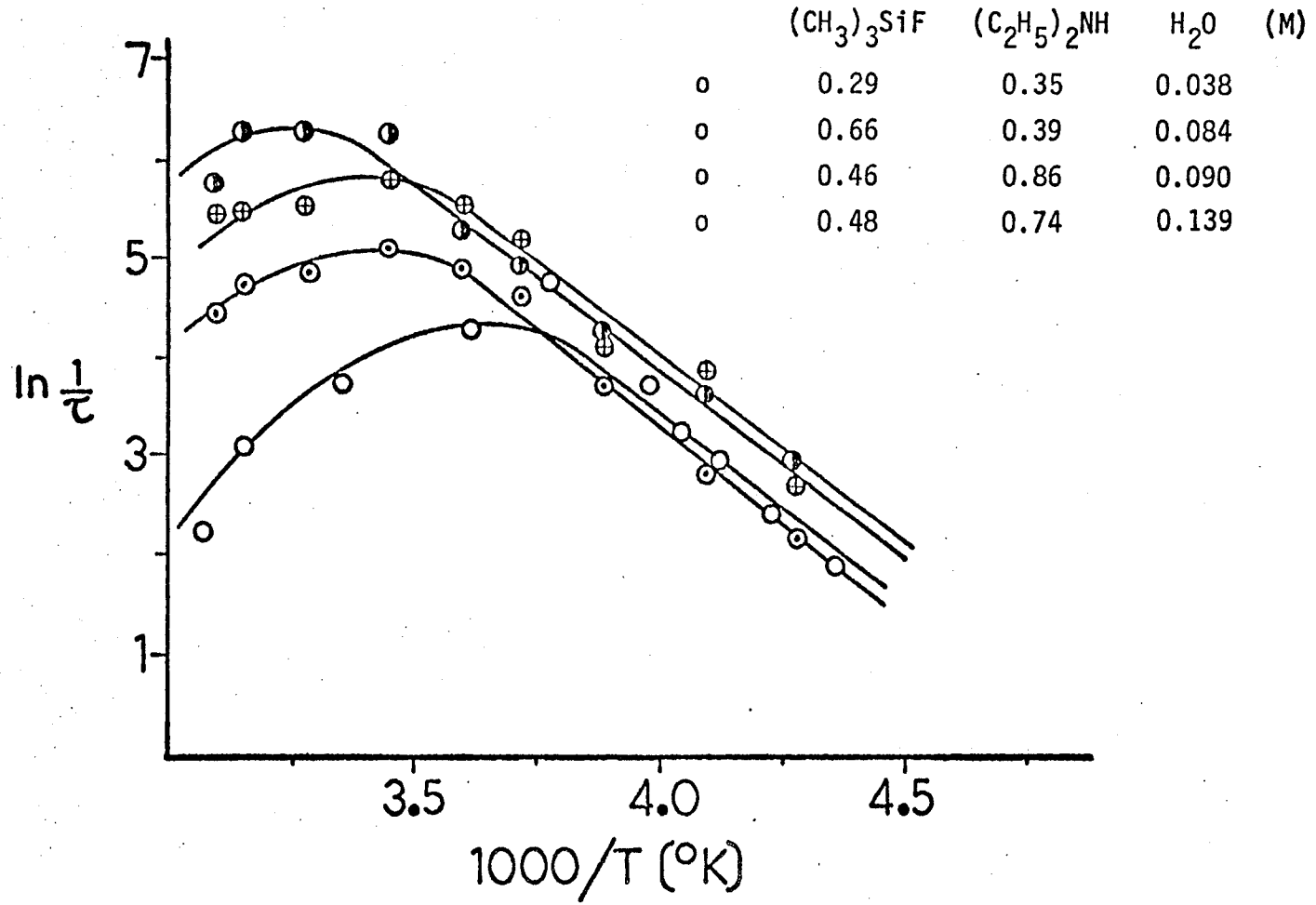


Figure [16]. Trimethylfluorosilane Exchange Study, Plot of $\ln \frac{1}{\tau}$ vs. 1000/T(°K)

four solutions shown all showed an initial increase in rate on cooling followed by a decrease in rate on further cooling. The solutions were all chosen where the order with respect to water would be ~1.5-2.0; the rate equation derived at $+38^{o}$ appeared to fit the data quite well at that temperature but a simple rate equation could not be found that would fit the observed rates at low temperatures. Two other temperature runs not included in the diagram to avoid cluttering showed similar temperature dependencies. The "inversion" temperatures for these two runs were 275±5 and 300±5 ^{o}K for, respectively, $[(C_2H_5)_2NH] = 0.28$, $[(CH_3)_3SiF] = 0.82$, $[H_2O] = 0.050$; and $[(C_2H_5)_2NH] = 0.87$, $[(CH_3)_3SiF] = 1.03$, $[H_2O] = 0.075$.

Trimethylsilanol was identified as a product at low temperatures from chemical shift measurements. This indicates the mechanism of exchange to be a simple base catalysed hydrolysis.

$$(CH_3)_3SiF + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3SiOH + HF$$

$$(C_2H_5)_2NH$$

The hydrolysis of organosilicon fluorides has been shown[97] to be an equilibrium process with,

$$K = \frac{[R_3SiOH][HF]}{[R_3SiF][H_2O]} = 10^{-2} \text{ to } 10^{-4}$$

Addition of small quantities of trimethylsilanol to an exchanging

system at low temperature produced an immediate increase in rate of exchange and a small quantity of hexamethyldisiloxane was observed to form.

Manual integration was carried out on one sample at three low temperatures, where the silanol peak was resolvable, in an attempt to calculate rough equilibrium constants for the hydrolysis. The results are shown in table [6], the concentration of HF (no doubt complexed with diethylamine) is assumed to be equal to the concentration of $(CH_3)_3SiOH$ from the stoichiometry.

T (^oK)	$[(CH_3)_3SiF]$ (M)	$[H_2O]$ (M)	$[(CH_3)_3SiOH] = [HF]$ (M)	K_{eq}
263	1.01	0.060	0.015	3.7×10^{-3}
252	1.01	0.057	0.018	5.6×10^{-3}
240	1.01	0.051	0.024	1.1×10^{-2}

Table [6]. Values of the Hydrolysis Equilibrium Constant for Trimethylfluorosilane at Various Temperatures

It was necessary to correct the "water added" concentration to give an actual water concentration as discussed earlier. The change amounted to some 30% at -33°; this fact alone may well explain why the low temperature plots of $\ln \frac{1}{\tilde{\tau}}$ vs. 1000/T(°K) could not be fitted to a simple kinetic expression where the water concentration is assumed to be equal to the amount added and no corrections for the establishment of an equilibrium system were applied.

Using the usual approximate expression:

$$\frac{d \ln K}{d (1/T)} = - \frac{\Delta H}{R}$$

By plotting ln K vs. 1/T it is possible to obtain a value for ΔH, the enthalpy of the reaction. The results of such a plot are shown in figure [17], the slope gave an estimate of ΔH of -6.0 kcal $mole^{-1}$. Some work has appeared in the literature on the thermodynamics of hydrolysis of trimethylsilyl derivatives[226,227] and this result is comparable with the ΔH values found for the hydrolysis of $(CH_3)_3SiOR$ derivatives; no fluorides were studied.

The value of ΔH of -6.0 kcal $mole^{-1}$ should be regarded with considerable caution, however, since the method can only be considered very approximate. Extrapolating the plot of ln K vs. 1/T to +38° indicated an equilibrium constant $\sim 1 \times 10^{-5}$ and therefore at this temperature $[H_2O]_{added} - [H_2O]_{actual}$ is very small and may be ignored.

It is clear, therefore, that the role of diethylamine in this

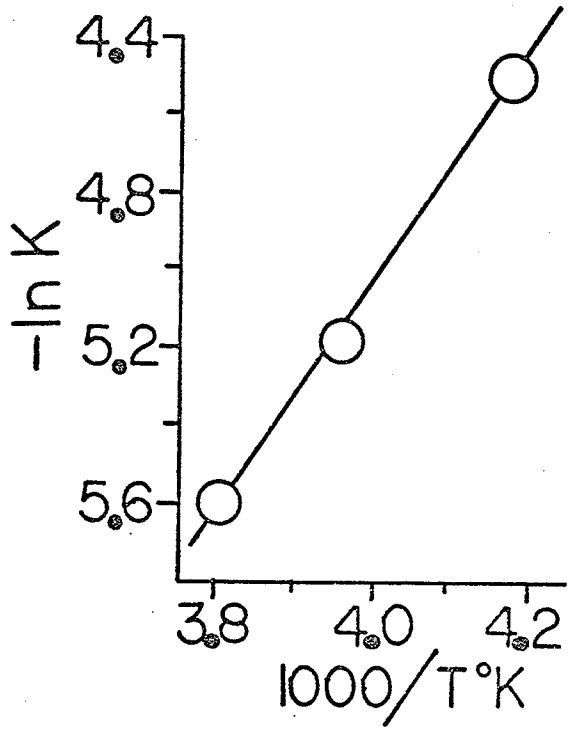


Figure [17]. Trimethylfluorosilane Exchange Study,
Plot of -lnK vs. 1000/T(^{o}K)

study is essentially catalytic and a large effect on the equilibrium constant is not observed.

Using all the data from the temperature and other studies an estimation of k_1 at +38^{o} was made for solutions suitable for the overall rate expression:

$$R = k_1 \left[(CH_3)_3SiF\right]\left[(C_2H_5)_2NH\right]\left[H_2O\right]^2$$

the results gave:

$$k_{1_{38^o}} = 4.0\pm1 \times 10^4\ l^3 mole^{-3} s^{-1}$$

Using the temperature studies only, a value for k_1 at 25^o was estimated as:

$$k_{1_{25^o}} = 4.5\pm1 \times 10^4\ l^3 mole^{-3} s^{-1}$$

A value of k_1 for the low temperature process could not be estimated since, as already mentioned, it was not possible to fit a simple kinetic expression to the low temperature data.

Of course, the usual additional information is obtainable from the plots of $\ln \frac{1}{\tau}$ vs. 1/T since:[128]

$$\frac{1}{\tau} \propto k_1 = A \exp\left(\frac{-E_a}{RT}\right)$$

therefore a plot of $\ln \frac{1}{\tau}$ vs. 1/T will give E_a as the slope.

Since the temperature effect is complex only rough estimates of E_a could be made for the "high temperature process" and the "low temperature process".

$$E_a = -5\pm2 \text{ kcal mole}^{-1}, \text{ "high temperature process"}$$

$$E_a = +8\pm1 \text{ kcal mole}^{-1}. \text{ "low temperature process"}$$

Obviously a negative activation energy is only an observed phenomenon and cannot have a true meaning, possible reasons for such an observation will be discussed later.

It is possible knowing k_1 and E_a to obtain other thermodynamic data, thus:[128]

$$k_1 = \frac{ek_b}{h} T e^{\Delta S^{\ddagger}/R} e^{-E_a/RT}$$

gives at $+25^{o}$:

$$\Delta S^{\ddagger}_{25^{o}} = -51\pm\sim5 \text{ e.u. "high temp. process"}$$

and since

$$\Delta G^{\ddagger}_{25^{o}} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

and

$$\Delta H^{\ddagger} = E_a - RT$$

$$\Delta G^{\ddagger}_{25^{o}} = 10\pm2 \text{ kcal mole}^{-1} \text{ "high temp. process"}$$

Again it should be stressed that these data be regarded with caution due to the approximations forced upon the experimental derivations. Once again it was not possible to calculate similar parameters for the low temperature process since k_1 could not be determined.

With the kinetic data at hand what sort of mechanism may now be proposed which is consistent with the experimental observations? The necessity for water rules out rapid displacement reactions analogous to the reaction of chlorosilanes with amines.[95]

$$(CH_3)_3SiCl + HNR_2 \rightleftharpoons (CH_3)_3SiNR_2 + HCl$$

i.e. $$(CH_3)_3SiF + HN(C_2H_5)_2 \rightleftharpoons (CH_3)_3SiN(C_2H_5)_2 + HF$$

In fact the total lack of reactivity of fluorosilanes towards amines is interesting in itself. One would have expected an equilibrium system with the equilibrium lying far over to the left, nevertheless the broadness of the N-H peak in very dry mixtures would indicate extremely low steady state HF concentrations. Indeed even on standing several months a dry solution sealed in an n.m.r. tube showed no collapse of the trimethylfluorosilane doublet and no sharpening of the N-H resonance.

The half height width of the N-H resonance found in the studies reported here does indeed suggest that the solutions are very dry (prior to addition of water, of course). It is interesting to compare

the N-H peak width found here (~5 Hz) with that reported by Springer and Meek[215] in an n.m.r. study of hydrogen bonding between acetonitrile and diethylamine. They observed a somewhat narrower N-H resonance indicating that the samples prepared by the technique described in this thesis were in fact dryer; their system was estimated to contain a 2×10^{-5} mole fraction of water.

The essentially hydrolytic nature of the exchange is confirmed by the low temperature observation of trimethylsilanol and the collapse of the ^1H n.m.r. singlet of this compound into the trimethylfluorosilane resonance on warming. It is also important to note that adding a drying agent, either chemical (e.g. $(CH_3)_3SiN(C_2H_5)_2$) or physical (molecular sieves), results in cessation of the exchange. The results of a typical experiment are shown in figure [18].

Silicon-nitrogen compounds are known[95,96] to react readily with water to give amines and hexamethyldisiloxane (when the Si-N compound is in excess).

$$2\ (CH_3)_3SiN(C_2H_5)_2 + H_2O \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + 2\ HN(C_2H_5)_2$$

Thus if the trimethylfluorosilane hydrolysis system is treated with N,N-diethylaminotrimethylsilane removal of water would be expected. In addition, HF or trimethylsilanol would be removed by similar reactions.

$$(CH_3)_3SiN(C_2H_5)_2 + HF \longrightarrow (CH_3)_3SiF + HN(C_2H_5)_2$$

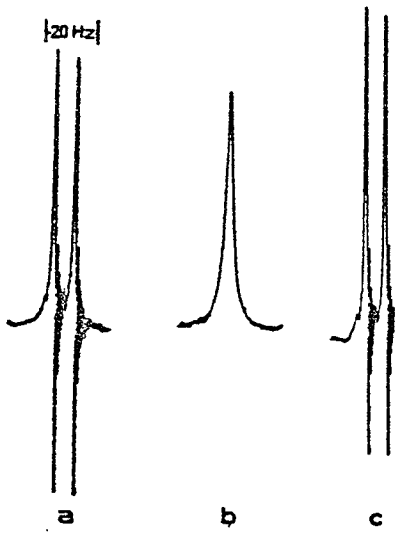


Figure [18]. Trimethylfluorosilane Exchange Study, Effects of a Drying Agent

Proton n.m.r. spectrum at $+38^{0}$ of (a) $(CH_3)_3SiF$ (0.58 mmoles) in 0.5 ml of acetonitrile solution, (b) after addition of H_2O (4.5×10^{-4} g, 0.025 mmoles) and $(C_2H_5)_2NH$ (0.41 mmoles) and (c) after further addition of $(CH_3)_3SiN(C_2H_5)_2$ (7.4×10^{-2} g, 0.51 mmoles).

$$(CH_3)_3SiN(C_2H_5)_2 + (CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + HN(C_2H_5)_2$$

Molecular sieves probably act as a more straightforward dehydrating agent,driving the hydrolysis equilibrium continuously to the left until no water is left in solution. The use of molecular sieves as a dehydrating agent in n.m.r. spectroscopy has been mentioned by Reeves et al.[228] It was found that dimethyltin dihalides sufferred rapid

exchange enhancement in the presence of traces of water; molecular sieves sealed in the n.m.r. tubes ensured continued dryness for periods of several months.

Although it has been positively shown that a hydrolysis of trimethylfluorosilane is occurring in the system under study there is the possibility that the collapse of the doublet is due to a fluoride-fluoride exchange.

$$H_2O + (CH_3)_3SiF \underset{(C_2H_5)_2NH}{\overset{\text{slow}}{\rightleftharpoons}} (CH_3)_3SiOH + (C_2H_5)_2NH_2^+ F^-$$

$$F^- + (CH_3)_3SiF^* \overset{\text{fast}}{\rightleftharpoons} (CH_3)_3SiF + F^{*-}$$

The quenching of the exchange by silicon-nitrogen compounds does not disprove such a mechanism since N,N-diethylaminotrimethylsilane was observed to react with diethylammonium fluoride to give trimethylfluorosilane and diethylamine. Indeed it was found that by adding diethylammonium fluoride to trimethylfluorosilane in acetonitrile collapse of the doublet could be induced.The effects of adding diethylammonium fluoride to trimethylfluorosilane are summarised in figure [19]. To collapse the doublet completely some 0.25 M F^- was necessary; a 0.01 M solution had little effect on the spectrum. However such a mechanism can be eliminated as the basis for the initially measured fluorine exchange by the following reasoning. At equilibrium the concentration of F^- present would be too low to

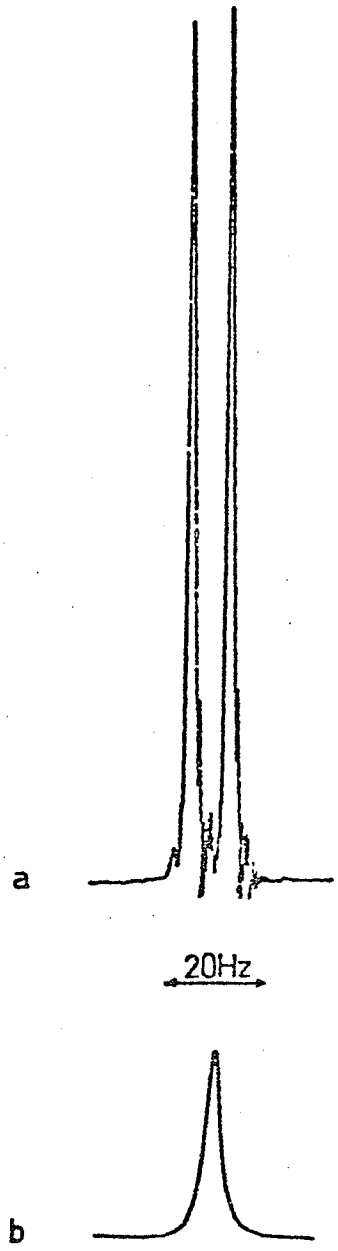


Figure [19]. Trimethylfluorosilane Exchange Study, Effect of Added F^-

(a) $(CH_3)_3SiF$ in CH_3CN (0.4 ml) + $4x10^{-4}$g $(C_2H_5)_2NH_2^+$ F^-

(b) $(CH_3)_3SiF$ in CH_3CN (0.4 ml) + 0.01 g $(C_2H_5)_2NH_2^+$ F^-

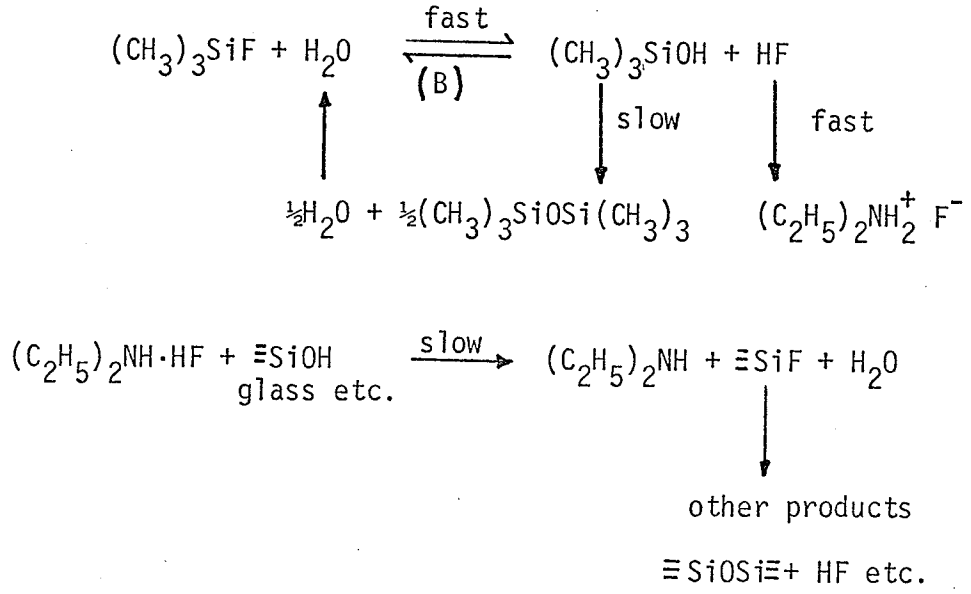
cause rapid exchange to be observed. From the hydrolysis equilibrium constant already discussed a rough value for the steady state concentration of F^- at $+38^0$ can be calculated. The concentration would be <0.01 M for the solutions studied and thus ineffective in causing fluorine exchange. It is very interesting to note that only alkylammonium fluorides were effective in collapsing the doublet if added in sufficient quantity; sodium fluoride, even aqueous, and ammonium fluoride had little effect on the spectrum.

Although fluoride-fluoride exchange can certainly be ruled out as the cause of the initially measured exchange such a mechanism provides an entirely plausible explanation of the observed rate enhancement on standing. Trimethylsilanol is known from previous studies[229,230] to condense slowly, particularly in the presence of acids and bases, to give hexamethyldisiloxane and water.

$$2\ (CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + H_2O$$

Sauer[229] found that the silanol condensed to hexamethyldisiloxane over the basic dehydrating agent K_2CO_3 with $t_{1/2} \sim 100$ hours at room temperature. Ishikawa[113] studied the condensation of the silanol produced from trimethylfluorosilane in the presence of 0.25 M H_2O and a 2:1 excess of n-propylamine. Some rate enhancement was produced by the presence of the base although very rough calculations based on the results given by Ishikawa would indicate $\sim 0.2\%$ condensation would occur within 5 minutes in the system under study in this thesis,

insufficient to affect the n.m.r. spectrum in any way. However on standing it is easy to see how rate enhancement might occur caused by the slow increase in fluoride concentration in solution due to the silanol condensation.



Thus the water concentration would decrease slightly or stay relatively constant while the concentration of fluoride ion would increase and, correspondingly, so would the hexamethyldisiloxane concentration. The observed rate enhancement on standing is therefore most probably due to the production of significant fluoride concentration and a more accurate overall rate expression should be:

$$R = k_1 \left[(CH_3)_3SiF\right]\left[(C_2H_5)_2NH\right]\left[H_2O\right]^n + k_1' \left[F^-\right]\left[(CH_3)_3SiF\right]$$

After only 5 minutes $k_1' \left[F^-\right]\left[(CH_3)_3SiF\right]$ is insufficiently large

to affect $\frac{1}{\tau}$. This type of rationale might explain some of the other experimental observations. For example at high amine concentration the rate of production of fluoride ion would be higher and less reproducibility from sample to sample would be expected. Indeed hexamethyldisiloxane was observed much more readily in such samples. It is also interesting that while molecular sieve was a good exchange quencher if added soon after the addition of water, it was less effective if the solution had been allowed to stand; presumably it is a poor fluoride ion scavenger. A condensation side reaction would explain the non-reversibility of the spectra if the samples were heated since the rate of condensation should increase with temperature. Finally the solid product that separated out on treatment of an "old" solution with a small quantity of methylene chloride gave an analysis consistent with the production of a 1:4 ratio of $(C_2H_5)_2NH_2F$ and $(C_2H_5)_2NH_2HF_2$.

It is interesting to compare the rate constant k_1 obtained in this study with previous work[97]. No rate studies have been made on base catalysed hydrolyses of fluorosilanes, presumably the rates are much too fast for conventional techniques. Acid catalysed hydrolysis is much slower and is first order in acid concentration, for example k_{obs} for triphenylfluorosilane was 0.34±.03 l mole^{-1} min^{-1} in 66.7% aqueous acetone. A very large sensitivity of rate to steric requirements was found; thus triethylfluorosilane reacted at some 120x the rate of tri-iso-propylfluorosilane. The rate constant for triethylfluorosilane hydrolysis was 2.5 l mole^{-1} min^{-1} and >10 l mole^{-1} min^{-1} for diethylmethylfluorosilane. Trimethylfluorosilane hydrolysis was presumably too

rapid to be measured by the titration technique used. It is interesting that formation of disiloxanes was not considered in the work reported. Base catalysed hydrolysis or alcoholysis of chlorosilanes is similarly unreported, such reactions presumably occurring at an even higher rate than fluorosilane hydrolysis.

Disregarding the variable order with respect to water for a moment, there are two general types of mechanism that may account for the observed kinetics.

I $$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$$

$$(CH_3)_3SiF + OH^- \rightleftharpoons (CH_3)_3Si(F)OH^- \rightleftharpoons (CH_3)_3SiOH + F^-$$

II $$(CH_3)_3SiF + H_2O \rightleftharpoons (CH_3)_3SiF\cdot H_2O$$

$$(CH_3)_3SiF\cdot H_2O + (C_2H_5)_2NH \rightleftharpoons (CH_3)_3Si(F)OH^- + (C_2H_5)_2NH_2^+$$

$$\Big\downarrow\Big\uparrow$$

$$(CH_3)_3SiOH + F^-$$

Pathway II is favoured over I for the following reasons. Typical OH^- concentrations may be calculated using the K_b value for diethylamine in water,[231] these would represent maximum OH^- concentrations since the K_b value would, in all probability, decrease in a solvent of lower dielectric constant such as acetonitrile. Thus typically at $[(C_2H_5)_2NH]$

= 0.5 M and $[H_2O]$ = 0.02 M there would be ~0.003 M $[OH^-]$. The effect of adding sodium hydroxide to trimethylfluorosilane in acetonitrile is shown in figure [20]. The reaction with solid sodium hydroxide at $+10^o$ occurred smoothly to give a singlet at -0.15 p.p.m. assumed to be $(CH_3)_3SiOSi(CH_3)_3$ or possibly $(CH_3)_3SiO^-Na^+$. The spectra are shown in figure [20] part A. During the course of the reaction no collapse of the trimethylfluorosilane doublet was observed. Addition of up to 10 µl of water after the reaction was complete had little effect on the remaining trimethylfluorosilane doublet.

Part B shows the effect of adding progressively larger quantities of aqueous sodium hydroxide to trimethylfluorosilane in acetonitrile at 0^o. For example spectrum d part B is the result of addition of 6µl of 0.5 M sodium hydroxide and allowing the solution to stand for 5 minutes at 0^o. The spectra in part B were all run at the same gain, the decrease in peak height and lack of ringing indicate the onset of slow exchange. 6 µl of 0.5 M sodium hydroxide in 0.2 ml of solution is approximately 0.015 M $[OH^-]$. This concentration of aqueous sodium hydroxide did <u>not</u> therefore significantly affect the spectrum at 0^o although condensation at $+38^o$ to give hexamethyldisiloxane was enhanced. This would tend to eliminate I as a possible mechanism since the direct nucleophilic displacement of F^- by OH^- by an S_N2-Si or S_N2^*-Si pathway is obviously too slow to be observed by the dynamic n.m.r. method. The highly associated intermediate in II is strongly supported by the $\Delta S^{\ddagger}$ value of -51 e.u., i.e. large and negative.

Mechanism II is thus preferred although OH^- could compete with

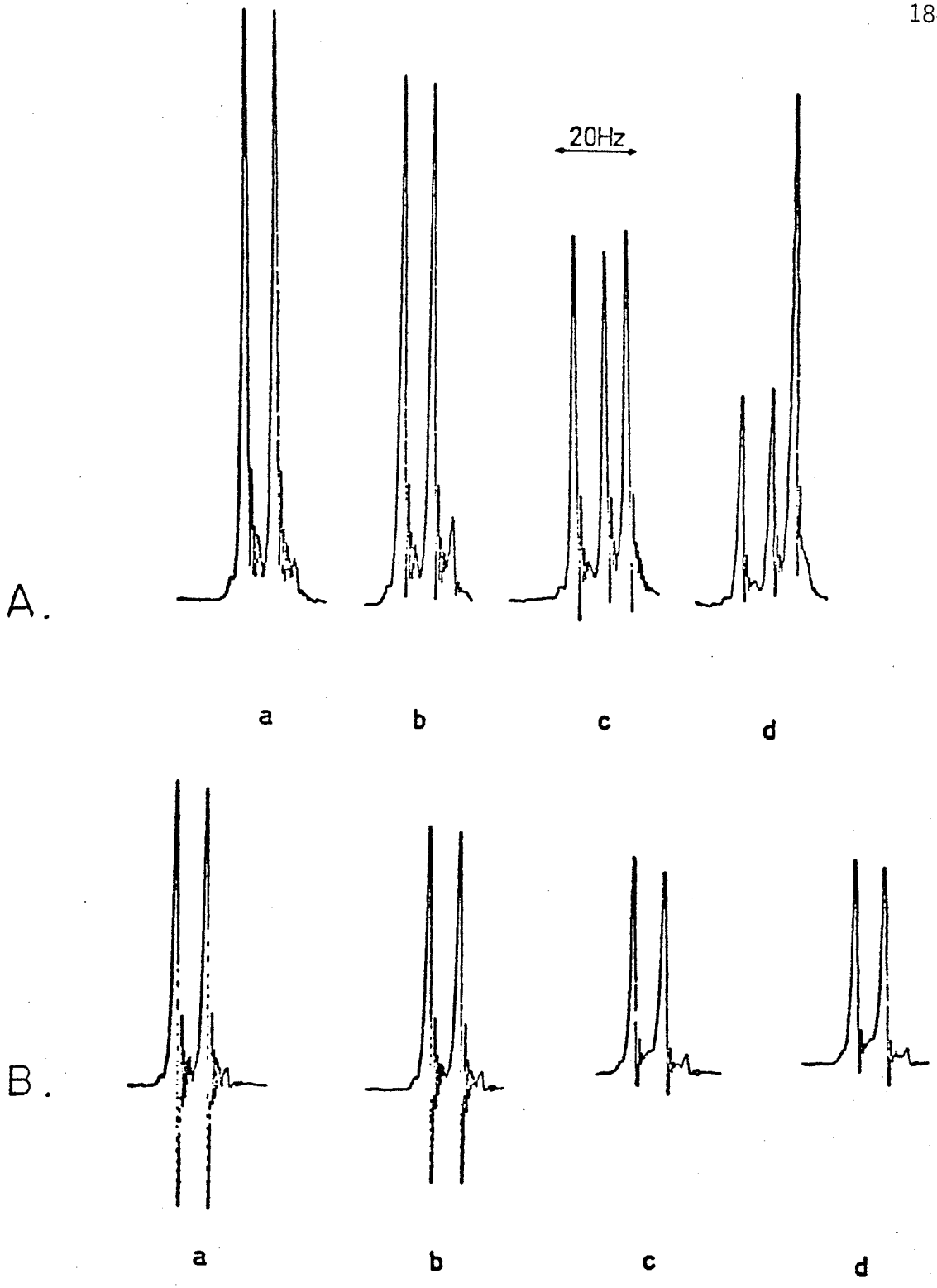


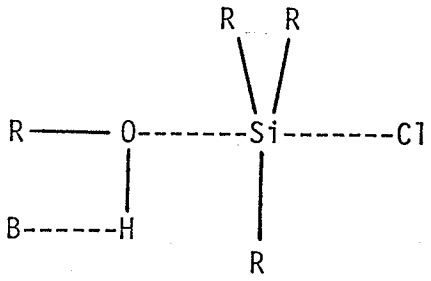
Figure [20]. Trimethylfluorosilane Exchange Study, Effect of Added OH^-

A. Reaction with solid NaOH at $+10^o$ (see text)

B. Addition of aqueous NaOH at 0^o (see text)

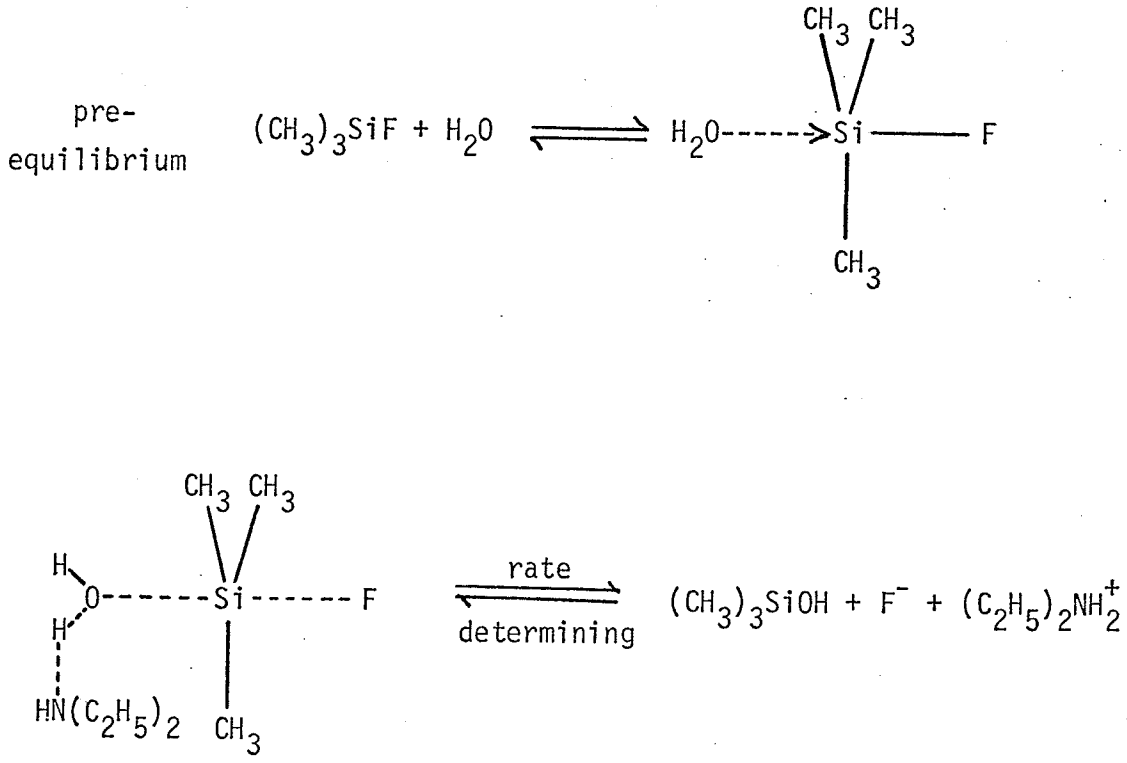
$(C_2H_5)_2NH$ for proton removal from $(CH_3)_3SiF \cdot H_2O$ but the diethylamine concentration is so much higher as to probably make this effect negligible. The very slight broadening of the trimethylfluorosilane doublet on addition of 0.015 M $[OH^-]$ could well be due to hydroxide acting as a base in scheme II.

The scheme outlined in II has been proposed several times in the literature to explain the kinetics of alcoholysis and hydrolysis of chlorosilanes[102—105] and fluorosilanes[106,97] and also partially to explain the racemisation of fluorosilanes by alcohols.[100] Similar aquated intermediates have been proposed for the acid cleavage of silicon hydrides.[154] Allen and Modena[102] proposed a general transition state as follows:



where B = any nucleophile capable of assisting proton removal, e.g. another molecule of ROH.

Clearly in the work reported in this thesis a similar transition state may be proposed:



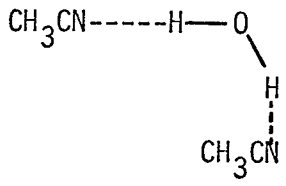
It is interesting to compare this intermediate to the trigonal bipyramidal intermediate proposed by Sommer and Baumann[100] for the racemisation of bulky optically active fluorosilanes by methanol by an S_N2^*-Si mechanism. Good evidence was presented that, in their particular case, the racemisation was the result of donor-acceptor interactions and was not the result of a silicon-fluorine bond cleavage step. It would be interesting to speculate on the effects of

traces of water in their systems although the possibility of impurity catalysis was never discussed.

Although the work reported here on the hydrolysis of trimethylfluorosilane seems to indicate a similar mechanism to alcoholysis or hydrolysis of chlorosilanes one perplexing problem remains. The order with respect to water for most of the studies was ~2 and decreased with increasing diethylamine concentration. This variable order with respect to solvolysis reagent is not new, and is discussed to some extent by Chipperfield & Prince[104] and Allen & Lavery[103]. Alcoholysis of silicon chlorides has been reported[104] to occur by a rate process involving an order with respect to alcohol of 7. The alcoholysis of triphenylchlorosilane with 2-propanol in carbon tetrachloride[103] gave an order with respect to alcohol of 2.4 and was autocatalytic in hydrogen chloride. Even the racemisations of optically active fluorosilanes[100] have orders with respect to methanol of ~3.

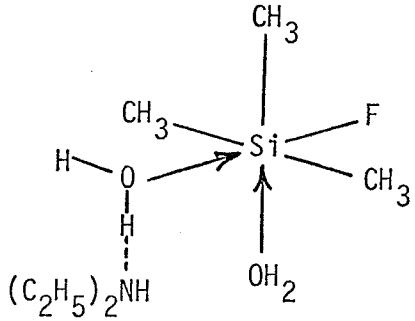
As well as a high order in nucleophile a negative temperature effect was found for the hydrolysis of trialkylchlorosilanes[104] which is similar to the initial increase in rate on cooling observed in the work reported here. The high order in water and the negative temperature effect was rationalised in terms of a heat of association of $(H_2O)_n$, an aggregate molecule. Presumably a similar mechanism could be invoked to explain the results reported here but there are several other possibilities that will be discussed. Firstly the observed dependance on water concentration does not exceed two and therefore the postulate of a

water aggregate $(H_2O)_n$ where $n > 2$ is unnecessary. Secondly acetonitrile has been shown to be a strong hydrogen bonding medium with amines[215] and there is infra red evidence for the formation of extensive hydrogen bonding with water,[232]

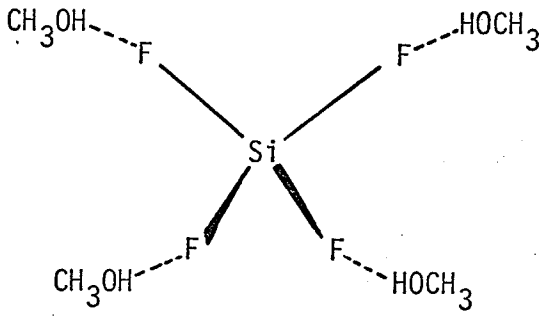


The possibility of water existing as a polymer in such solutions is remote, particularly when the concentration is low as was the case in this work.

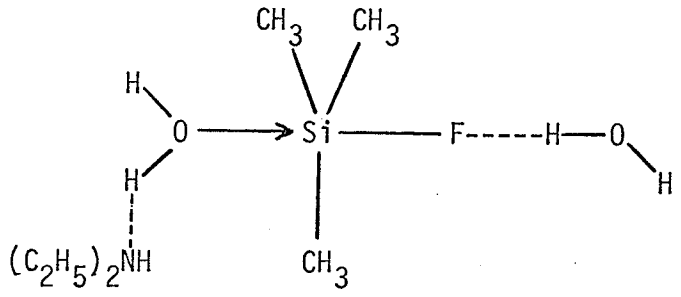
Two other possibilities come to mind; the ability of silicon to expand its coordination to six has been mentioned previously, a six coordinate intermediate with 2 coordinated water molecules could be considered:



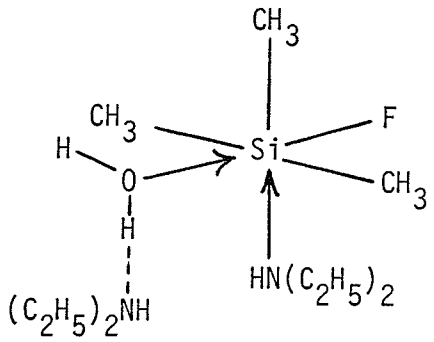
Secondly the interaction of alcohols with silicon tetrafluoride has been studied[233] and a 4:1 complex isolated, rationalised as:



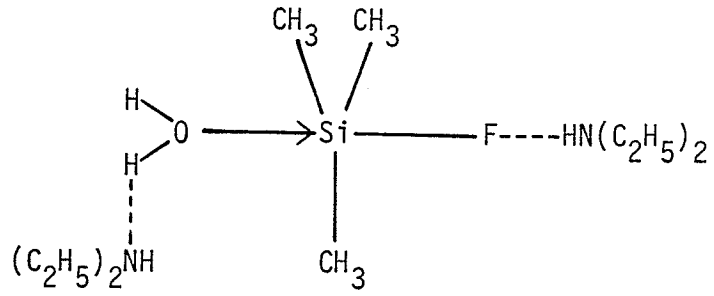
Thus the second water molecule could be envisaged as complexing or assisting in the removal of F^-.



Why would the order with respect to water decrease on increasing the diethylamine concentration? One possibility is that diethylamine competes with the second water molecule for the sixth coordination site.



Or alternatively could compete in forming a hydrogen bond with the fluorine.



In this case one might expect the order with respect to diethylamine to increase to 2 at high diethylamine concentrations. It was not possible to test this suggestion because of the poor reproducibility of the results at high base concentrations. The corresponding decrease in order with respect to water would tend to offset an increase in order with respect to base and the effect may not be as noticeable as

might be expected.

Finally, as an example only, the effect of competing equilibria on an observed activation energy will be considered. Consider, for example, the system:

$$(CH_3)_3SiF + H_2O \underset{k_2^a}{\overset{k_1^a}{\rightleftharpoons}} (CH_3)_3SiF\cdot H_2O \qquad K^a$$

$$(CH_3)_3SiF\cdot H_2O + H_2O \underset{k_2^b}{\overset{k_1^b}{\rightleftharpoons}} (CH_3)_3SiF\cdot 2H_2O \qquad K^b$$

$$(CH_3)_3SiF\cdot H_2O + B \underset{k_2^c}{\overset{k_1^c}{\rightleftharpoons}} (CH_3)_3SiOH + F^- + BH^+ \qquad K^c$$

$$(CH_3)_3SiF\cdot 2H_2O + B \underset{k_2^d}{\overset{k_1^d}{\rightleftharpoons}} (CH_3)_3SiOH + H_2O + BH^+ + F^- \qquad K^d$$

Therefore rate of exchange

$$= k_1^d\left[(CH_3)_3SiF\cdot 2H_2O\right][B] + k_1^c\left[(CH_3)_3SiF\cdot H_2O\right][B]$$

$$= K^a\cdot K^b\cdot k_1^d\left[(CH_3)_3SiF\right]\left[H_2O\right]^2[B] + K^a\cdot k_1^c\left[(CH_3)_3SiF\right]\left[H_2O\right][B]$$

Now $$\ln K \triangleq -\frac{\Delta H}{RT}$$

Therefore $$\text{Rate} = k_1^d \left[(CH_3)_3SiF\right]\left[H_2O\right]^2\left[B\right]e^{\frac{-(\Delta H^c+\Delta H^d)}{RT}} + k_1^c \left[(CH_3)_3SiF\right]\left[H_2O\right]\left[B\right]e^{\frac{-(\Delta H^c)}{RT}}$$

Now $$k = Ae^{-E_a/RT}$$

Therefore $$\text{Rate} = A \left[(CH_3)_3SiF\right]\left[H_2O\right]^2\left[B\right]e^{\frac{-(\Delta H^c+\Delta H^d+E_a^d)}{RT}} + A^* \left[(CH_3)_3SiF\right]\left[H_2O\right]\left[B\right]e^{\frac{-(\Delta H^c+E_a^c)}{RT}}$$

Thus there are two terms which would act as observed activation energies,

$$(\Delta H^c + \Delta H^d + E_a^d) \quad \text{and} \quad (\Delta H^c + E_a^c)$$

It may well be that the first is -ve and the second +ve, the overall observed activation energy is a resultant of the two depending on the concentration of the various species present and could well account for an observed negative activation energy at high temperatures becoming positive at low temperatures.

The derivative, $\frac{d\ln(\text{Rate})}{d(1/T)}$, gives a very complex expression which when set to zero gives a real answer for T ("inversion temp").

$$\frac{d \ln (\text{rate})}{d\ (1/T)} = \frac{Le^{+L/T} - YMe^{-M/T}}{e^{+L/T} + Ye^{-M/T}}$$

Where $L = -\frac{(\Delta H^c + \Delta H^d + E_a^d)}{R}$

$M = +\frac{(\Delta H^c + E_a^c)}{R}$

Y = a constant where the concentrations of the reactants are the same.

Where $\frac{d \ln (\text{rate})}{d\ (1/T)} = 0$

We have $T = \frac{(L + M)}{(\ln \frac{YM}{L})}$

It may be shown that for constant diethylamine and trimethylfluorosilane concentrations then :

$$Y \propto \frac{1}{[H_2O]^{\S}} \qquad \S = 1\text{-}2$$

Therefore as the water concentration increases the "inversion

temperature" should also increase. Surprisingly enough this trend is found in the temperature studies previously reported although the diethylamine and trimethylfluorosilane concentrations were not kept very constant.

The preceeding, again it will be stressed, was presented in order to explain how such a complex $\ln \frac{1}{\tilde{\tau}}$ vs. 1/T plot could be obtained. The low precision of the method precludes any more detailed analysis of the results obtained, however a pre-equilibrium or a series of pre-equilibria in solution would appear to be most consistent with the observed data.

The effects of pre-equilibria, and other related effects on the Arrhenius equation have been summarised by Hulett[234] and others.[235,236]

The mechanism involved in the trimethylfluorosilane hydrolysis is obviously complex and the effects of other higher coordinated intermediates such as $(CH_3)_3SiF \cdot 2(HN(C_2H_5)_2)$ have not been considered (cf. $SiF_4 \cdot 2NH_3$ etc.). Indeed no mention has been made of the role of the solvent acetonitrile in the mechanism. Acetonitrile is known to complex to metal ions[237] and metal halides[238-240] and almost certainly would form weak transient complexes with trimethylfluorosilane. Nevertheless the overall mechanism presented seems reasonable in view of current concepts in organosilicon chemistry. However the problem of deriving a mechanism from a rate expression is fraught with pitfalls and one should always be looking to alternative interpretations.

5.3 TETRA-N-PROPYLAMMONIUM PENTAFLUOROSILICATE

A few comments should be made on the preparation of this interesting derivative, in particular on the ability of the intermediates to abstract boron from pyrex glassware. In their original preparation Clark and co-workers[217] attributed this property to the platinum hydride/hydrogen fluoride mixture present in solution. The work reported here strongly suggests that a solution of $[(n\text{-}C_3H_7)_4N][SiF_5]$ in aqueous methanolic HF is a powerful fluorinating agent towards boron in glass. If hydrogen fluoride alone is allowed to contact pyrex glassware the major product is silicon tetrafluoride; little boron trifluoride is observed. It is suggested here that hydrogen fluoride solutions of pentafluorosilicates may have novel fluorinating ability, particularly as a substitutive fluorinating agent; no work has appeared in this area.

The pentafluorosilicate ion has been assumed to have a trigonal bipyramidal structure[72,173] by analogy with phosphorus pentafluoride, this assumption is strongly supported by the ^{19}F n.m.r. spectrum of the $(C_6H_5)_2SiF_3^-$ ion which shows axial and equatorial fluorine environments at low temperature. The coupling between axial and equatorial fluorines in this molecule must be very low as no coupling was observed even at -90^o, this agrees with the work of Klanberg and Muetterties[72] who concluded that the coupling was <5 Hz.

The ^{19}F n.m.r. spectra of pentacoordinate silicon fluorides have been reported and discussed at some length by Klanberg and Muetterties. The anions exhibited both inter- and intramolecular fluorine exchange,

for example the methyltetrafluorosilicate anion ($CH_3SiF_4^-$) gave only one fluorine resonance (coupled to the CH_3 group) at low temperatures, thus intramolecular exchange is rapid. As the solution was warmed to $+25^o$ partial loss of F-H coupling was observed due to an intermolecular exchange. Klanberg and Muetterties showed that the rate of intermolecular exchange is highly susceptible to the degree of purity of the samples and, very interestingly, suggested the existence of a ($CH_3SiF_4 \cdot H_2O^-$) anion. Protonic solvents such as methanol considerably enhanced intermolecular exchange. The pentafluorosilicate ion was observed to be rapidly exchanging by an intermolecular mechanism above -60^o and exchanging by an intramolecular mechanism below this temperature.

Some of the work by Klanberg and Muetterties was repeated with the type of exchange found for trimethylfluorosilane in mind. With untreated methylene chloride as a solvent it was possible to reproduce almost exactly the spectra for SiF_5^-, $CH_3SiF_4^-$ and $(C_6H_5)_2SiF_3^-$. Addition of a drying agent (hexamethyldisilazane) had little effect on the diphenyltrifluorosilicate anion, a marginal effect on the methyltetrafluorosilicate anion, but a very significant effect on the spectrum of the pentafluorosilicate species. There was an improvement of some 20^o in the temperature needed to resolve the ^{19}F n.m.r. spectrum of $[(n\text{-}C_3H_7)_4N][SiF_4CH_3]$ to the same extent as previously reported.

The effects of adding hexamethyldisilazane as a drying agent to a solution of tetra-n-propylammonium pentafluorosilicate in methylene chloride at $+38^o$ are shown in figure [21]. Addition of hexamethyldi-

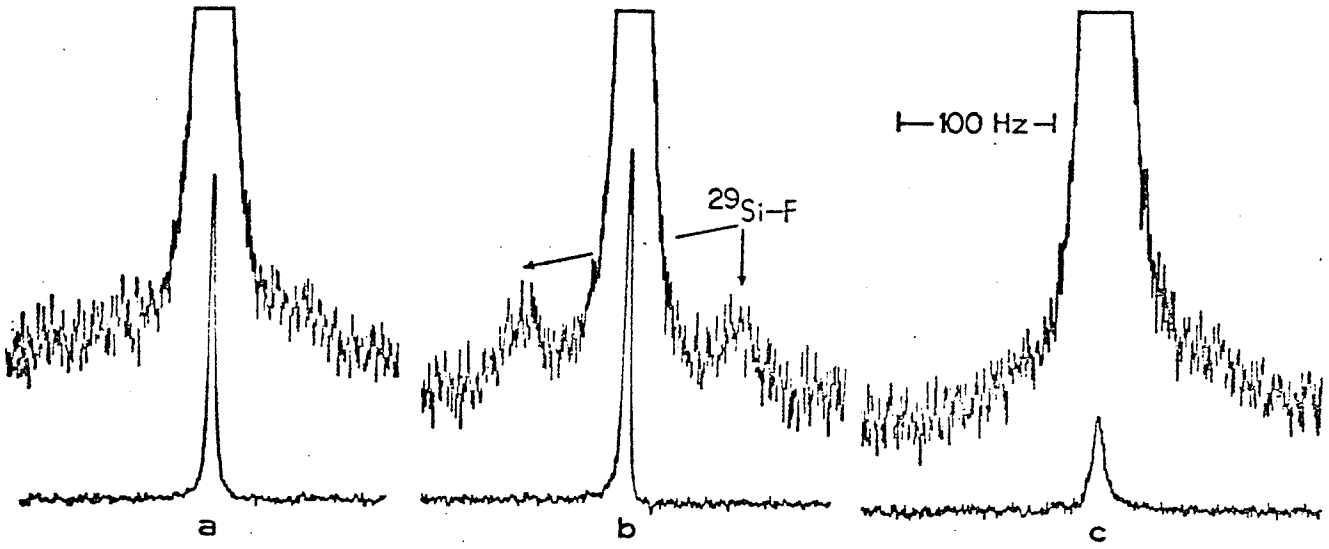


Figure [21]. ^{19}F N.M.R. Spectra of $[(n\text{-}C_3H_7)_4N][SiF_5]$ at +38°

(a) $[(n\text{-}C_3H_7)_4N][SiF_5]$ (0.094 g, 0.30 mmoles) in CH_2Cl_2 (0.32 g)

(b) As in (a), + $(CH_3)_3SiNHSi(CH_3)_3$ (0.0062 g, 0.04 mmoles)

(c) As in (b), + H_2O (0.001 g, 0.056 mmoles)

silazane led to the observation of ^{29}Si-F satellites, thus intermolecular exchange has been halted on the n.m.r. time scale. Further addition of a trace of water resulted in loss of ^{29}Si-F coupling and hence a resumption of intermolecular exchange. The halting of intermolecular exchange at $+38^{o}$ (and even at $+45^{o}$) meant that the temperature improvement in this case was $>100^{o}$ over the previous work.

Klanberg and Muetterties proposed several types of mechanism to explain intermolecular exchange. The alkylfluorosilicates were suggested as exchanging by a dissociative process and/or S_N2-Si displacement.

$$RSiF_4^- + F^{*-} \rightleftharpoons RSiF_3F^{*-} + F^-$$

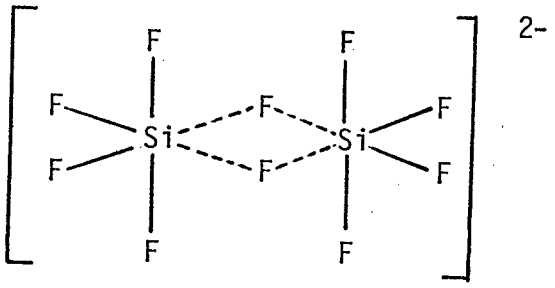
$$R_2SiF_3^- \rightleftharpoons R_2SiF_2 + F^-$$

Thus weak acceptors such as dimethyldifluoro- or trimethylfluorosilane did not form stable five coordinate compounds. Dissociative mechanisms were considered less attractive for the pentafluorosilicate anion since this species does in fact possess acceptor power as does the dissociation product silicon tetrafluoride.[173,241,242]

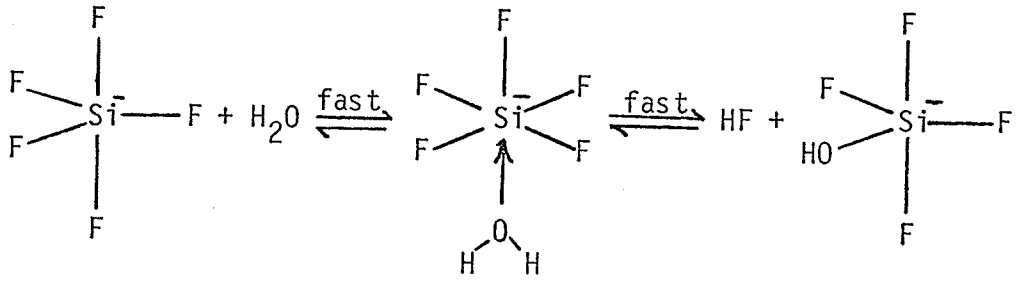
$SiF_5^- \rightleftharpoons SiF_4 + F^-$ unlikely due to the high acceptor power of SiF_4

$SiF_5^- + F^- \rightleftharpoons$ exchange unlikely since SiF_6^{2-} is kinetically inert[74]

Thus a bimolecular fluorine bridged mechanism was considered most likely:



The work reported in this thesis proves conclusively that intermolecular exchange in the SiF_5^- species is due to traces of water in the solvent. A mechanism is proposed based on, (i) the knowledge that SiF_5^- can act as an acceptor, (ii) the kinetic investigation reported previously on intermolecular exchange in trimethylfluorosilane. The proposed mechanism is as follows:



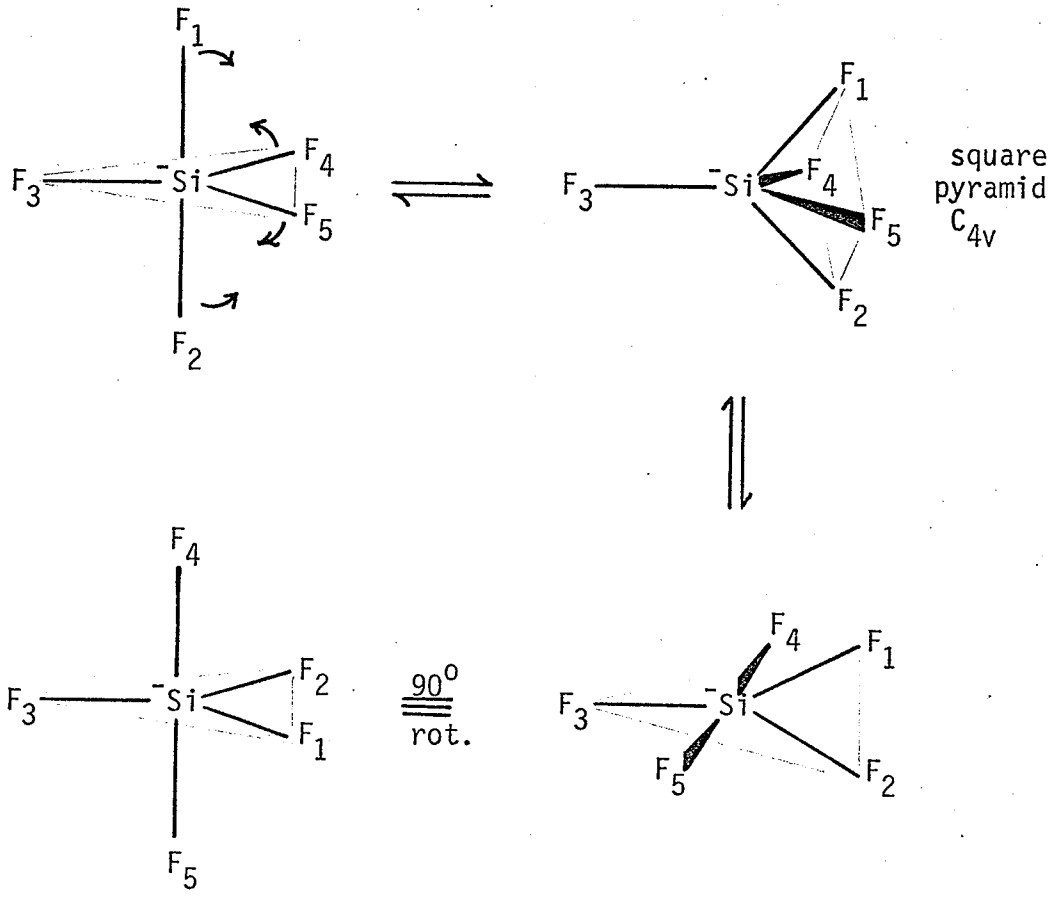
Addition of hexamethyldisilazane, a powerful drying agent,[87] stopped exchange; addition of further water initiated exchange once

again. Rough calculations indicate <0.01 M $[H_2O]$ (less than 0.02% wt) is sufficient to cause rapid exchange. In fact additional experiments indicated the actual quantity of water necessary to be <0.002 M (0.004% wt); indeed an impurity catalysed exchange.

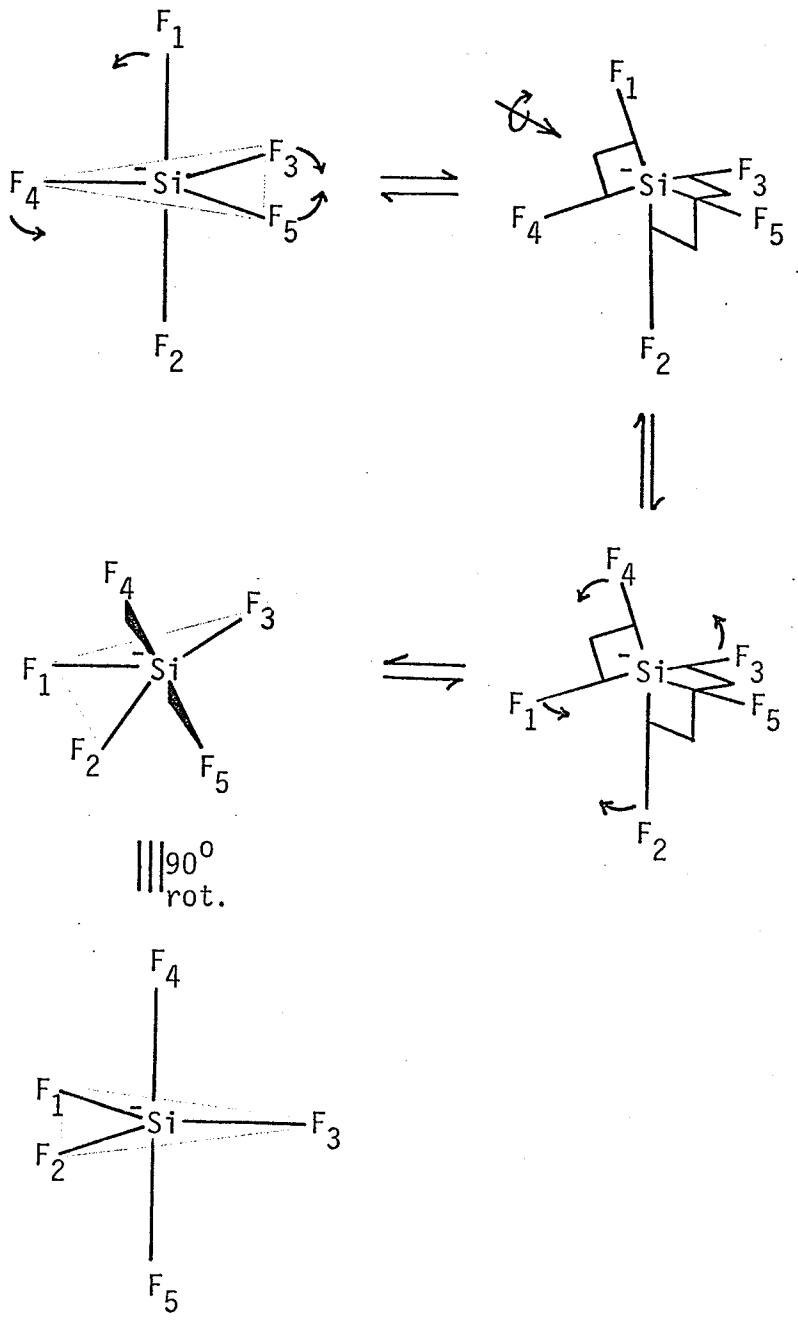
The origin of the small peak at +126 p.p.m. observable at low temperatures after addition of silazane is interesting. Although the chemical shift is close to that of SiF_6^{2-} the assignment of the peak to this species is not favoured for the following reasons. On warming from -60^{o} the peak disappears at $\sim -30^{o}$, appearing to coalesce into the main SiF_5^- resonance. Since F-^{29}Si coupling is retained throughout the temperature range an intermolecular exchange cannot explain the coalescence. Any collapse of an SiF_5^- resonance could only conceivably occur via an intermolecular exchange, in fact rapid exchange between these species would not be expected at all. Thus the peak at +126 p.p.m. is assigned to $SiF_5^-\cdot B$ where B = excess hexamethyldisilazane or ammonia. Ammonia would be the expected product from the reaction of hexamethyldisilazane with water.

The first step in the proposed mechanism of <u>inter</u>molecular exchange could also be put forward to explain the rapid <u>intra</u>molecular exchange observed. All MF_5 molecules have been found to show spectroscopic equivalence of fluorine atoms, most favoured explanations for this phenomenon have been the Berry pseudorotation[243–246] mechanism or turnstile rotation[247,248]. A detailed discussion of these mechanisms involving bond deformations will not be made, the coverage is more than adequate

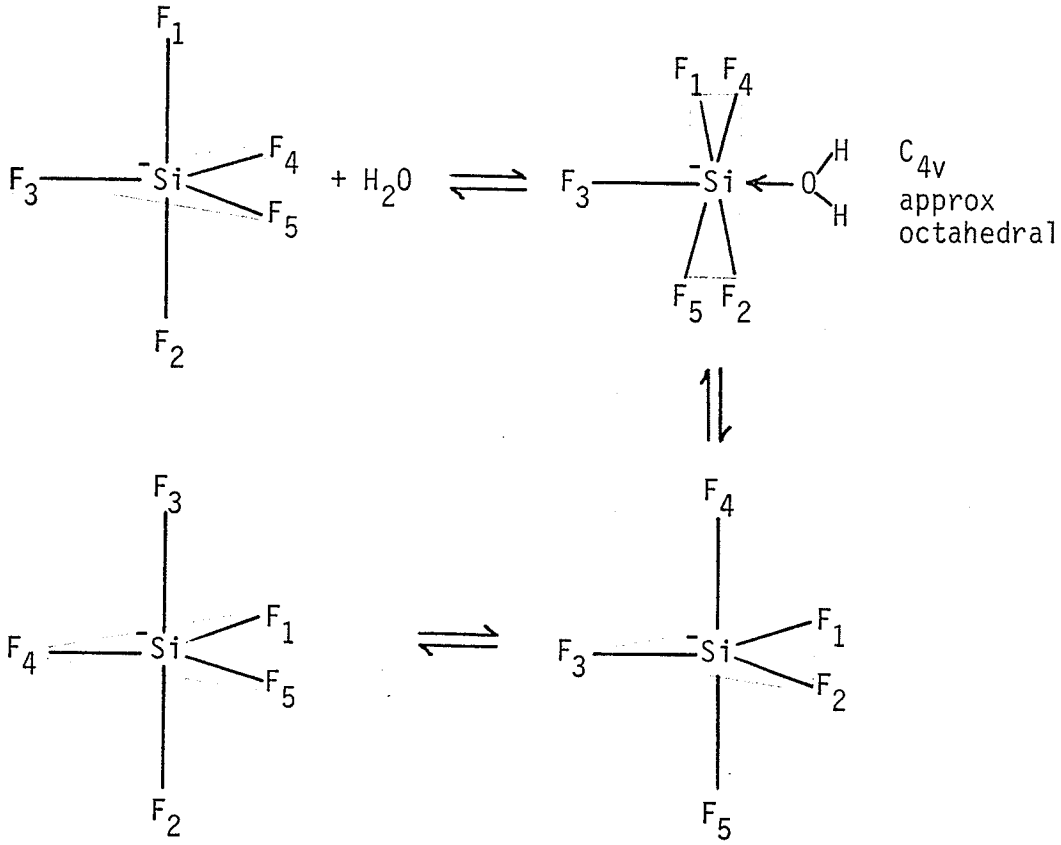
in the literature. As an example however a Berry pseudorotation as applied to an SiF_5^- species would be proposed to occur via a square pyramidal transition state.



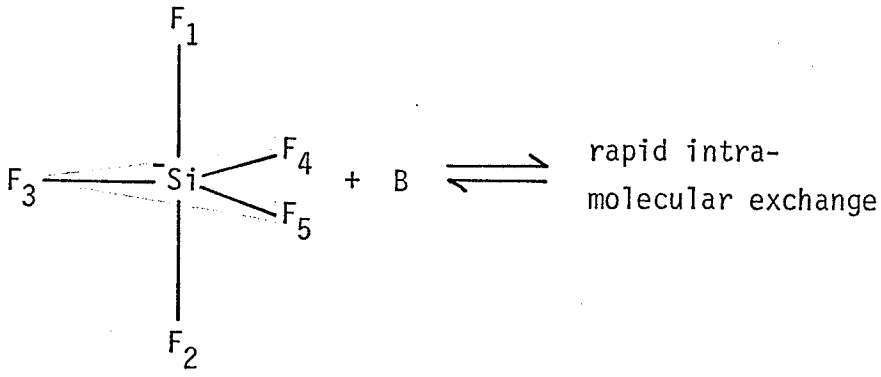
Turnstile rotation requires a complex series of small ligand movements accompanied by a rotational switching of two ligands.



Thus another mechanism could be proposed using water as a Lewis base to equilibrate axial and equatorial environments.



It was hoped by drying the system that such an exchange would stop and separate axial and equatorial fluorine environments might be observable in the ^{19}F n.m.r. spectrum. This was found not to be the case. However this does not disprove such a mechanism since traces of other Lewis bases, NH_3, $((CH_3)_3Si)_2NH$, $((CH_3)_3Si)NH_2$, etc. had now been introduced, thus a more general mechanism could be proposed.



The interaction of bases with SiF_5^- was studied in greater detail. The effect of temperature on the ^{19}F n.m.r. spectrum of tetra-n-propylammonium pentafluorosilicate in the presence of diethylamine is shown in figure [22]. Although not shown ^{29}Si satellites were clearly visible down to -10^o but below this temperature the signal was so broad as to preclude positive identification of the F-^{29}Si coupling. At -60^o the chemical shift was ~9.5 p.p.m. downfield from that of a sample containing no diethylamine, and some resharpening of the peak had occurred. The small peak at +126 p.p.m. is the result of treatment with hexamethyldisilazane and has been mentioned previously.

The results may best be interpreted as a dynamic equilibrium with the position of the equilibrium shifting to the right with decreasing temperature.

$$SiF_5^- + B \underset{}{\overset{\text{fast}}{\rightleftharpoons}} SiF_5^- \cdot B$$

The $SiF_5^- \cdot B$ resonance, as might be expected, is shifted downfield towards that of SiF_6^{2-}. From the peak position several values of

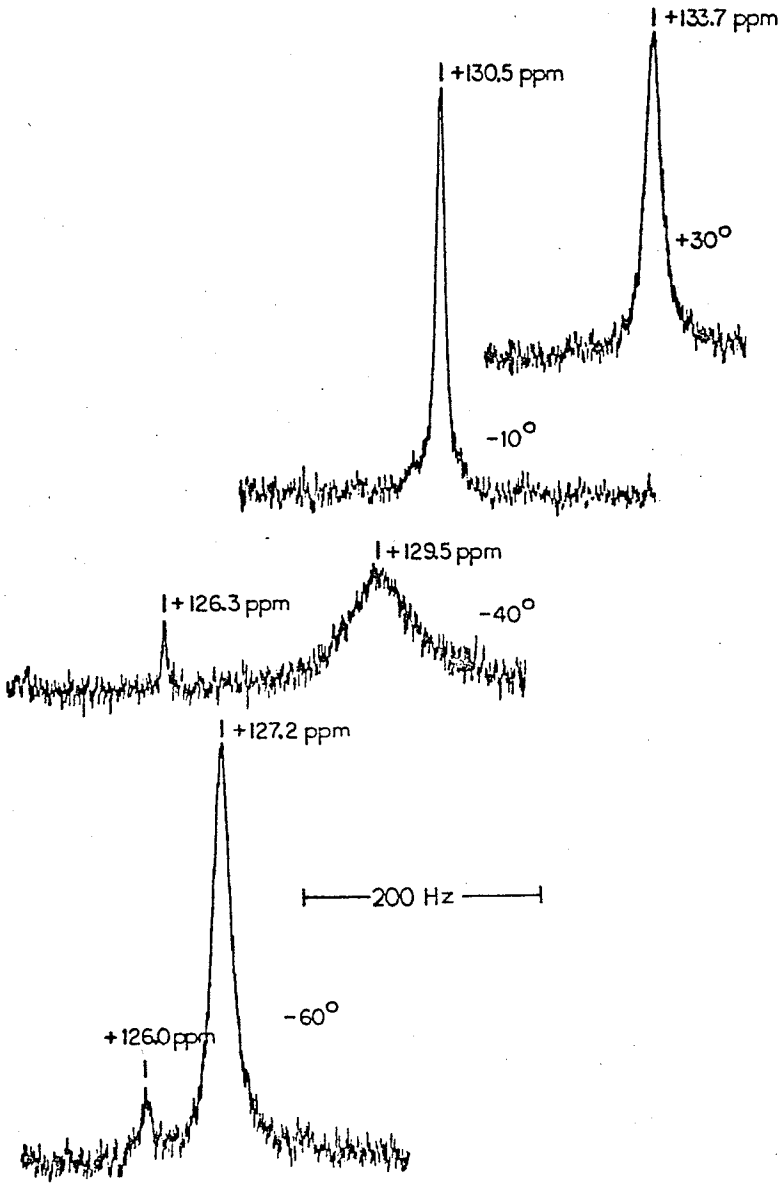


Figure [22]. Temperature Dependant ^{19}F N.M.R. Spectrum of $[(n\text{-}C_3H_7)_4N][SiF_5]$ in CH_2Cl_2 in the Presence of Diethylamine

Solution contained $[(n\text{-}C_3H_7)_4N][SiF_5]$ (0.113 g, 0.36 mmoles), $(C_2H_5)_2NH$ (0.083 g, 1.13 mmoles) and CH_2Cl_2 (0.35 g)

the equilibrium constant were roughly estimated and a plot of ln K vs. 1/T gave values for ΔH, the enthalpy of dissociation, close to those found by previous workers[241,242]; an accurate study was not undertaken.

An intermolecular mechanism may be ruled out since F-^{29}Si coupling was retained, no splitting into axial and equatorial environments (either A_2B_3 or AB_4) was observed even at -85^{o}. Presumably the activation energy for dissociation is low and a stereochemically rigid complex is not observed even at this low temperature. Thus it is possible to suggest that traces of weak bases may well cause intramolecular exchange by lowering the barrier to site permutation. This is shown schematically in figure [23], the pseudorotation is assumed to have a transition state rather than a stabilised intermediate. This thesis does not offer proof of the hypothesis summarised in figure [23] but in view of the current interest in the literature on the question of intramolecular exchange it is included for discussion.

For powerful bases the intermediate will be stabilised sufficiently to have quite large equilibrium constants but the activation energy may still be very low (for diethylamine at least), this is also shown schematically in figure [23]. The activation energies and equilibrium constants for such processes could depend on several factors such as base strength, steric requirements, etc.

As mentioned previously, adducts of pentafluorosilicates with bases are known; Wharf and Onyszchuk have measured the enthalpies of dissociation of a number of amines complexed to the SiF_5^- moiety by

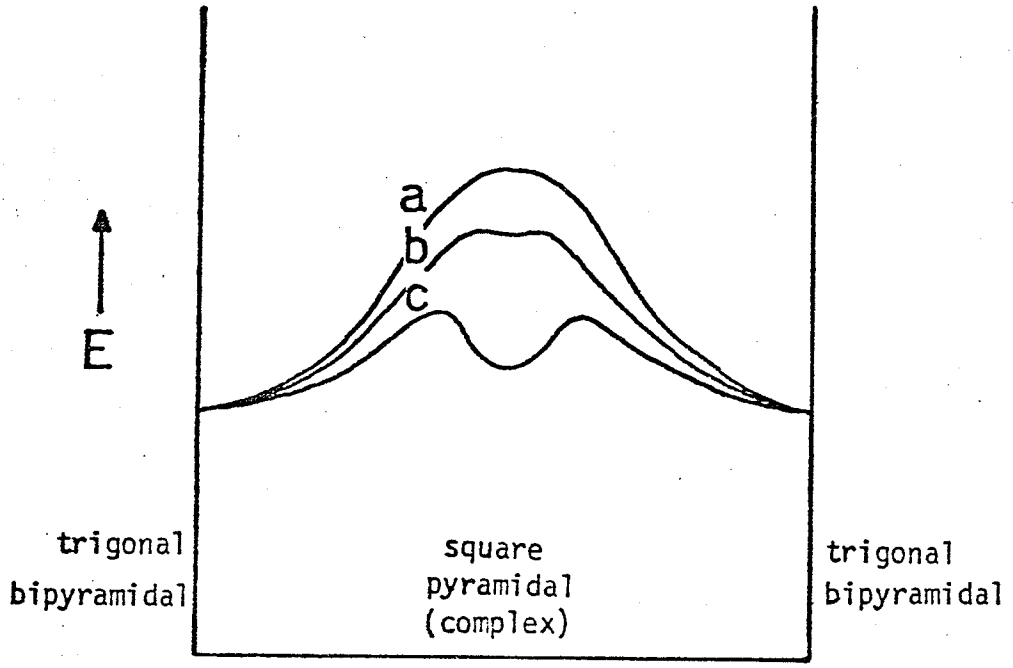


Figure [23]. Schematic Representation of the Interaction of Bases with Pentafluorosilicates

vapour pressure measurements.[241,242] Clark studied the effects of amines on the infra red spectrum of the pentafluorosilicate anion and also the vapour pressure curve of the compound $[(n\text{-}C_3H_7)_4N][SiF_5.NH_3]$.[173] The most effective donor was judged to be diethylamine from the infra red studies.

5.4 PHOSPHORUS PENTAFLUORIDE

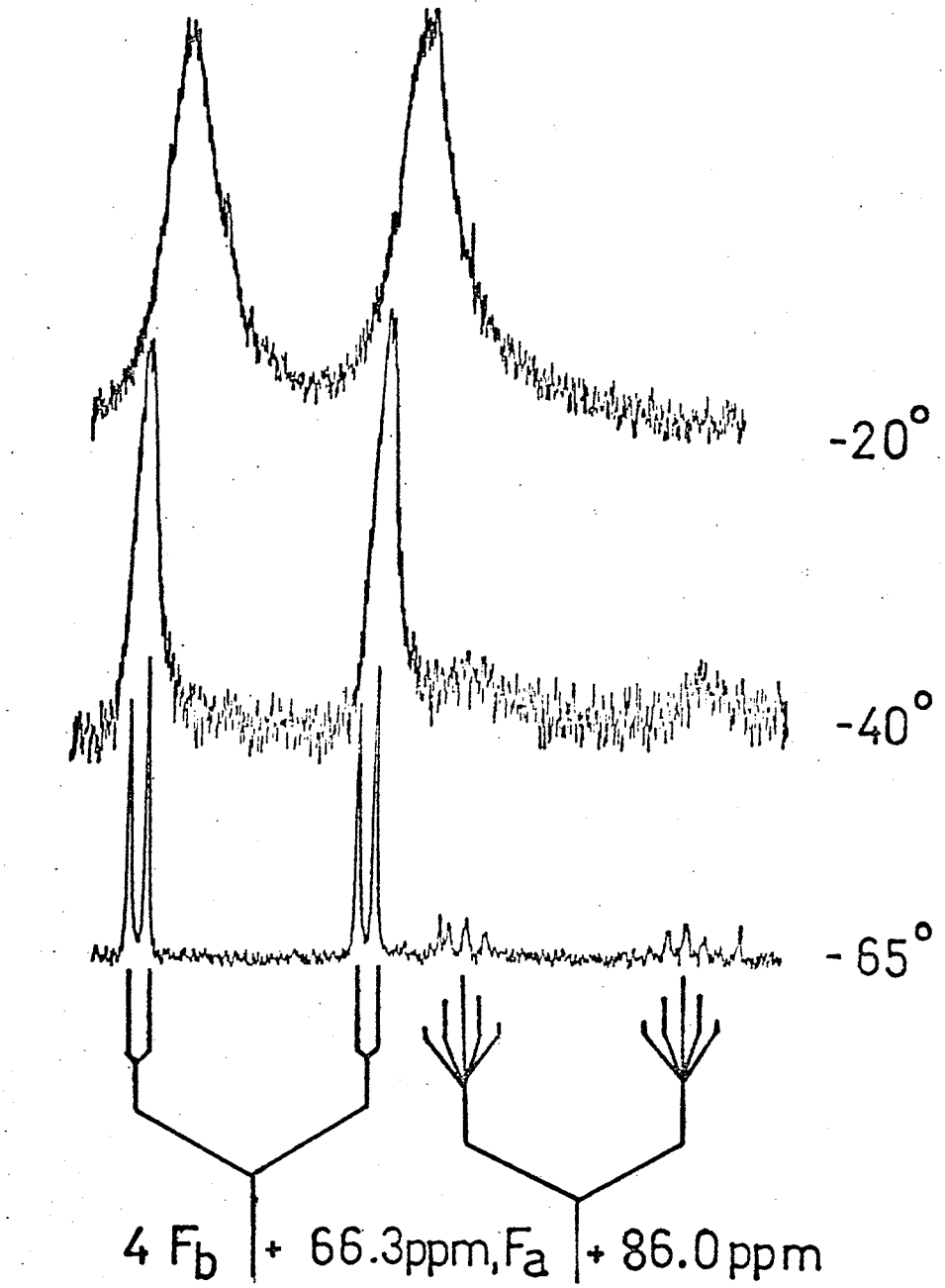
The hypothesis that traces of bases, such as water, may lead to a lowering of the barrier to intramolecular exchange was extended to phosphorus pentafluoride. Intramolecular exchange is very common in phosphorus V fluorides, particularly RPF_4 derivatives.[249] Intermolecular exchange is relatively uncommon, a notable exception being the intermolecular exchange observed in trimethyldifluorophosphorane and dimethyltrifluorophosphorane.[250] It has recently been suggested, however, that this work may be the result of impurities generated by heating the fluorophosphoranes in glass n.m.r. tubes.[251]

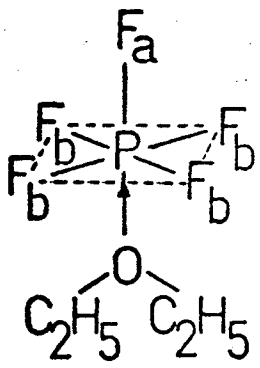
The interaction of phosphorus pentafluoride with bases has been studied by several workers[219,252-255] although only two nuclear magnetic resonance studies appear to have been reported.[219,255] Muetterties et al. studied the interaction of phosphorus pentafluoride with sulphoxides, amines, oximes, amides, thioamides, ethers, esters and nitriles. Very little n.m.r. data was presented but they indicated that complexes with strong donors gave AB_4X (X=P) spectra, i.e. a doublet of doublets and a doublet of quintets. Weaker donors such as ethers, esters and nitriles did not give resolvable AB_4X spectra except for diethylether which gave a doublet of doublets at

-78^{o} but the doublet of quintets was not observed. Other workers have obtained an AB_4X spectrum from the interaction of dimethylether with phosphorus pentafluoride at low temperature.[255]

The complexation of phosphorus pentafluoride with diethylether was restudied. The work presented in this thesis represents a considerable improvement in overall resolution of the spectrum. The temperature dependant ^{19}F n.m.r. spectrum of phosphorus pentafluoride in diethylether is shown in figure [24]. At -65^{o} both a doublet of doublets and a doublet of quintets was observed. The spectrum may be interpreted on a first order basis as an AB_4X system where X is phosphorus. The chemical shifts and coupling constants were as shown. As the solution was warmed from -65^{o} an intramolecular scrambling was observed and at -20^{o} only a doublet was found.

The coupling constants and chemical shifts for the phosphorus pentafluoride-diethylether complex are interesting. The weighted mean P-F coupling constant at -65^{o} was 780 Hz, at -20^{o} the averaged coupling constant was 820 Hz. These values lie between the P-F coupling constant found for phosphorus pentafluoride (940 Hz in $CFCl_3$) and that reported for PF_6^- (706 Hz in H_2O).[60] Similarly the weighted mean chemical shift at -65^{o} was +70.2 p.p.m. and at -20^{o} the averaged chemical shift was ~+70.5 p.p.m. These values lie below the chemical shift of phosphorus pentafluoride (+75.5 p.p.m. in $CFCl_3$) and close to that reported for PF_6^- (+72.2 p.p.m. in H_2O).[60] The AB_4X nature of the spectrum identifies the complex as pseudo-octahedral. It is suggested here that the chemical shifts and coupling constants may be a sensitive guide to the averaged molecular geometry about phosphorus. Thus in the case of the phosphorus





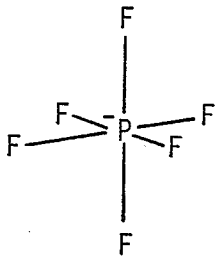
$J_{P-F_a} = 745\,Hz$

$J_{P-F_b} = 790\,Hz$

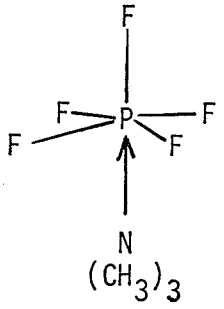
$J_{F_a-F_b} = 65\,Hz$

Figure [24]. Temperature Dependant ^{19}F N.M.R. Spectrum of Phosphorus Pentafluoride in Diethylether

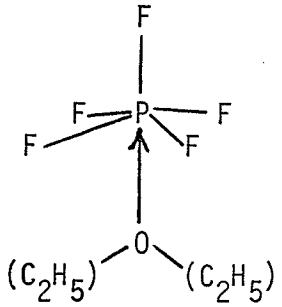
hexafluoride anion true octahedral symmetry is present. However with the PF_5·base complexes the "average" structures are probably distorted with the phosphorus atom above the plane of the four F_b atoms. The amount of distortion would depend on several factors such as base strength,etc. The averaged coupling constants observed would in turn depend on both the position of the equilibrium, base strength and steric factors. However it is possible to see general trends :



J_{F-P}= 706 Hz



av.J_{F-P}= 740 Hz
+20° [219]

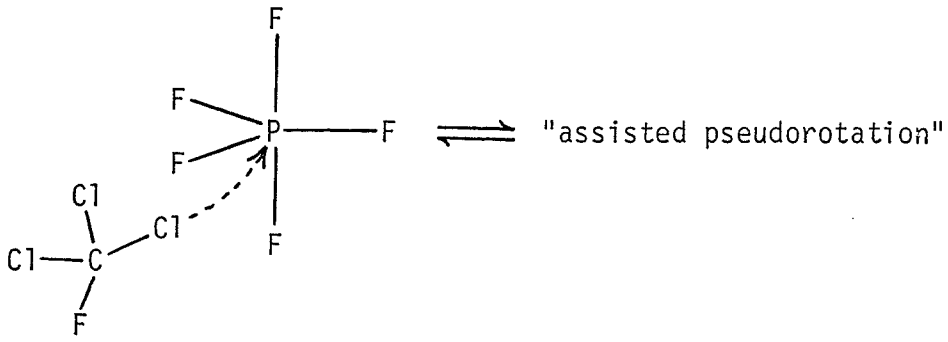


av.J_{F-P}= 820 Hz
-20°

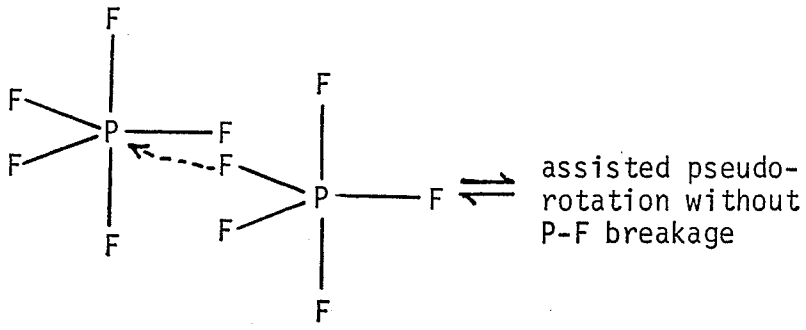
av.J_{F-P}= 781 Hz
-65°

To evaluate such a proposal fully would require a more extensive quantitative study. However it is reasonable to suggest that the weaker the base the closer the complex will approach the Berry pseudo-rotation transition state. Therefore, depending on the activation energy and enthalpy of formation of the complex, weak bases in trace amounts could provide a lower energy to intramolecular exchange than

Berry pseudorotation. It is difficult to define weak base in this context, presumably it should be less basic than $(C_2H_5)_2O$ or an AB_4X spectrum would be seen. Finally it is interesting to see if this concept can be widened somewhat speculatively. For example, is freon-11 a sufficiently strong donor to "lower" the barrier to intramolecular exchange?



It is interesting that Brownstein[256], in a line width study on phosphorus pentafluoride, suggests that an intermolecular association of PF_5 molecules may be the pathway to intramolecular exchange. Incorporating this into the hypothesis presented here, this would simply be:

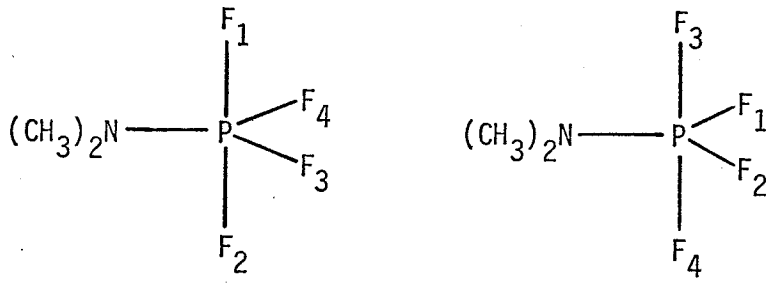


It is not easy to see how one could distinguish between pure pseudorotation and "base" assisted pseudorotation experimentally. Plots of rates vs. concentration are not possible where the rate of intramolecular exchange is too high to be measured by the dynamic n.m.r. technique.

5.5 CONCLUSIONS

Organosilicon fluorides and pentafluorosilicates have been shown to undergo rapid intermolecular exchange by a hydrolytic process. Rate expressions have been derived indicating an analogous mechanism to previously studied chlorosilane hydrolyses. The studies reported in this thesis have contributed to the understanding of organosilicon hydrolyses and, in particular, stress the reversible nature of such hydrolytic processes. Whereas organosilicon fluorides require base catalysis, other systems are much more susceptible and rapid intermolecular exchange may occur in the presence of only traces of water.

The generally accepted theory of intramolecular exchange by ligand vibration mechanisms,such as Berry pseudorotation, has been questioned. An alternative mechanism based on weak Lewis acid-Lewis base interactions has been suggested. Unfortunately no experimental proof has been forthcoming in strong support of such a mechanism since, in its simplest form, it can merely be described as an "assisted" Berry pseudorotation. It is interesting that one experiment in the literature[76] has been suggested by many workers as confirmatory evidence for a pseudorotation mechanism. Using ^{31}P n.m.r. spectroscopy Whitesides and Mitchell showed that equilibration of fluorine environments in N,N-dimethylaminotetrafluorophosphorane occurs by a simultaneous exchange of both axial equatorial fluorines .



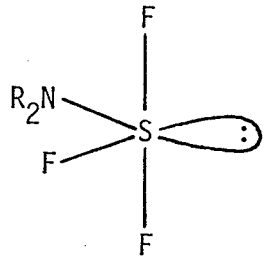
Such an observation is necessary for but does not prove the Berry pseudorotation mechanism. Whitesides and Mitchell themselves point this out, "we will arbitrarily refer to any exchange reaction resulting in interchange of both pairs of fluorines as a "Berry" pseudorotation without implying further details of the interchange". Thus the suggestion by other workers that this experiment confirms the Berry mechanism is not justified. Exactly the same observations would be expected as the result of acid-base assisted exchange.

The postulate that weak acid-base interactions are responsible for lowering the barrier to intramolecular exchange may explain many of the observations found in the literature. Trace catalysis would be more effective with fluorides of greater reactivity and Lewis acidity such as PF_5, SF_4, ClF_3, SeF_4 etc. Reaction of glass with these materials could produce traces of water sufficient to act as a base. RPF_4 compounds are much more susceptible than R_2PF_3 compounds to intramolecular exchange[249] although a very recent paper describes the intramolecular exchange of diphenyltrifluorophosphorane[251] at high temperature. Such effects can be ascribed to the greater Lewis acidity of RPF_4 derivatives compared to

R_2PF_3 compounds. It is also interesting that Treichel et al. obtained good spectra for HPF_4 and H_2PF_3 in the gas phase but broadened spectra in the liquid phase.[257]

The experimental testing of the hypothesis presented here would probably require considerable work. The best approach would be to take a compound with a known temperature dependant spectrum (e.g. $(CH_3)_2NPF_4$) and study the effects of weak bases on the coalescence temperature, etc. Then attempts could be made to run the spectra in non-donor solvents under rigorously anhydrous conditions to see if improvement to previously reported work could be obtained.

Finally it is worth re-examining the results obtained in this laboratory on the n.m.r. spectra of sulphur IV fluoride derivatives run under rigorously anhydrous conditions.[87–89] Sulphur has no spin and it is not possible to distinguish between inter- and intramolecular exchange using ^{19}F n.m.r. spectroscopy. Sulphur IV derivatives have a pseudo-trigonal bipyramidal structure due to the presence of a lone pair in the equatorial plane.



Running the spectra of R_2NSF_3 (R = CH_3, C_2H_5, $(CH_3)_2CH$) and SF_4

under anhydrous conditions led to considerable improvement in spectral resolution. However in view of the fact that the drying procedure was bound to introduce traces of other bases it is the opinion of this author that the exchange observed in these species is intermolecular rather than intramolecular.

Ibbott[87] suggested that the resolution of phosphorus pentafluoride into axial and equatorial ^{19}F n.m.r. environments would depend on a "search for the ultimate drying agent". It is the proposal of this thesis that the situation may be more complex still, improvement of spectra by reducing intramolecular exchange would depend on removal of all materials suitable as Lewis bases in the system under study. Until the ^{19}F n.m.r. spectrum of a trigonal bipyramidal MF_5 molecule has been resolved into axial and equatorial environments the purely ligand motion processes, such as pseudorotation, must still be considered attractive due to their relative simplicity.

APPENDIX

I. RATE EXPRESSION DERIVATION

Proof of the rate expression:

$$\frac{1}{B_o - 2A_o} \ln \frac{A_o B}{B_o A} = kt$$

where B_o = initial concentration of species B

A_o = initial concentration of species A

B = concentration of B after time t

A = concentration of A after time t

For a second order reaction, first order in A, first order in B, with overall stoichiometry:

$$A + 2B \longrightarrow \text{products}$$

Frost and Pearson[128] do not give a treatment of this example and only consider the reaction:

$$A + B \longrightarrow \text{products}$$

Laidler[129] quotes a rate expression for this process which is in error, the rate expression given in his book should read:

$$\frac{1}{b_o - 2a_o} \ln \frac{a_o (b_o - 2x)}{b_o (a_o - x)} = kt$$

Proof

$$-\frac{dA}{dt} = kAB \qquad \text{identity} \qquad \ldots\ldots\ldots(1)$$

$$2(A_o - A) = (B_o - B) \qquad \text{identity} \qquad \ldots\ldots\ldots(2)$$

$$\text{therefore} \quad B = B_o - 2(A_o - A) \qquad \ldots\ldots\ldots(3)$$

$$-\frac{dA}{dt} = kA\left[B_o - 2(A_o - A)\right]$$

$$-\frac{dA}{A\left[B_o - 2(A_o - A)\right]} = kdt \qquad \ldots\ldots\ldots(4)$$

using the method of partial fractions one may write:

$$\frac{1}{A\left[B_o - 2(A_o - A)\right]} \equiv \frac{p}{A} + \frac{q}{B_o + 2A - 2A_o} \qquad \ldots\ldots\ldots(5)$$

equating numerators gives:

$$1 \equiv p\left[B_o + 2A - 2A_o\right] + qA \qquad \ldots\ldots\ldots(6)$$

equating constant terms gives:

$$1 = p(B_o - 2A_o) \qquad \ldots\ldots\ldots(7)$$

equating coefficients of A gives:

$$2p + q = 0 \qquad \text{.....(8)}$$

solving for p and q gives the only solutions as:

$$q = -\frac{2}{B_o - 2A_o} \qquad \text{.....(9)}$$

$$p = \frac{1}{B_o - 2A_o} \qquad \text{.....(10)}$$

therefore from (5):

$$\frac{1}{A\,[B_o - 2(A_o - A)]} = \frac{1}{(B_o - 2A_o)A} - \frac{2}{(B_o - 2A_o)(B_o + 2A - 2A_o)}$$

and from (4):

$$kt = -\,dA\left[\frac{1}{A(B_o - 2A_o)} - \frac{2}{(B_o - 2A_o)(B_o + 2A - 2A_o)}\right] \qquad \text{.....(11)}$$

or:

$$(B_o - 2A_o)\,kdt = -\,dA\left[\frac{1}{A} - \frac{2}{(B_o + 2A - 2A_o)}\right] \qquad \text{.....(12)}$$

integrating from $A_o \rightarrow A$ gives:

$$(B_o - 2A_o)\,kt = -\ln\frac{A}{A_o} + 2\int_{A_o}^{A}\frac{dA}{B_o + 2A - 2A_o}$$

therefore:

$$(B_o - 2A_o)\, kt = \ln \frac{A_o}{A} + \int_{x=B_o}^{x=B+2A-2A_o} \frac{dx}{x}$$

therefore:

$$(B_o - 2A_o)\, kt = \ln \frac{A_o}{A} + \ln \left(\frac{B_o + 2A - 2A_o}{B_o} \right) \qquad \text{.....(13)}$$

simplifying gives from (3):

$$\ln \frac{A_o B}{B_o A} = (B_o - 2A_o)\, kt$$

or:

$$\frac{1}{B_o - 2A_o} \cdot \ln \frac{A_o B}{B_o A} = kt \qquad \text{.....(14)}$$

Alternate Proof

$$\frac{dA}{dt} = -kAB \qquad \text{.....(1)}$$

also:

$$\frac{dB}{dt} = -2kAB \qquad \text{.....(2)}$$

and:

$$B - B_o = 2(A - A_o) \qquad \text{.....(3)}$$

consider $\frac{d}{dt}\left(\frac{A}{B}\right)$:

$$\frac{d}{dt}\left(\frac{A}{B}\right) = \frac{B\,\frac{dA}{dt} - A\,\frac{dB}{dt}}{B^2}$$

$$= \frac{B\,(-kAB) - A\,(-2kAB)}{B^2}$$

simplifying:

$$\frac{d}{dt}\left(\frac{A}{B}\right) = -k\left(\frac{A}{B}\right)(B - 2A) \qquad \text{.....(4)}$$

however the sum B - 2A is a time independant quantity and we may write:

$$B - 2A = B_o - 2A_o$$

therefore:

$$\frac{d}{dt}\left(\frac{A}{B}\right) = -k\left(\frac{A}{B}\right)(B_o - 2A_o)$$

$$\frac{d\left(\frac{A}{B}\right)}{\left(\frac{A}{B}\right)} = -k(B_o - 2A_o)\,dt \qquad \text{.....(5)}$$

integrating gives:

$$\ln\left(\frac{A}{B}\right) - \ln\left(\frac{A_o}{B_o}\right) = -k(B_o - 2A_o)\,t \qquad \text{.....(6)}$$

$$\ln \frac{B_o A}{A_o B} = -(B_o - 2A_o)\,kt$$

or:

$$\frac{1}{B_o - 2A_o} \cdot \ln \frac{A_o B}{B_o A} = kt \qquad \text{.....(7)}$$

II. CALCULATION OF $[(C_2H_5)_2NH]$, $[(CH_3)_3SiF]$ and $[H_2O]$.

Standard solutions were not made up for n.m.r. studies for two principal reasons:

(i) Trimethylfluorosilane is volatile (b.p. 5^o) and solution concentrations would tend to decrease rapidly on standing.

(ii) Making up solutions would mean exposure of materials to the atmosphere and to additional glassware leading to contamination by traces of water.

The concentrations of diethylamine and trimethylfluorosilane were determined by n.m.r. integration prior to introduction of water (the volumes of H_2O/CH_3CN mixtures added were small and changes in $[(C_2H_5)_2NH]$ and $[(CH_3)_3SiF]$ could be neglected). The determination of molarities from n.m.r. integration is not as simple a step as might be anticipated and the method of calculation is outlined below.

The method ignores changes in volume upon mixing since this cannot be allowed for. Such errors are likely to be small for solutions of simple organic,or organometallic,compounds .

	a. CH_3CN	b. $(CH_3)_3SiF$	c. $(C_2H_5)_2NH$
Mole ratio from n.m.r. integration (approp. allowances for no. of protons in each molecule)	p	q	r
therefore wt ratios = (M=molecular wt)	pM_a	qM_b	rM_c
therefore vol ratio = (ρ = density)	$\frac{pM_a}{\rho_a}$	$\frac{qM_b}{\rho_b}$	$\frac{rM_c}{\rho_c}$
Volumes "normalised" to 1 litre total =	$\frac{\frac{pM_a}{a} \cdot 10^3}{\frac{pM_a}{\rho_a}+\frac{qM_b}{\rho_b}+\frac{rM_c}{\rho_c}}$	$\frac{\frac{qM_b}{b} \cdot 10^3}{\frac{pM_a}{\rho_a}+\frac{qM_b}{\rho_b}+\frac{rM_c}{\rho_c}}$	$\frac{\frac{rM_c}{c} \cdot 10^3}{\frac{pM_a}{\rho_a}+\frac{qM_b}{\rho_b}+\frac{rM_c}{\rho_c}}$
therefore Molarity =	-	$\frac{q \cdot 10^3}{\frac{pM_a}{\rho_a}+\frac{qM_b}{\rho_b}+\frac{rM_c}{\rho_c}}$	$\frac{r \cdot 10^3}{\frac{pM_a}{\rho_a}+\frac{qM_b}{\rho_b}+\frac{rM_c}{\rho_c}}$

Compared below are four solutions of diethylamine made up as standards in acetonitrile, the actual molarity is compared with the molarity as measured by n.m.r. integration.

Actual Molarity.	Molarity by n.m.r.
0.22	0.24
0.44	0.40
0.72	0.71
1.22	1.29

estimated standard deviation ±10%

The molarity of water in the mixtures was calculated by determining the total volume (±0.02 ml) of the mixture in the n.m.r. tube and calculating the molarity directly from the number of μl of water added.

$$[H_2O] = \frac{\text{no. of } \mu l \ H_2O \text{ added}}{v \times 18}$$

v = volume of mixture

estimated standard deviation ±10%

The overall errors involved in the kinetic studies from the above discussions are obviously large; with insufficient data a detailed statistical treatment is not warranted, errors due to non-random fluctuations are discussed, where relevant, in chapter 4.

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