ACID CATALYSED ACETYLENE-ALLENE ISOMERISATIONS

by

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ABSTRACT

The isomerisations of 1-, 2- and 3-hexyne and of 1,2- and 2,3-hexadiene have been studied in various acid catalysts, all of which were anhydrous solutions in sulpholane. The principal catalysts were HBF_4 and HPF_6 while others used were BF_3, PF_5, PF_5/H_2O, $HClO_4$, HSO_3F, AsF_5, $HAsF_6$, AsF_5/SO_3, and H_2SO_4.

The evidence for all catalysts favours a stepwise hexyne-hexadiene-hexyne pathway. In the case of the protonic acids it is proposed that vinyl cations were formed by protonation of the isomers and that the subsequent deprotonation occurred from another site in the molecule:

$$-C\equiv C-CH_2- + H^+ \rightleftharpoons -CH=\overset{+}{C}-CH_2- \rightleftharpoons -CH=C=CH- + H^+$$

The most probable explanation for the Lewis acid catalysed reaction is that a co-catalyst (such as water) is present so that the true catalyst is a protonic acid; however, alternative mechanisms are discussed.

The isomeric conjugated dienes were found to be unstable in the reaction media. The implications of this for the reaction mechanisms are discussed.

Free energy changes in the isomerisations could not be determined since equilibration studies were not carried out due to irreversible side reactions. However, a kinetic analysis leads to an order of stability consistent with published data.

The side reactions also prevented the calculation of accurate kinetic data and the reaction order.

The addition products formed in the HBF_4 catalysed reactions were identified as 2,2- and 3,3-difluorohexane.

Nmr, conductivity and solvent extraction studies provided evidence on the nature of the acid species and suggested that complex formation occurred between the isomers and the acids. It is proposed that the complex formation is responsible for the production of hexanones in the HPF_6 catalysed reactions.

Hexanone production in the H_2SO_4 catalysed reaction was found to occur before water was added to quench the reaction, contrary to the mechanism proposed previously. A possible alternative mechanism is discussed.

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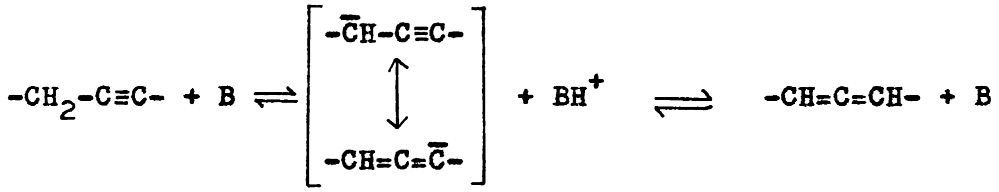
CHAPTER ONE

INTRODUCTION

1.1 ACID CATALYSED ACETYLENE-ALLENE ISOMERISATIONS

Base catalysed acetylene-allene isomerisations have long been known, having been first observed in 1887[1]. Since that time a number of studies have been made and the field has recently been reviewed[2]. The generally accepted mechanism for these isomerisations was first postulated by Jacobs et. al[3]. It involves the formation of carbanions as reaction intermediates:



$$-CH_2-C\equiv C- + B \rightleftharpoons \left[\begin{array}{c} -\bar{C}H-C\equiv C- \\ \updownarrow \\ -CH=C=\bar{C}- \end{array}\right] + BH^+ \rightleftharpoons -CH=C=CH- + B$$

Weedon[4] has noted that there are many examples of acetylene-allene isomerisations in vitro.

The first report of acid catalysed acetylene-allene isomerisations under homogeneous conditions was as a side reaction to addition to allenes. During the addition of HCl (neat, -78^{o}) to allene ($BiCl_3$ catalyst required) and to 1,2-butadiene some rearrangement to propyne and 2-butyne respectively occurred. Addition of HCl to the two acetylenes resulted in some rearrangement back to the allenes. The formation of vinyl cation intermediates was proposed to account for the products of the addition reactions and it was pointed out that the same intermediates could account for the isomerisations[5].

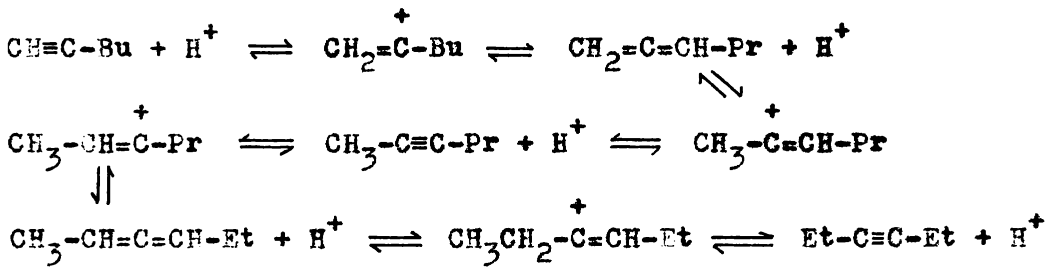
An allene-propyne isomerisation has been implicated in the mechanism of the chlorination of allene in the presence of boron trifluoride diethyletherate catalyst. However the intermediates in the isomerisation reaction were not discussed[6].

Deprotonation of vinyl cations has been studied by Noyce et. al.[7a] and by Grob and Cseh[7b]. Noyce found that during the acid catalysed hydration of phenylacetylene a small amount (ca. 1%) of exchange of the acetylenic hydrogen occurred; Grob and Cseh observed that the solvolysis of α-bromostyrene to acetophenone was accompanied by the formation of phenylacetylene. Formation of a vinyl cation followed by deprotonation would explain the results of both of these groups.

Some acid catalysed isomerisations under heterogeneous conditions have been reported; e.g. propyne was isomerised to allene over a silica catalyst[8].

The first direct study of acid catalysed acetylene-allene isomerisations under homogeneous conditions has been carried out by the group of which this author is a member.

The project was commenced by Reid[9]. In a very brief study each of the five straight chain C_6H_{10} isomers (1-hexyne, 1,2-hexadiene, 2-hexyne, 2,3-hexadiene, 3-hexyne) was reacted with an anhydrous sulpholane solution of p-nitrobenzene sulphonic acid. Except for 2-hexyne, isomerisation occurred and it was tentatively suggested that the reaction occurred via a protonation-deprotonation sequence involving vinyl cation intermediates:



$$\begin{tikzcd}
CH\equiv C-Bu + H^+ \arrow[r, rightleftharpoons] & CH_2=\overset{+}{C}-Bu \arrow[r, rightleftharpoons] & CH_2=C=CH-Pr + H^+ \arrow[d, rightleftharpoons] \\
CH_3-CH=\overset{+}{C}-Pr \arrow[r, rightleftharpoons] \arrow[d, rightleftharpoons] & CH_3-C\equiv C-Pr + H^+ \arrow[r, rightleftharpoons] & CH_3-\overset{+}{C}=CH-Pr \\
CH_3-CH=C=CH-Et + H^+ \arrow[r, rightleftharpoons] & CH_3CH_2-\overset{+}{C}=CH-Et \arrow[r, rightleftharpoons] & Et-C\equiv C-Et + H^+
\end{tikzcd}$$

Considerable product destruction occurred, limiting the usefulness of this acid as a catalyst.

The isomerisation of the same compounds using H_2SO_4 in sulpholane as the catalyst was the subject of a very much more extensive study by Hei[10].

The two allenes were the main products of the initial isomerisation of the acetylenes; 1-hexyne gave 1,2-hexadiene, and both 2- and 3-hexyne gave 2,3-hexadiene. The allene proportions passed through a maximum in each case. The products from the allene isomerisations were exclusively the three acetylenes; 1,2-hexadiene gave 1- and 2-hexyne, and 2,3-hexadiene gave 2- and 3-hexyne. The products of the later stages of the acetylene isomerisations were in accord with the results of the allene isomerisations.

Thus 1,2-hexadiene was the precursor of 2-hexyne in the 1-hexyne isomerisation; similarly 2,3-hexadiene was the precursor of 2-hexyne in the 3-hexyne isomerisation and of 3-hexyne in the 2-hexyne isomerisation.

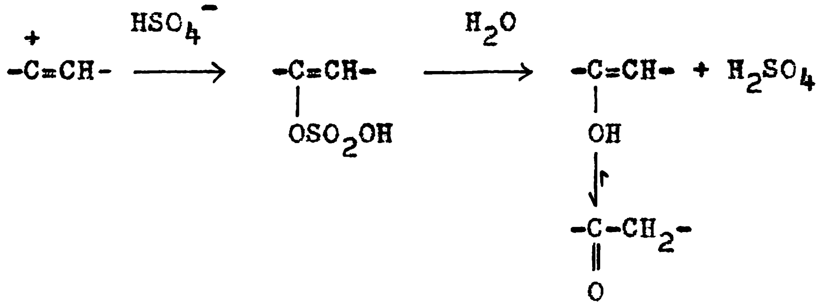
This data indicated that the isomerisation occurs by the following stepwise sequence:

$$\text{1-hexyne} \rightleftharpoons \text{1,2-hexadiene} \rightleftharpoons \text{2-hexyne} \rightleftharpoons \text{2,3-hexadiene} \rightleftharpoons \text{3-hexyne}$$

This sequence was explained by the protonation-deprotonation mechanism involving vinyl cations as outlined above.

No traces of the isomeric conjugated dienes 1,3- and 2,4-hexadiene were found although these were readily detectable on the glc column used for product analysis[11].

Large amounts of 2- and 3-hexanone were produced, thus preventing equilibration of the isomers. This competing reaction was also accounted for by implicating vinyl cation intermediates:



$$\overset{+}{-C{=}CH-} \xrightarrow{HSO_4^-} \underset{\displaystyle OSO_2OH}{-C{=}CH-} \xrightarrow{H_2O} \underset{\displaystyle OH}{-C{=}CH-} + H_2SO_4 \quad \rightleftharpoons \quad \underset{\displaystyle \overset{\|}{O}}{-C-}CH_2-$$

i.e. water used in the work up of the reaction products attacks a sulphate ester formed via a vinyl cation. By this mechanism 2-hexanone would be formed from a cation with positive charge on carbon atom number two in the chain (C-2), and 3-hexanone from a cation with charge at C-3.

The actual distribution of the two ketones formed was as follows:

1-hexyne:	mostly 2-hexanone, but with some 3-hexanone after 40% reaction.
1,2-hexadiene:	mostly 2-hexanone, but with some 3-hexanone after 50% reaction.

2-hexyne: the 3-:2-hexanone ratio was approximately equal to 1.2 throughout the observed reaction.

2,3-hexadiene: mostly 3-hexanone, but with some 2-hexanone after 80% reaction.

3-hexyne: exclusively 3-hexanone.

These results are consistent with the vinyl cations postulated in the protonation-deprotonation mechanism. For example, 1,2-hexadiene would form vinyl cations with the charge at C-2 and 2-hexanone would be produced as a result; however its main isomerisation product is 2-hexyne which gives cations with charge at both C-2 and C-3 thus forming 3-hexanone at a later stage in the reaction.

The rates of the reactions corresponded approximately to the expected thermodynamic stabilities of the isomers[12]. Thus the allenes were expected to be the least stable and these indeed gave the fastest reactions. The internal acetylenes reacted more slowly than 1-hexyne, again as expected.

The proposed protonation-deprotonation mechanism involves attack of a single proton on a single isomer molecule. If, as seems likely, this is the rate determining step the kinetics would be first order in both isomer and catalyst.

The reaction was found to be first order in the isomers as expected, but approximately fourth order in the acid. This was possibly due to complexity of the catalyst system.

Product destruction occurred during the reaction; e.g. in the reaction of 3-hexyne (with 0.959 M H_2SO_4) there was about 65% product recovery after 15% reaction.

Beale[13] extended this work to the HBF_4/sulpholane catalyst system.

A similar isomerisation pattern to that for H_2SO_4/sulpholane was observed and once again the protonation-deprotonation sequence involving vinyl cations was invoked.

No traces of conjugated dienes were found, either by inspection of the chromatograms or by a uv analysis of the reaction products.

Considerable side reactions occurred. It was found at first that an unknown compound, labelled X, occurred in the reactions with 2- and 3-hexyne and with 2,3-hexadiene (also to a small extent after 80% reaction of 1,2-hexadiene). The isomers were then reacted with a strong HBF_4 solution (0.99 M, 12 hour reaction) and apart from a small amount of 3-hexyne in the 2-hexyne reaction only two compounds were formed; these were X and a compound, labelled Z, with the same retention time as 1-hexyne. Z could not be 1-hexyne as that compound had already been found to isomerise in a much weaker (0.1 M) HBF_4 solution. The product analysis gave the following result:

isomer	%Z	%X	Other
1-hexyne	70	30	
1,2-hexadiene	49	51	
2-hexyne	45	54	1% 3-hexyne
2,3-hexadiene	29	71	
3-hexyne		100	

These results are consistent with the formulation of Z as 2,2-difluorohexane and X as 3,3-difluorohexane, these compounds being formed by successive additions of two HF molecules according to Markovnikov addition.

3-Hexyne, being symmetrical, will only form 3,3-difluorohexane while 2-hexyne will form both 2,2- and 3,3-difluorohexane depending on the orientation of the initial addition. The remaining three results can be explained by postulating addition competing with fast isomerisation. For example, 1-hexyne would form only 2,2-difluorohexane by Markovnikov addition[14]; however if fast isomerisation to 1,2-hexadiene and thence to 2-hexyne occurred, addition to the 2-hexyne so produced would yield both 2,2- and 3,3-difluorohexane.

Furthermore, if the addition occurs via the vinyl cations postulated for the protonation-deprotonation sequence the results are also as expected. For example, 2-hexyne gives vinyl cations with the positive charge at C-2 and C-3; Markovnikov addition would then result in the formation of both 2,2- and 3,3-difluorohexane:

$$\text{i.e. } CH_3\text{-}C{\equiv}C\text{-}CH_2CH_2CH_3 + H^+ \longrightarrow CH_3\text{-}CH{=}\overset{+}{C}\text{-}CH_2CH_2CH_3 \xrightarrow{2HF} CH_3CH_2CF_2CH_2CH_2CH_3$$

$$+ \quad CH_3\overset{+}{C}{=}CH\text{-}CH_2CH_2CH_3 \xrightarrow{2HF} CH_3CF_2CH_2CH_2CH_2CH_3$$

Small amounts (ca. 6% maximum) of a third side product, labelled Y, were noted in the 3-hexyne isomerisation. It was tentatively suggested that Y was the result of anti Markovnikov addition, i.e. 3,4-difluorohexane.

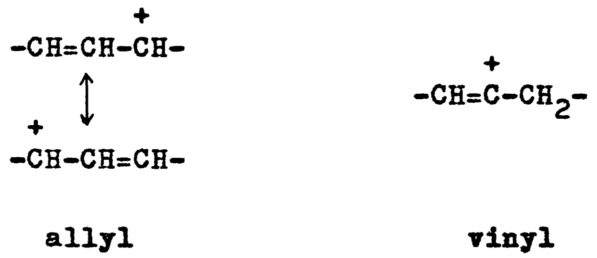
The isomerisations were much faster than with H_2SO_4. For example, 20% reaction of 3-hexyne took about 40 hours with 0.959 M H_2SO_4 but only about 20 minutes with 0.1 M HBF_4. However the relative rates for the five isomers were approximately those expected from the thermodynamic stabilities[12].

The occurrence of the side reactions was an obstacle to kinetic studies. However it was possible to study the reactions of 1,2- and 2,3-hexadiene before significant amounts of the addition products had been formed. Approximately third order kinetics were found.

In the 1-hexyne reaction the very reactive 1,2-hexadiene built up to a high maximum proportion (ca. 20%). This correlated with the third order kinetics as a lower concentration then implies an increase in the time for half reaction.

1.2 ALLYL AND VINYL CATIONS

Jacobs[5] and the members of this group[9,10,13], have all discussed the possibility of the formation of allyl cations. These are resonance stabilised species and would be expected to be more stable than the isomeric vinyl cations.



$$\text{-CH=CH-}\overset{+}{\text{C}}\text{H-} \updownarrow \overset{+}{\text{C}}\text{H-CH=CH-} \qquad \text{-CH=}\overset{+}{\text{C}}\text{-CH}_2\text{-}$$

allyl vinyl

There are two possibilities for the formation of allyl cations in the present system.

Firstly, a hydride shift could occur in a vinyl cation.

$$\text{-CH=}\overset{+}{\text{C}}\text{-CH}_2\text{-} \rightleftharpoons \text{-CH=CH-}\overset{+}{\text{C}}\text{H-} \longleftrightarrow \overset{+}{\text{C}}\text{H-CH=CH-}$$

Whiting[15] has observed that reactions involving secondary <u>alkyl</u> cations are invariably accompanied by hydride shifts. However, only one example of a hydride shift in a vinyl cation has so far been reported and in this case an allyl cation was not formed[16].

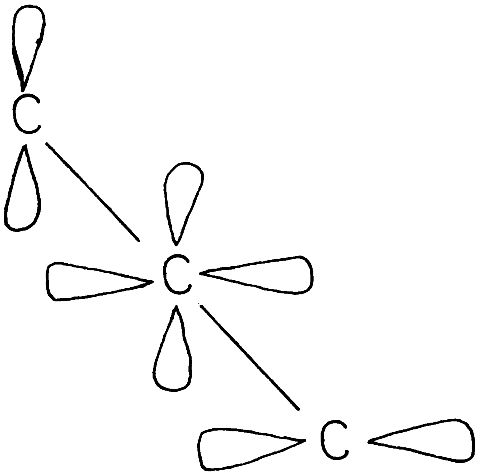
$$\text{Ad-CH=}\overset{+}{\text{C}}\text{H} \rightleftharpoons \text{Ad-}\overset{+}{\text{C}}\text{=CH}_2 \quad (\text{Ad = adamantyl})$$

The second possibility is protonation on the central carbon atom of the allene system.

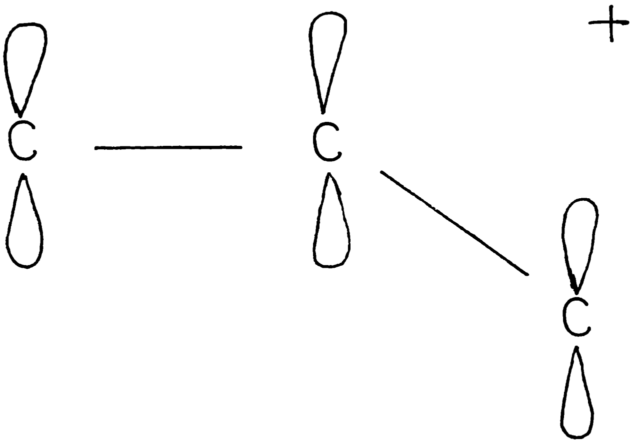
$$\text{-CH=C=CH-} + \text{H}^+ \rightleftharpoons \text{-CH=CH-}\overset{+}{\text{C}}\text{H-} \longleftrightarrow \overset{+}{\text{C}}\text{H-CH=CH-}$$

Two factors mitigate against this reaction. Firstly, the polarization of the bonds in the allene molecule favours electrophilic attack on the terminal carbon atom[17]. Secondly[5], the geometry of the allene system favours the formation of a vinyl cation.

In the parent allene the two π orbitals are perpendicular to each other, as are the groups at each end of the allenic system.



In an allyl cation however the two orbitals, and the substituent groups, are coplanar so that a considerable change in the geometry of the molecule is required.

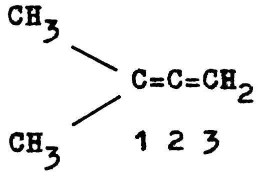


Without a 90° rotation of one of the allene π bonds resonance stabilisation can not occur; hence the transition state in the formation of the intermediate allyl cation may not reflect the stability of that intermediate.

It might be expected that the presence of electron donating groups at the ends of the allene system would favour the formation of allyl cations; this has in fact been found to be the case. Several studies of protonation, and other electrophilic attack, have been made and some typical examples will be discussed here.

Jacobs[5], studied the addition of HCl to the following allenes:

$CH_2{=}C{=}CH_2$ $CH_3{-}CH{=}C{=}CH_2$



unsubstituted monosubstituted 1,1-disubstituted

The first two were protonated at the terminal C atom (with concurrent isomerisation to propyne and 2-butyne respectively) and the third at the central C atom (with concurrent isomerisation to the conjugated diene isoprene). Bianchini[18] extended this study to HBr addition to 1,1-, 1,3-, tri- and tetrasubstituted allenes; protonation of the 1,3-substituted compounds (2,3-pentadiene, -hexadiene and -heptadiene) was 80% central and 20% terminal, while all the other compounds were protonated exclusively at the central C atom.

An example of a similar variation in attack by electrophiles other than the proton has been given by Sethi et. al.[19]. Electrophilic attack of disiamylborane, $\left[(CH_3)_2CHCHCH_3\right]_2BH$, occurred preferentially at the less substituted terminal C atom of 1,2-nonadiene, phenylpropadiene and 3-phenyl-1,2-butadiene; preferentially on the central C atom of 4,5-nonadiene; and exclusively on the central C atom of tetramethylallene.

Further examples of similar variations in the position of protonation and other electrophilic attack are noted in the list of references[5,6,20-29].

In general, when a substituent can stabilise a positive charge at the terminal C atom electrophilic attack at the central carbon atom is favoured[17].

Until about 1960 it was thought that vinyl cations were very unstable because of the difficulty of solvolysing vinyl halides[30]. However they have since been shown to have properties similar to alkyl cations and have been implicated in many reactions; extensive reviews have been published[17,31]. Vinyl cations are now considered to be intermediate in stability between ethyl and methyl cations[31] although they have not yet been prepared in solution with lifetimes sufficient to permit their observation by spectral methods[31,32].

1.3 THE NATURE OF THE ACID SOLUTIONS

The solvent used by this group is sulpholane (tetrahydrothiophene-1,1-dioxide or tetramethylene sulphone), one of the dipolar aprotic solvents. Parker[33] has defined these as "solvents with dielectric constants greater than fifteen, which, although they may contain hydrogen atoms, can not donate suitably labile hydrogen atoms to form strong hydrogen bonds with an appropriate species".

Because of this lack of hydrogen bonding anions are less solvated in aprotic solvents than in protic solvents. Moreover, solvation is stronger for large than for small anions (since larger anions are more polarisable). A consequence of this is that in aprotic solvents the order of the acid strengths of the hydrogen halides is

$$HI > HBr > HCl > HF$$

i.e. the order of the strengths of the H-X bonds is reinforced, the acid with the weakest H-X bond being the strongest proton donor[33]. Thus aprotic solvents are known as differentiating solvents[34]. However, in protic solvents anion solvation is strongest for small anions; thus dissociation of acids with stronger H-X bonds is favoured. For instance, the hydrogen halides in methanol are of approximately equal strength[33]. Thus protic solvents are known as levelling solvents[34].

The trends in cation solvation are different. Cations are most strongly solvated in highly polar solvents having a negative charge localised on a bare oxygen atom[33]. The following list of strengths of cation solvation was taken from a larger list suggested for some solvents[33]:

DMSO (aprotic) > water (protic) > sulpholane (aprotic) > methanol (protic) ≫ acetonitrile (aprotic)

It is evident from the list that it is not possible to generalise about solvation of cations as it was for anions.

An important observation from the list however is that sulpholane solvates cations less efficiently than water. A weakly solvated proton would be expected to be more active than a strongly solvated proton; this supposition is borne out by the following H_0 values for aqueous[35] and sulpholane[36] solutions (1 mole/litre in both cases) of some common acids.

acid	aqueous solution	sulpholane solution (from a graph)
HCl	-0.20	-2.9
HBr	-0.20	-6.0
H_2SO_4	-0.26	-4.5
$HClO_4$	-0.22	-8.0

The advantage of a dipolar aprotic solvent such as sulpholane for acid catalysis is therefore obvious. An example of its use is the isomerisation of trans-Δ^1-octalin to Δ^9-octalin by HBF_4[37]; the reaction in benzene:sulpholane (1:2 by volume) is 8×10^4 times as fast as in benzene:acetic acid (1:2 by volume). It should also be noted that the present group uses water to quench the isomerisation reactions (s = sulpholane):

$$\underset{\text{strong acid}}{sH^+} \quad + \quad H_2O \longrightarrow \underset{\text{weaker acid}}{sH_3O^+}$$

Parker[33,38] has reviewed the field of dipolar aprotic solvents and Dack[39] has summarised the factors affecting the choice of solvent in organic reactions.

Whiting[36] has carried out H_o measurements on various acids in sulpholane. The order of acidity was

$$HCl < H_2SO_4 < HBr < HSO_3F \sim HBF_4 < HClO_4 < HPF_6 \quad \text{(0.1 mole/litre)}$$

$$\text{and} \quad " < " < " < " < HClO_4 < HBF_4 < " \quad \text{(1 mole/litre)}$$

From the slopes of the $-H_o$ against log $[HA]$ plots it was deduced that HSO_3F, $HClO_4$ and HPF_6 dissociate to form simple ion pairs of the type $sH^+ \ldots A^-$ (s = sulpholane) while HCl, HBr and H_2SO_4 form $H^+ \ldots H\bar{A}_2$. The slope of the plot for HBF_4 was intermediate between these two types and an equilibrium of the type

$$s + HF + BF_3 \rightleftharpoons sH^+ \ldots BF_4^-$$

was postulated. This accords with the low heat of mixing of sulpholane solutions of HF and BF_3[36], and with the obvious vapour pressures of HF and BF_3 over HBF_4 solutions[40].

Solutions of BF_3 and PF_5 in sulpholane were studied by Jones[41] using ir and ^{19}F nmr techniques. Sulpholane and BF_3 formed a 1:1 complex (white, square, plate-like crystals), the boron atom probably being tetrahedrally bonded. Sulpholane and PF_5 did not form a complex (except perhaps at high pressure) but nmr indicated that rapid intermolecular exchange of fluorine atoms occurred. Auto-ionisation was postulated to explain this:

i.e. $\quad PF_5 \rightleftharpoons PF_4^+ + F^-$

or $\quad 2PF_5 \rightleftharpoons PF_4^+ + PF_6^-$

The average exchange lifetime of a fluorine nucleus was found to be 2.76×10^{-5} seconds.

Using ^{19}F nmr, Brownstein[42] found evidence of fluorine exchange in PF_5/CH_2Cl_2 solutions. An intramolecular exchange by an intermolecular mechanism was postulated; however no detailed mechanism was outlined. Macomber[43] criticised this interpretation and suggested that intermolecular exchange explained the results;

autoionisation of PF_5 to PF_4^+ and PF_6^- was tentatively suggested.

Kolditz and Rehak[44], on the basis of conductivity and hydrolysis studies, suggested that autoionisation occurred in CH_3CN solutions of CH_3CN complexes of PF_5, AsF_5 and SbF_5. However, Tebbe and Muetterties[45] studied the same systems with ^{19}F nmr and found no fluorine exchange in PF_5 solutions at room temperature while exchange at 80° was explained by the presence of PF_6^- impurity; it was further found that without a rigourous purification procedure the solutions could contain up to 10% PF_6^- and it was on this basis that Kolditz and Rehak's results were explained. Similarly, no evidence was found for fluorine exchange in AsF_5 and SbF_5 solutions.

Lewis acid catalysts have long been used in organic chemistry, e.g. Friedel-Crafts reactions. These catalysts require the presence of a co-catalyst so that reaction can take place; co-catalysts react with the Lewis acid to form a protonic acid which is the actual catalyst[46a,47a];

$$\text{e.g.}\quad \underset{\text{Lewis acid}}{BI_3} + \underset{\text{co-catalyst}}{H_2O} \longrightarrow \underset{\text{actual catalyst}}{H^+(BF_3O\bar{H})}$$

Although the need for a co-catalyst is now accepted it has, due to experimental difficulties, been demonstrated in only a few cases. One such is the polymerisation of isobutylene by BF_3 (which is very difficult to dry completely[46b]); the reaction does not occur with dry BF_3 but the addition of traces of water results in a very fast reaction[48].

The proportion of catalyst to co-catalyst which gives maximum reaction rate varies from case to case. Consider, for example, the $SnCl_4$ catalysed polymerisation of styrene with water as co-catalyst; the maximum rate occurs at $[H_2O]/[SnCl_4]$ values of 0.002 in CCl_4 solution and 1.0 in nitrobenzene/CCl_4 (30:70 by volume) solution. This was interpreted as being due to catalysis by stannic chloride mono- and dihydrate respectively[47b]; an alternative explanation is that water can also act as a polymerisation terminator, a reaction which results in a lowering of the co-catalyst concentration, so that the maximum rate occurs at some optimum co-catalyst concentration[47c].

1.4 THE AIM OF THE PRESENT WORK

The work described in this thesis is an attempt to solve some of the problems associated with the previous work of this group and to use new catalyst systems.

Hei[10] did not make a detailed study of the mechanism of ketone formation in the H_2SO_4 catalysed reactions. Furthermore, equilibration studies were not possible due to product destruction and the formation of side products.

Beale[13] presented only indirect evidence to show that the side products formed in the HBF_4 catalysed reactions were 2,2- and 3,3-difluorohexane. The kinetics of the isomerisation were puzzling. The stability of conjugated dienes in the reaction systems was not studied. Equilibration studies were not feasible because of the formation of side products.

Thus a catalyst which does not promote side reactions would be desirable. Whiting's[36] H_o measurements suggested the use of sulpholane solutions of HPF_6, HSO_3F and $HClO_4$, which are of comparable acid strength to HBF_4. Their use would overcome any problems connected with the complexity of the HF/BF_3 system. Also, Beale[13] has suggested the use of BF_3/sulpholane as a catalyst.

CHAPTER TWO

EXPERIMENTAL

2.1 THE ISOMERISATION REACTIONS

The following procedure was used for the isomerisation reactions unless otherwise stated.

The catalyst solution (1 ml) was introduced into a test tube (13 mm od) in a dry nitrogen atmosphere. The tube was sealed with a serum cap, withdrawn from the nitrogen atmosphere and placed in a water bath held at 25.0°C. After allowing 15-30 minutes for thermal equilibration one of the isomers (10μl) was injected into the solution through the serum cap. The tube was then shaken to ensure even mixing of the isomer and the catalyst solution; homogeneous solutions were always obtained.

At the chosen time the reaction was quenched with water (0.5 ml). The reaction products were then extracted by shaking the aqueous mixture with petroleum spirits (1 ml; see appendix 1.7). If necessary the petroleum spirits layer was separated and stored in a refrigerator freezer in a sample bottle.

A sample of the petroleum spirits layer (2 μl) was taken for analysis by gas liquid chromatography (glc) as described in section 2.2.

2.2 PRODUCT ANALYSIS BY GAS CHROMATOGRAPHY

The gas chromatograph used was a Perkin Elmer model 800, a dual column instrument equipped with a flame ionisation detector.

The details of the sensing column used are as follows:

Liquid phase	20% polypropylene glycol LB-550-X
Stationary phase	chromosorb W, 60/80 mesh
Length	24 feet
Size	$\frac{1}{8}$ inch od
Material	stainless steel

A column temperature of 50° and a carrier gas (nitrogen) flow rate of 24 ml/min gave the following retention times (the relative retention times are based on 2-hexyne as 1.00):

isomer	retention times (minutes)	relative retention times
1-hexyne	44.0	0.72
1,2-hexadiene	40.5	0.66
2-hexyne	61.0	1.00
2,3-hexadiene	39.0	0.64
3-hexyne	51.5	0.84

Other retention times of interest are:

Compound	relative retention times	
1,3-hexadiene	0.60 0.69	geometrical isomers
2,4-hexadiene	0.81 0.91 0.98	geometrical isomers

(continued...)

(continued..)

Compound	relative retention times
2-hexanone	3.63
3-hexanone	3.23
2,2-difluorohexane	0.72
3,3-difluorohexane	0.76
Y	0.62

Temperature programming was usually used to elute the two hexanones. The oven temperature was changed from 50° to 100° at 40°/min as soon as the 2-hexyne peak had eluted. Under these conditions the relative retention times of 2- and 3-hexanone were 1.51 and 1.49 respectively.

The amount of a particular component of a sample is proportional to the area of its chromatographic peak and several methods have been developed to estimate such areas[49]. The method used in this work is due to Pecsok[50] who showed that the product of peak height and retention time is (to a good approximation) proportional to the area under the peak.

In addition, since different compounds have different responses to the flame ionisation detector it is necessary to calculate a response factor by using known amounts of each compound. This was done for the five isomers by Reid[9] and, assigning 2-hexyne the arbitrary value of 1.00 the following results were obtained:

isomer	response factor
1-hexyne	1.19
1,2-hexadiene	0.96
2-hexyne	1.00
2,3-hexadiene	1.03
3-hexyne	1.04

The response factors of the other compounds of interest were arbitrarily taken to be 1.00.

The method for obtaining the relative amounts of each isomer from the chromatogram is as follows:

1. The compounds are identified by their retention times.
2. The signal attenuation from the detector and the peak height are noted for each compound.
3. The product of the peak height, relative retention time, attenuation, and response factor is calculated for each compound.
4. This is expressed as a percentage of the sum of all such products in the mixture.

The yield of the reaction is calculated by means of an internal standard; a solvent peak which eluted at a relative retention time of 0.31 was used for this purpose. Experiment showed that for 100% product recovery the total area under the peaks (calculated as above) divided by the height of the internal solvent peak was equal to 2.4; if a lower value, x say, was obtained the product recovery was given by

$$\% \text{ recovery} = \frac{x}{2.4} \times 100$$

This estimate proved to be reliable only to within 10%.

The labour involved in these calculations was greatly reduced by the use of a Hewlett Packard 9100A programmable calculator. A program was written (incorporating the retention times and response factors) so that by input of the peak heights of the various compounds and the internal standard, the percentages of each compound and the product recovery were easily and quickly calculated.

The results of the isomerisation reactions are presented in tabular form and the abbreviations given in the table below are used for the column headings.

compound	abbreviation
1-hexyne	1-
1,2-hexadiene	1,2-
2-hexyne	2-
2,3-hexadiene	2,3-
3-hexyne	3-
2,2-difluorohexane	Z
3,3-difluorohexane	X
2-hexanone	2-one
3-hexanone	3-one

In the body of the text however the full names will be used unless otherwise stated, except where names are differentiated by numbers only:

e.g. 2- and 3-hexyne

but not 2- and 2,3-hexadiene.

In the figures illustrating the results of the reactions the percentage of each product is plotted against the percentage reaction; the percentage reaction at time t is defined as

100 - (percentage of reactant isomer at time t).

If the reactant is not isomerically pure the percentage reaction at zero time will not be zero; e.g. the 3-hexyne sample (see appendix 1.5) contains 1.1% 2-hexyne and 0.7% 2,3-hexadiene. Thus the extent of reaction at t = 0 is 1.8%.

2.3 SOME TESTS OF THE REACTION PROCEDURE

To ensure that the reaction procedure gave meaningful results several tests were carried out. The aspects that were checked were:

1) the completeness of the extraction of the isomers,

2) the possibility of leakage of the volatile isomers through the serum caps during reaction,

and 3) the possibility of leakage when the reaction product was stored in the refrigerator freezer.

Experimental

1) Two petroleum spirits solutions were made up as follows;

a) 3-Hexyne (10 μl) was added to petroleum spirits (1 ml).

b) 3-Hexyne (10 μl) was added to sulpholane (1 ml), water (0.5 ml) was then added, and the 3-hexyne was extracted with petroleum spirits (1 ml).

Both solutions gave 100% 3-hexyne.

2) 3-Hexyne (10 μl) was injected into test tubes of sulpholane (1 ml) and left for varying times, the tubes being stoppered with serum caps. The usual extraction procedure was carried out with the following results:

time (hr)	% extraction
0	100
4.4	95
16	82
27.5	71
64	61
96	53

3) The products from an isomerisation of 3-hexyne with HPF_6 (see chapter 4) were analysed,

a) immediately after extraction,

b) after 3 days storage in the refrigerator freezer

with the following results:

	product composition %					%
	2-	2,3-	3-	X	3-one	recovery
a)	8.8	11.5	76.4	1.3	2.0	47
b)	8.6	12.0	76.6	0.9	1.8	47

Discussion

Experiment 1 shows that petroleum spirits extract 3-hexyne completely from sulpholane/water.

From experiment 2 it can be seen that leakage of isomer occurs through the serum caps. However, most of the reactions carried out occupied less than three hours and in this time a maximum of approximately 3% loss could be expected. As will be seen this is considerably less than the product destruction which occurs in all reactions in the equivalent time; however some reactions were allowed to proceed for considerably longer and in such cases the loss through leakage will be considered.

The results of experiment 3 show that storage in a refrigerator freezer of the reaction products has virtually no effect on the product composition.

CHAPTER THREE

TETRAFLUOROBORIC ACID AS A CATALYST

3.1 INTRODUCTION

Beale[13] has already demonstrated (see section 1.1) that solutions of tetrafluoroboric acid (HBF_4) in sulpholane catalyse acetylene-allene isomerisations.

The work described in this chapter is an attempt to solve some of the problems associated with the use of this catalyst and to gain further insight into the nature of the reaction mechanism and of the catalyst solution.

The preparation of sulpholane solutions of HBF_4 from solutions of HF and BF_3 is described in appendix 1.11. Only sulpholane solutions have been used for this catalyst.

3.2 THE ISOMERISATION OF 3-HEXYNE AND 2,3-HEXADIENE

These reactions were studied as a check that the solutions prepared for this work are comparable to those used by Beale[13].

Experimental

1) 3-Hexyne (10 μl) was reacted with HBF_4 (0.1 M, 1 ml) at 25°C.

The complete procedure for analysing the chromatograms is here illustrated for this isomerisation at t = 10 min.

product	a	b	ab
X	0.76	30.5	23.2
Y	0.62	7.3	4.5
2-	1.00	2.8	2.8
2,3-	0.66	48.2	31.8
3-	0.87	332.0	289.0

In this table, a = relative retention time x response factor,

b = peak heights on same attenuation.

Now, % compound i $= \dfrac{a_i b_i}{\sum a_i b_i}$

In this case, $\sum a_i b_i = 351.3$

$\therefore \quad \%X = \dfrac{23.2 \times 100}{351.3} = 6.6\%;$

Similarly, %Y = 1.3% , %2- = 0.8%

%2,3- = 9.1% , %3- = 82.2%

The height of the internal standard peak was 155.5. The overall recovery was then given by

$$\% \text{ recovery} = \frac{351.3}{155.5} \times \frac{1}{2.4} \times 100$$

$$= 94\%$$

As has already been pointed out (see section 2.2) the above procedure is carried out automatically with the aid of the Hewlett Packard 9100A programmable calculator. Only the results of such calculations will be presented for all remaining examples.

The complete results for the reaction are as follows:

time min.	product composition %						% recovery
	1-	2-	2,3-	3-	X	Y	
0		1.1	0.7	98.2			100
10		0.8	9.1	82.2	6.6	1.3	94
30		4.0	11.1	66.3	17.2	1.2	98
90		8.0	8.1	47.5	35.5	0.9	88
360	2.0	15.5	7.2	23.8	49.3	2.2	51

2) 2,3-Hexadiene (10 μl) was reacted with HBF_4 (0.1 M, 1 ml) at 25°C.

time min.	product composition %					% recovery
	2-	2,3-	3-	X	Y	
0		100	-			100
1	14.3	75.3	10.4			90
2	20.9	64.0	14.5	0.3	0.3	85
4	26.6	53.3	19.1	0.7	0.2	82
6	31.4	44.8	22.5	0.9	0.3	76
8	34.5	38.4	25.0	1.6	0.4	79
10	35.7	35.8	26.1	2.0	0.4	71

In both experiments 1 and 2 the solutions darkened as the reaction proceeded.

Discussion

The product patterns in the two reactions are as expected from the proposed protonation-deprotonation sequence; i.e. 3-hexyne produces 2,3-hexadiene initially, with a subsequent rise in the proportion of 2-hexyne, while the main products from 2,3-hexadiene are 2- and 3-hexyne with the former predominating.

However, in the 3-hexyne reaction 3,3-difluorohexane is produced to a greater extent than in the earlier work (compare 49% difluorohexane at 76% reaction with 33% at 80% reaction). Also, the amount of compound Y does not increase sharply to 7% at 80% reaction as found previously.

In the 2,3-hexadiene reaction a small amount of Y is produced; none was reported in the earlier work.

In this work there is definite evidence for product destruction, the magnitude of which cannot be accounted for by isomer leakage through the serum caps (see section 2.3). Previously it was reported that no product destruction occurred.

There are kinetic differences also.

The 3-hexyne reaction is faster than in the earlier work (compare 34% reaction at 30 min. with 24% reaction at 32 min.). The slower reaction could be accounted for by postulating the incursion of small amounts of water into the reaction system.

The situation is the reverse in the 2,3-hexadiene reaction. Here the reaction is slower than reported previously (compare 25, 36 and 62% reaction after 1,2 and 8 min. respectively with the previous figures of 33, 41 and 64% after the same times). This reaction was carried out one year after the 3-hexyne reaction and in this time the catalyst system may have become water-contaminated.

In general however the reactions are sufficiently similar to the earlier work to enable conclusions drawn here to apply to that work as well.

Notes

1) This account assumes that X is 3,3-difluorohexane (see section 3.3).

2) The compound labelled 1-hexyne in the 3-hexyne isomerisation results may well be compound Z (2,2-difluorohexane, see section 3.3).

3.3 THE IDENTIFICATION OF X AND Z

Beale[13] proposed that the unknown compounds X and Z were 3,3- and 2,2-difluorohexane respectively. It was noted that final proof of their identities awaited synthesis of authentic samples.

Experimental

2,2- and 3,3-difluorohexane were prepared by the method of Grosse and Linn[14] (see appendix 1.17).

2,2-Difluorohexane gave no precipitate when subjected to the silver acetylide test.

The relative retention time of 2,2-difluorohexane was found to be the same (0.72) as that of 1-hexyne, both by chromatography of 2,2-difluorohexane alone and by co-chromatography with 1-hexyne.

The relative retention time of 3,3-difluorohexane was found to be the same (0.76) as that of compound X.

Some time after this initial work the opportunity arose to study these compounds with ^{19}F nmr (see appendix 2). Fresh samples were prepared but, due to a shortage of 3-hexyne, 2,3-hexadiene was used in the preparation of 3,3-difluorohexane (see appendix 1.17).

The spectrum of 2,2-difluorohexane (Fig. 3.1) consists of a single signal split into a sextet

δ = -73.0 ppm (relative to C_6F_6)

J_{H-F} = 2.7 ppm

The spectrum of 3,3-difluorohexane is displayed in Fig. 3.2. The main signal is split into a pentet

δ = -62.6 ppm (relative to C_6F_6)

J_{H-F} = 2.8 ppm

There is also a small signal at δ = -72.5 ppm.

Discussion

Grosse and Linn[14] found that the reaction of neat HF with 1- and 3-hexyne resulted in the addition of 2 moles of HF to one of alkyne in each case. Markovnikov addition was assumed and the products were then identified as 2,2- and 3,3-difluorohexane respectively. The ^{19}F nmr experiments described here were carried out to confirm that Markovnikov addition did occur.

Compound Z gives the expected spectrum for 2,2-difluorohexane; i.e. a single signal split into a sextet by the five adjacent protons in the CH_3-CF_2-CH_2- grouping; the observed hyperfine splitting is probably due to the non identity of the methyl and methylene protons in this grouping, but no detailed analysis was carried out.

Similarly compound X gives the expected spectrum of 3,3-difluorohexane; i.e. a signal split into a pentet by the four adjacent protons in the grouping -CH_2-CF_2-CH_2-. Hyperfine splitting is less evident in this case, probably because the two sets of protons in $-CH_2-CF_2-CH_2-$ are more nearly identical than the two sets in $CH_3-CF_2-CH_2-$. The small resonance at -72.5 ppm is probably 2,2-difluorohexane (the small difference in δ being ascribed to a solvent shift); 2,2-difluorohexane could be formed if isomerisation of 2,3-hexadiene to 2-hexyne occurs in competition with the addition of HF (cf. the addition of neat HCl to allene[5]).

The silver acetylide test confirms complete conversion of 1-hexyne into 2,2-difluorohexane. Thus the peak which occurs at the same retention time as 1-hexyne is indeed 2,2-difluorohexane.

Similarly X is identified as 3,3-difluorohexane from its retention time.

This combination of nmr and glc evidence unequivocally confirms Beale's conclusion that

compound Z is 2,2-difluorohexane,

and compound X is 3,3-difluorohexane.

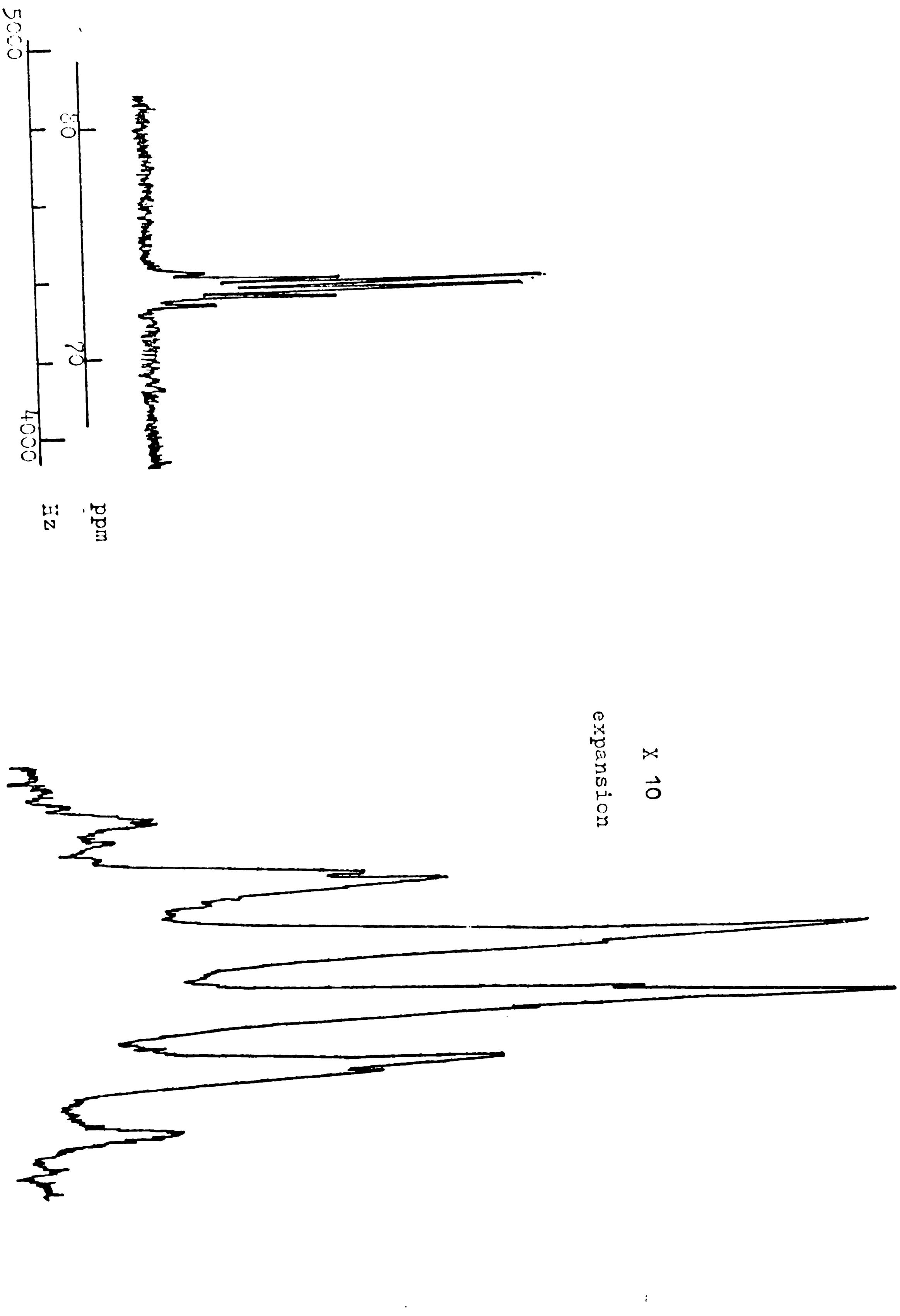


Fig. 3.1 ^{19}F nmr spectrum of compound Z

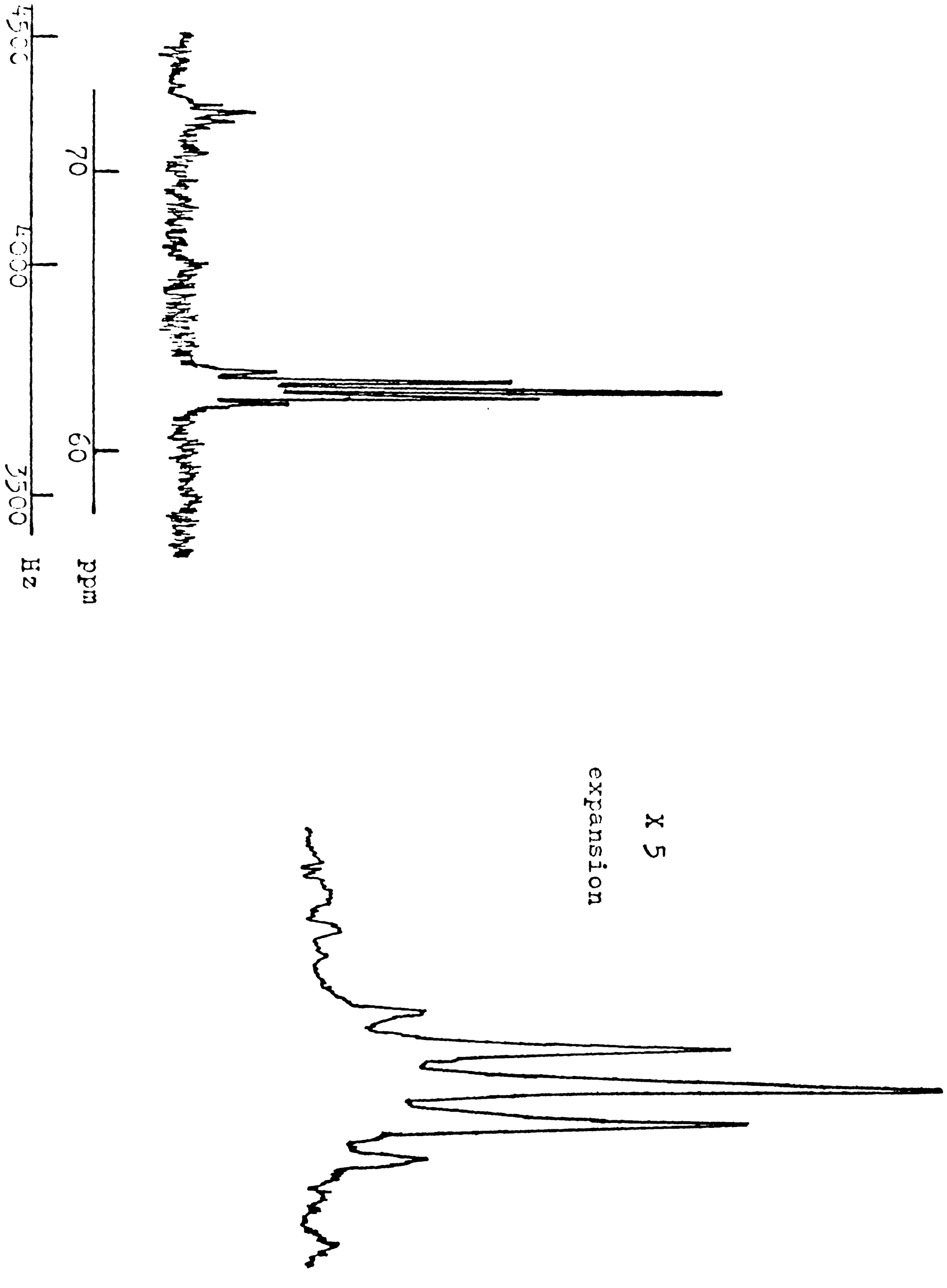
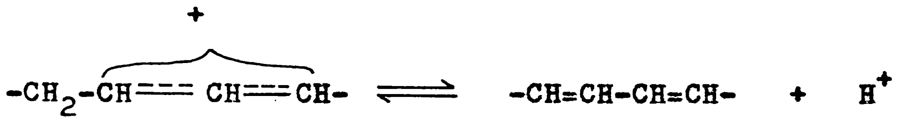


Fig. 3.2 ^{19}F nmr spectrum of compound X

3.4 THE REACTION WITH CONJUGATED DIENES

As described in section 1.1 the workers in this group have found evidence that the isomeric conjugated dienes 1,3- and 2,4-hexadiene are not formed during the isomerisation reactions.

Theoretically these compounds could be generated by proton loss from allyl cations thus:



$$-CH_2-\overset{+}{\overbrace{CH \mathrel{=\!=\!=} CH \mathrel{=\!=\!=} CH}}- \rightleftharpoons -CH{=}CH-CH{=}CH- \quad + \quad H^+$$

It is possible that the conjugated dienes are not formed because of their instability in the reaction medium and that allyl cations lead to some other product. However if it could be shown that conjugated dienes are stable in HBF_4/sulpholane there would be convincing evidence that allyl cations are not formed in the acetylene-allene isomerisations.

Reactions with the conjugated dienes were thus carried out.

Experimental

2,4-Hexadiene was synthesised as described in appendix 1.6. As pointed out in the appendix 2,4-hexadiene made by this method contains ca. 20% 1,3-hexadiene.

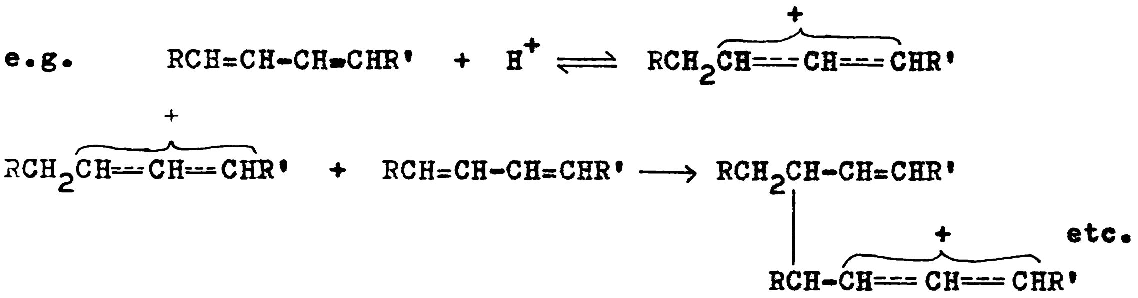
Reactions were carried out for 1 minute and 30 minutes using the experimental method described in section 2.1. Darkening of the catalyst solution occurred, as it did during the acetylene-allene isomerisations.

Both reactions resulted in complete product destruction.

Discussion

The experiments show that neither 1,3- nor 2,4-hexadiene is stable in HBF_4/sulpholane.

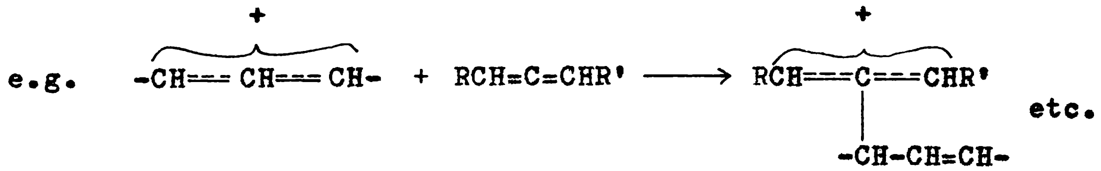
A likely explanation for this result is polymerisation via an allyl cation:



$$\begin{array}{l}
\text{e.g.}\quad RCH{=}CH{-}CH{=}CHR' + H^{+} \rightleftharpoons RCH_2\overbrace{CH{\equiv}CH{\equiv}CHR'}^{+} \\
RCH_2\overbrace{CH{\equiv}CH{\equiv}CHR'}^{+} + RCH{=}CH{-}CH{=}CHR' \longrightarrow \begin{array}[t]{l} RCH_2CH{-}CH{=}CHR' \\ \quad | \\ RCH{-}\overbrace{CH{\equiv}CH{\equiv}CHR'}^{+} \end{array} \quad \text{etc.}
\end{array}$$

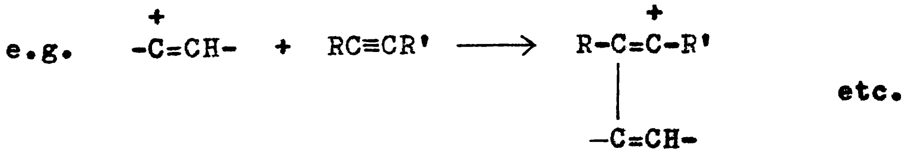
This carries the implication for the acetylene-allene isomerisation reaction that should allyl cations be generated, proton loss to form conjugated dienes will not occur.

Therefore this work indicates a possible mechanism for product destruction. Allyl cations if formed could react as shown above or with acetylenes or allenes to initiate polymerisation thus causing product destruction:



$$\text{e.g.}\quad {-}\overbrace{CH{\equiv}CH{\equiv}CH}^{+}{-} + RCH{=}C{=}CHR' \longrightarrow \begin{array}[t]{c} R\overbrace{CH{\equiv}C{\equiv}CHR'}^{+} \\ | \\ {-}CH{-}CH{=}CH{-} \end{array} \quad \text{etc.}$$

However it should be remembered that product destruction mechanisms involving only vinyl cations may also be written:



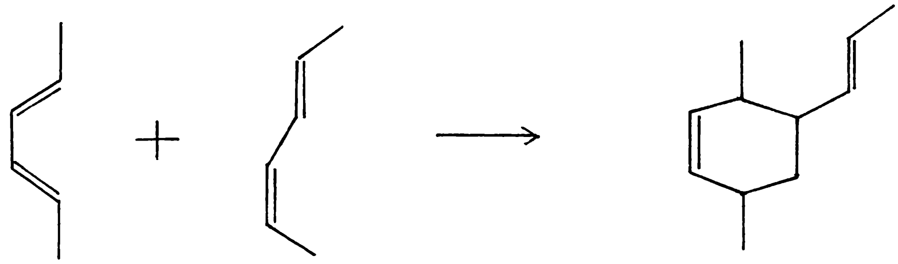
$$\text{e.g.}\quad {-}\overset{+}{C}{=}CH{-} + RC{\equiv}CR' \longrightarrow \begin{array}[t]{c} R{-}\overset{+}{C}{=}C{-}R' \\ | \\ {-}C{=}CH{-} \end{array} \quad \text{etc.}$$

In summary there is insufficient evidence to determine whether or not allyl cations are formed in the isomerisation reactions; a structural study of the compounds formed in the product destruction reactions would be necessary.

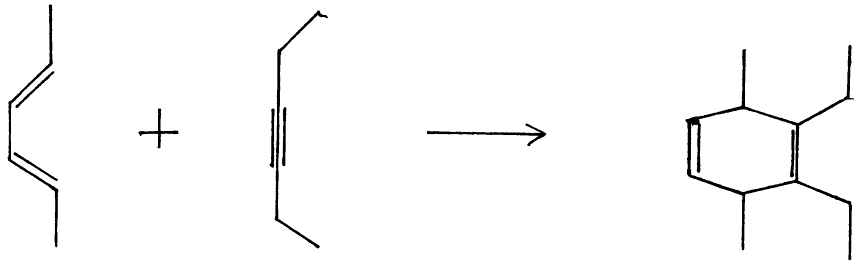
Note

It has been found that solutions of Lewis acids (such as BF_3) in dichloromethane can catalyse Diels-Alder reactions[51]. Thus it is possible that the conjugated dienes undergo self condensation in this manner:

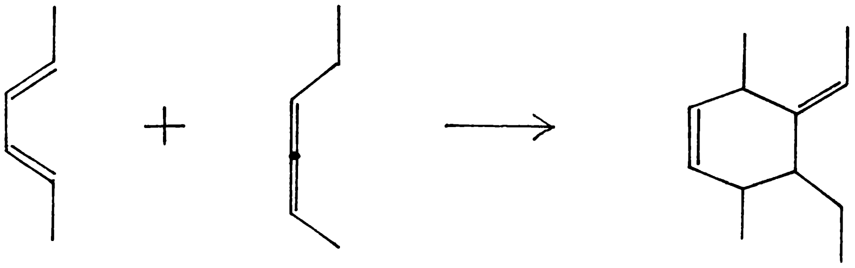
e.g.



In addition both acetylenes and allenes may be dienophiles in this class of reaction so that the isomerisation reactions may lead to reactions such as



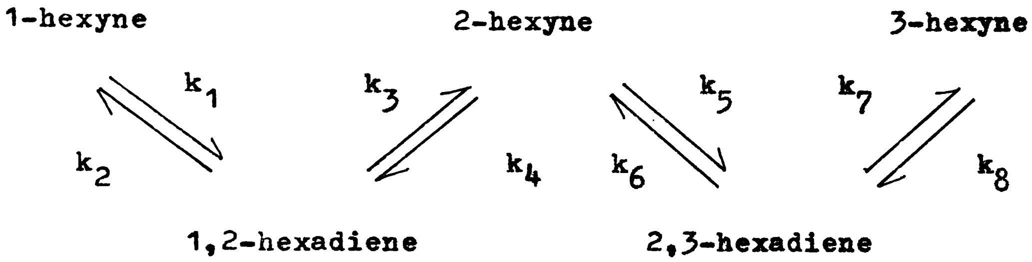
and



Such products however, while probably having long retention times, might well have been detectable by glc.

3.5 THE KINETICS OF THE ISOMERISATIONS

It is expected (see section 1.1) that each step in the isomerisation should be first order in both isomer and catalyst. Since the catalyst concentration is constant the reaction scheme may be written as



where the k_i are the pseudo first order rate constants. The kinetics of such a system are complex and are made even more so by addition reactions which consume both isomer and substrate. However, Beale found that the addition reactions were very much slower than the allene isomerisations; accordingly, he analysed his results for the 1,2- and 2,3-hexadiene isomerisations and found pseudo third order kinetics.

A kinetic analysis was carried out on the present results for 2,3-hexadiene. Since 1-hexyne and 1,2-hexadiene are not formed the system under study can be reduced to

$$\text{2-hexyne} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \text{2,3-hexadiene} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} \text{3-hexyne.}$$

It is pertinent to investigate the form the kinetic plots should take if all the reactions were first order, as expected. The kinetics of this system can be solved exactly (see appendix 3.1 for brief details) and the solution is of the form

$$\left[2,3\text{-hexadiene}\right] = B_1e^{nt} + B_2e^{mt} + B_3$$

where B_1, B_2, B_3, m and n are constants.

Treatment of data

The figures for percentage of 2,3-hexadiene given in section 3.2 are percentages of the recovered product, and are thus not proportional to $\left[2,3\text{-hexadiene}\right]$. For instance, at t = 1 minute the amount of 2,3-hexadiene is 75.3% of a 90% total recovery. Thus if we set the original $\left[2,3\text{-hexadiene}\right]$ at 100 (arbitrary units), $\left[2,3\text{-hexadiene}\right]$ at t = 1 minute is given by

$$\left[2,3\text{-hexadiene}\right] = 75.3 \times \frac{90}{100}$$

$$= 67.6 \text{ (arbitrary units)}$$

Similar treatment of the remaining data using percentage recovery figures from the curve in Fig. 3.3a gives the following results :

time min.	2,3-hexadiene
0	100
1	67.6
2	54.5
4	42.5
6	33.0
8	28.5
10	26.0

A plot of the reciprocal of $\left[2,3\text{-hexadiene}\right]^2$ against time (i.e. a third order plot) is shown in Fig. 3.3b.

The theoretical and observed results can be compared by evaluating the four rate constants and inserting them into the kinetic equation.

The rate constants can be estimated from Beale's results by the following procedure.

a) The time for a given amount of initial isomerisation (in this case 15%) is noted (an adjustment being made for 2-hexyne, see note 1 at end of this section).

b) The reciprocals of these times are calculated and taken as relative values of the rate constants for decomposition (the units of first order rate constants are time^{-1}); i.e. values of $k_4 + k_5$, $k_6 + k_7$, and k_8 are calculated.

c) Relative values of the rate constants are then calculated from the amounts of each product formed (e.g. 2-hexyne initially gives approximately 3:1 of 2,3-: 1,2-hexadiene; hence if the rate constant for decomposition is x (= $k_4 + k_5$) the rate constant for formation of 1,2-hexadiene (k_4) is 0.25x and for 2,3-hexadiene (k_5) is 0.75x).

This procedure leads to the following relative rate constants

k_5 = 1
k_6 = 20
k_7 = 13
k_8 = 2

If these values are correct the final equilibrium mixture would consist of 73% 2-hexyne, 4% 2,3-hexadiene and 24% 3-hexyne. Inspection of Beale's results and subsequent work (see chapter 4) indicates that 4% is a reasonable figure for 2,3-hexadiene, although it should be regarded as an upper limit, and 24% is possibly rather large for 3-hexyne.

Using a program written for the Hewlett Packard 9100A calculator these values were inserted into the kinetic equation. The results were plotted (Fig. 3.4) on a graph of log [2,3-hexadiene] against time (i.e. a first order plot), together with the observed results given above.

Discussion

The third order plot (Fig. 3.3b) gives a good straight line fit, confirming Beale's result.

Fig. 3.4 shows that with the set of theoretical rate constants derived above the first order plot is a good approximation to a straight line until about 90% reaction; then with increasing time and as the equilibrium point is approached there is wide deviation from a straight line. Substitution of other sets of rate constants into the kinetic equation confirmed that deviation from the straight line is in general greater as equilibrium is approached.

The observed and theoretical results match well in the early stages of the reaction but subsequently deviate widely (see Fig. 3.4). The deviations are such that large changes in the rate constants are required to give a close fit.

The rate constants can be changed so that the final equilibrium state may or may not be altered.

If the final equilibrium state is changed a good fit can be obtained with the following rate constants.

$k_5 = 15$

$k_6 = 22$

$k_7 = 13$

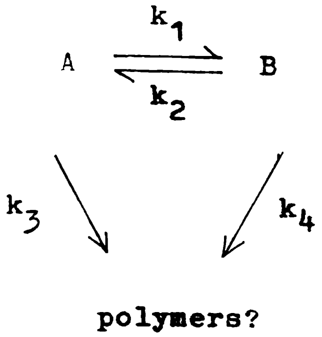
$k_8 = 15$

The main difference between this set and the one above is that k_5 and k_8 are much larger; as a result the final equilibrium state would contain a large amount (30%) of 2,3-hexadiene.

If the final equilibrium state is not to be changed the relative rates of the two reversible reactions can still be changed (e.g. if k_5 is multiplied by 10 then so must k_6; likewise k_7 and k_8 must be changed by an equal factor). It was not found possible to obtain a reasonable fit by such a procedure.

Thus the (relatively) simple first order analysis will not fit the observed results unless a set of rate constants which is unlikely, on the basis of both observed rates and the likely final equilibrium mixture, is used.

Attempts were also made to assess the effect of product destruction on the form of the kinetic plots. The system chosen for analysis was



(see appendix 3.2 for brief details of the solution)

The much more complex system involving two reversible reactions and three product destruction reactions was not analysed; justification for the chosen system is given in appendix 3.2.

In a clean system (i.e. no product destruction) deviation from "first order" behaviour is more apparent as equilibrium is approached (see above). In this case however product destruction occurs; thus the reaction proceeds to completion. Substitution of various values of the rate constants into the kinetic equations leads to the result which may thus have been expected intuitively; the reaction becomes more nearly first order.

Therefore, first order product destruction cannot account for the kinetics of the 2,3-hexadiene isomerisation.

Exact solutions are not possible for systems of first order isomerisation and higher order product destruction. However, from the argument above it would be expected that the order of the product destruction reaction would be the dominant factor in determining the overall reaction order. Fig. 3.5 shows that the product destruction reaction is in fact of higher order than three.

In summary, it is not possible, considering the complexity of the system, to define the order of the isomerisation. The deviation from first order behaviour of the experimental results may well be due to the product destruction reaction.

Notes

1) The time for 15% reaction of 2-hexyne is halved to account for the fact that Beale's sample was 1:1 2-hexyne: petroleum spirits.

2) A good technique for further elucidating the kinetics of the isomerisations would be isotope exchange. If the isomers were substituted with deuterium or tritium in various well defined parts of the molecules, the rates of incorporation of these isotopes into the other isomers could be measured; this would lead to values of rate constants for which it would be easier to take account of back reactions to the starting isomer. In addition, the isotope effect could be used to gain mechanistic information.

Fig. 3.3a

Percentage recovery in the 2,3-hexadiene isomerisation

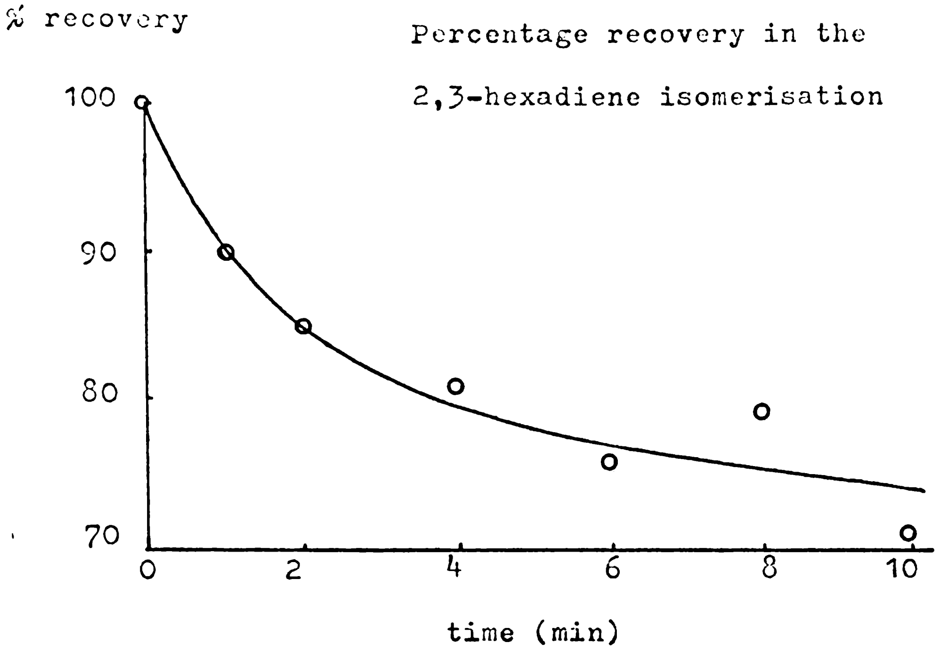
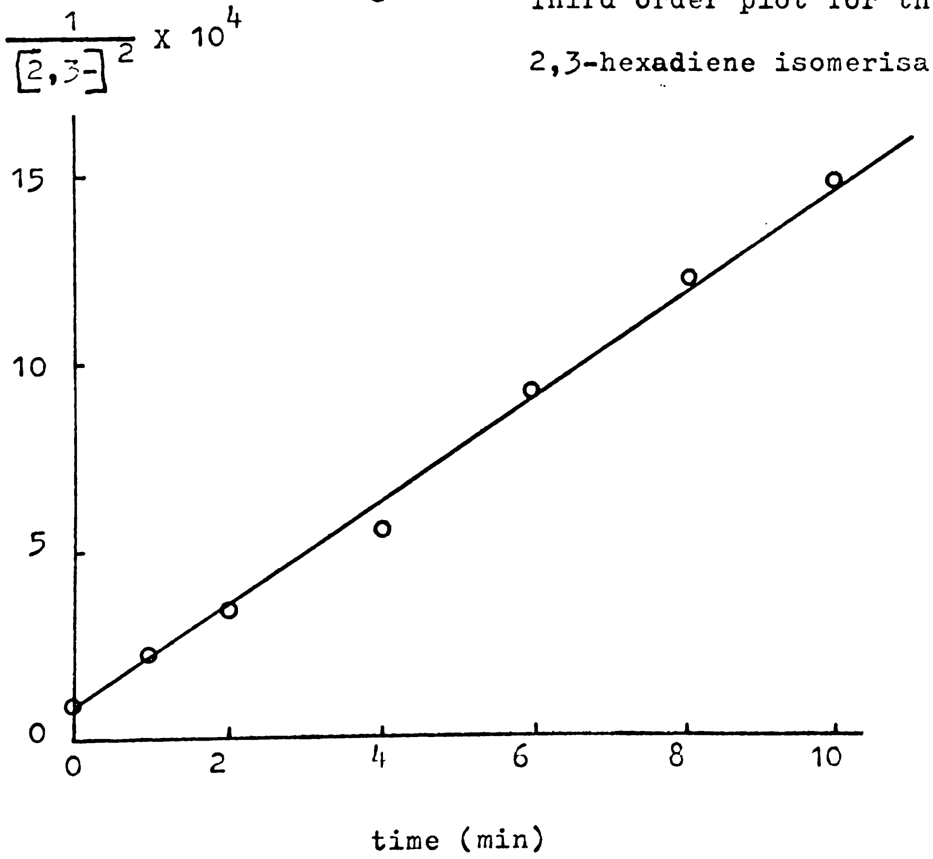


Fig. 3.3b Third order plot for the 2,3-hexadiene isomerisation



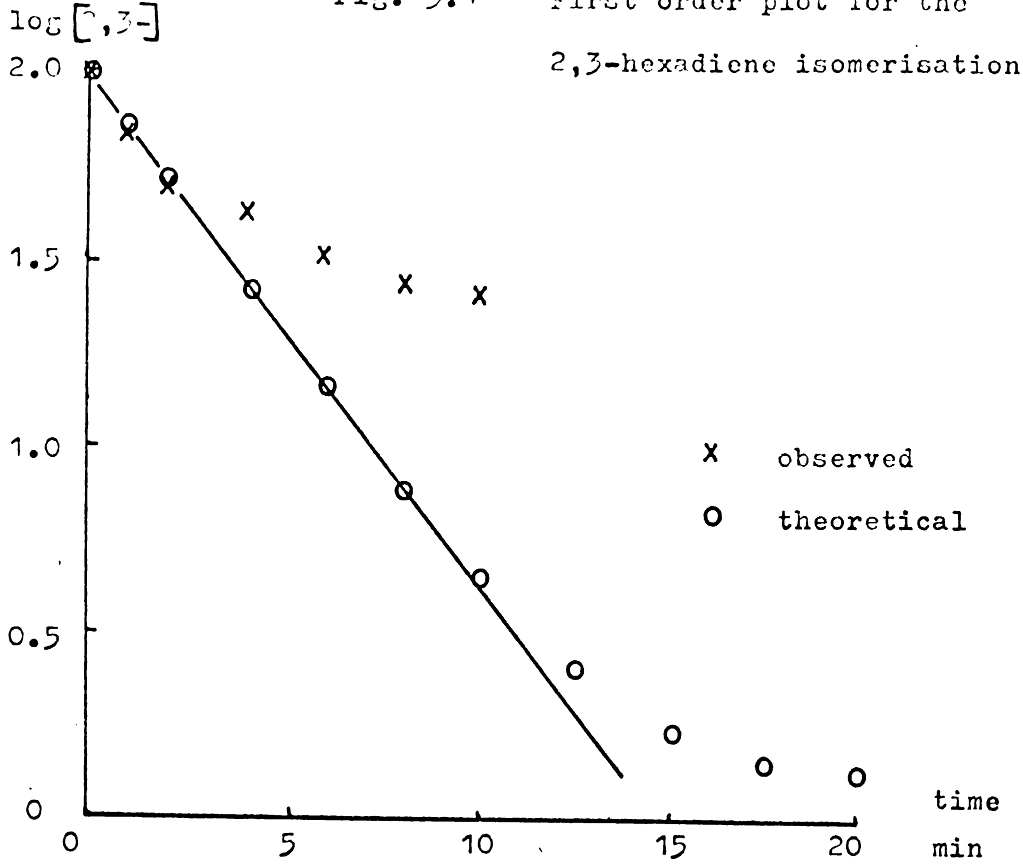


Fig. 3.4 First order plot for the 2,3-hexadiene isomerisation

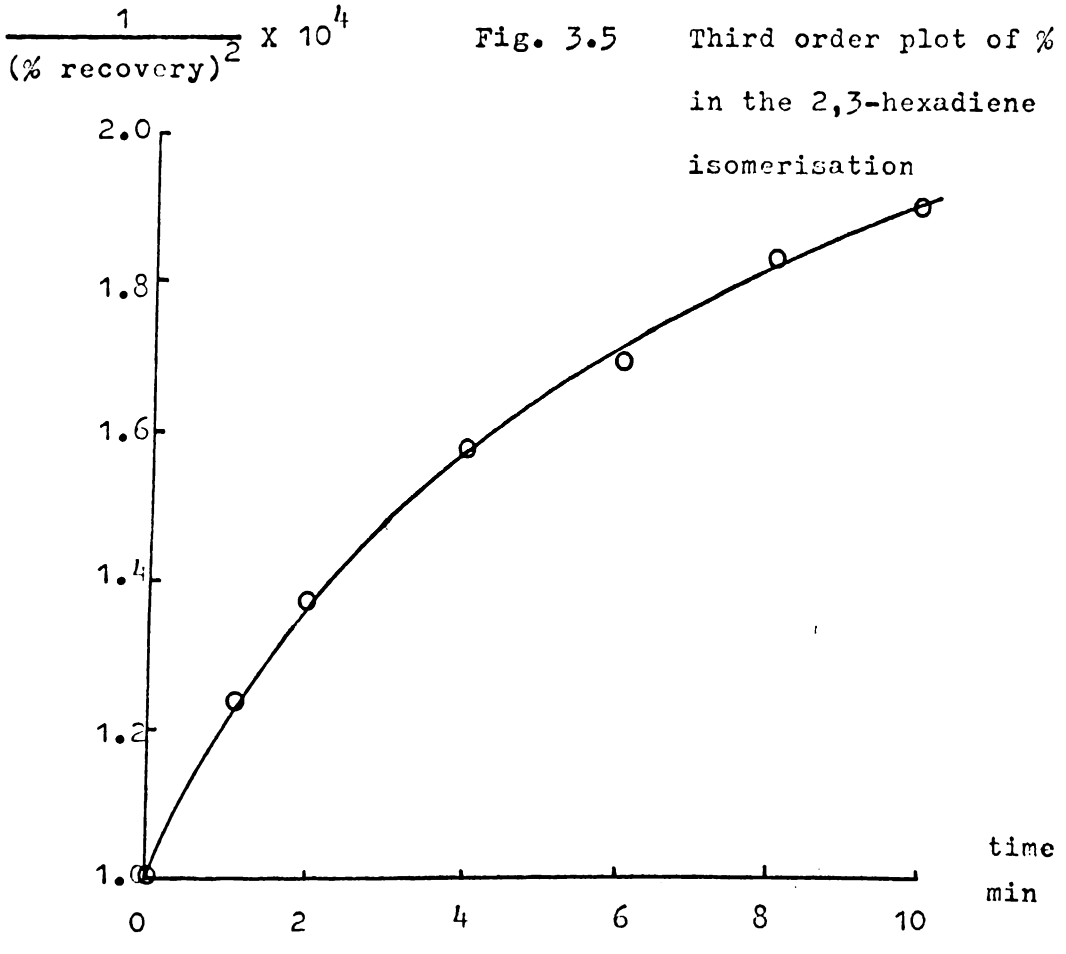


Fig. 3.5 Third order plot of % recovery in the 2,3-hexadiene isomerisation

3.6 ISOMERISATIONS WITH BORON TRIFLUORIDE

Beale[13] suggested that an alternative catalyst for the isomerisation might be BF_3/sulpholane. This section describes some experiments which test the use of this catalyst.

Experimental

1) 3-Hexyne (10 μl) was reacted with BF_3 (1 ml; varying concentrations, see table) at 25°C.

BF_3 mole.litre^{-1}	time hr	product composition %						% recovery
		1-	2-	2,3-	3-	X	Y	
	0		1.4	1.0	97.6			100
0.22	0.5		1.5	2.7	95.8			100
0.22	22	0.7	17.0	8.3	72.4	0.2	1.4	70
1.89	17	3.8	42.5	23.2	18.0	5.5	7.1	16
1.89	168							0

2) 1-Hexyne (10 μl) was reacted with BF_3 (1.89 M, 1 ml) for 17 hr at 25°.

product composition %					% recovery
1-	1,2-	2-	2,3-	3-	
43.6	9.7	41.7	4.8	0.3	38

3) 1,2-Hexadiene (10 μl) was reacted with BF_3 (0.22 M, 1 ml) for 2 hr at 25°C.

product composition %			%
1-	1,2-	2-	recovery
4.8	51.1	44.1	75

4) 3-Hexyne (10 μl) was reacted with an equimolar mixture of BF_3 and water (1 ml of 0.22 M BF_3 + 4 μl H_2O) for 50 minutes at 25°C. No detectable reaction (i.e. $< 0.1\%$) occurred.

Discussion

It is apparent from these results that BF_3/sulpholane catalyses the isomerisation.

The reaction is slow in comparison with the HBF_4 reaction. For example 3-hexyne is 28% isomerised after 22 hours in BF_3 (0.22 M) whereas less than 30 minutes is required for the same amount of isomerisation in HBF_4 (0.1 M).

A similar sequential pattern to that of the HBF_4 reactions is indicated. After about 50% reaction 1-hexyne has formed 2-hexyne as the major product with a smaller amount of 1,2-hexadiene; 2,3-hexadiene and 3-hexyne are present in only small amounts. After a similar extent of reaction 1,2-hexadiene has formed 2- and 1-hexyne with the former predominating. The data for 3-hexyne suggest that the initial product is 2,3-hexadiene and that this is a precursor to 2-hexyne (although the amount of 2,3-hexadiene at 82% reaction is much higher than in the HBF_4 reaction).

3,3-Difluorohexane, or another compound with the same retention time, is formed in the 3-hexyne isomerisations after some time. This poses mechanistic problems since its formation requires the addition of two HF entities to a molecule of isomer; in the present system the only sources of protons are the solvent and other isomer molecules.

The reaction between 3-hexyne and an equimolar mixture of BF_3 and water was carried out because other experiments had shown that similar mixtures of PF_5 and water (see section 4.5) caused considerable isomerisation. However, in this case the same amount of water quenched the reaction.

Like HBF_4, this catalyst causes product destruction. Comparison with the experiment described in section 2.3 indicates that leakage through the serum caps cannot account for this effect although there would be some contribution from it.

The isomerisation may be explained on the basis of water contamination; it has already been pointed out that BF_3 is very difficult to dry completely (see section 1.3). Thus it is possible that the BF_3 solutions used here contain co-catalyst water which reacts with BF_3 to form the protonic acid $H^+(BF_3OH^-)$. This should catalyse the reaction in a similar manner to HBF_4 so that both the stepwise sequence and the production of addition products (with the water as the source of protons) can be explained; it is worth noting that only small amounts of addition products are formed (e.g. the maximum amount of 3,3-difluorohexane is 5.5% of a 16% recovery) so that only a small amount of water contamination need be invoked.

It is very difficult to suggest a reason for the lack of catalytic activity of the equimolar mixture of BF_3 and water on this basis however. The possibility that the dihydrate $H_3O^+(BF_3OH^-)$ (i.e. a species with a hydrated proton) is formed is contrary to nmr evidence (as will be shown in the next section). The other possibility is that BF_3 does not require a co-catalyst in this system; this possibility will be discussed in section 4.5, but it should be pointed out here that the production of 3,3-difluorohexane is very difficult to explain by such an approach (a problem which does not arise in the case yet to be discussed).

3.7 THE NATURE OF THE CATALYST SOLUTIONS

The properties of the catalyst solutions were studied both with and without the addition of isomers. The techniques used were ^{19}F nmr and conductivity measurements.

Experimental

1) ^{19}F nmr. All chemical shifts recorded here were determined with respect to C_6F_6. All samples were solutions in sulpholane.

BF_3 (0.22 M) gave a singlet at $\delta = -20.3$ ppm; an equimolar solution of BF_3 and water (1 ml 0.22 M BF_3 + 4 μl H_2O) gave a singlet at $\delta = -13.9$ ppm; and HBF_4 (0.1 M) gave a singlet at $\delta = -13.7$ ppm, although the precise position of this signal was uncertain due to the low signal to noise ratio.

The spectra are displayed in Fig. 3.6 (the spectrum of HBF_4 was run through several times to confirm the existence of the signal).

2) Conductivity. The conductivities of the solutions were measured with a Philips PR 9501 conductivity bridge and in a cell (capacity ca 1 ml) with platinum wire electrodes coated with platinum black (as outlined by Vogel[52]).

a) The conductivities of the HF, BF_3 and HBF_4 solutions were as follows (relative to that of HF being one; the absolute conductivity of the HF solution was in the order of $10^{-6}\,\Omega^{-1}\,cm^{-1}$):

solution	concentration	relative conductivities
HF	0.18 mole.litre^{-1}	1
BF_3	0.22 " "	7
HBF_4	0.10 " "	75

b) 1-Hexyne (10 μl) was added to HBF_4 (0.1 M, 1 ml) in the conductivity cell. A gradual increase in conductivity to approximately twice the original value was found.

Addition of the saturated C_6 hydrocarbon n-hexane caused no change in the conductivity of HBF_4.

Note

^{19}F nmr chemical shifts are measured with respect to a variety of compounds, the most common being $CFCl_3$, CF_3COOH (TFA), and C_6F_6. Emsley and Phillips[53] give the following conversion factors

$C_6F_6 \longrightarrow CFCl_3$	+ 163 ppm
$TFA \longrightarrow CFCl_3$	+ 77 ppm

All literature values of chemical shifts will be adjusted using these factors. The values so obtained will be rounded off to the nearest whole number; greater precision is not possible because of instrumental differences, concentration effects, solvent shifts, etc.

The reference compound with respect to which the chemical shift was actually measured will be given in brackets.

E.g., $\delta = -40$ ppm ($CFCl_3$) means that the chemical shift is -40 ppm with respect to C_6F_6 but was originally measured with respect to $CFCl_3$.

This system will be used for the remainder of this thesis.

Discussion

The value of -20.3 ppm for the BF_3 singlet agrees well with Jones's[41] figure of -19 ppm ($CFCl_3$). The lack of structure due to ^{11}B-^{19}F splitting was ascribed by Jones to quadrupole broadening with perhaps some effect due to fluorine exchange.

Addition of an equimolar amount of water to BF_3 causes an upfield shift to $\delta = -13.9$ ppm. This presumably is due to the formation of the monohydrate $H^+(BF_3OH^-)$; the dihydrate $H_3O^+(BF_3OH^-)$ cannot be formed (see section 3.7) since in that case half the BF_3 would be unreacted and there is no sign of any signal at $\delta = -20.3$ ppm.

The strong acid HBF_4 gives a signal very close to the signal from BF_3/H_2O. Despite the low signal to noise ratio it appears that the peak is broader than for BF_3 or BF_3/H_2O (the peak is lower than expected for a solution containing approximately two thirds the number of F atoms as in the BF_3 solutions). Although there is no signal from BF_3 it is possible that the broadened peak is due to intermolecular F exchange brought about by the reaction proposed by Whiting[36] (and modified here to take account of the formation of the 1:1 complex of BF_3 and sulpholane[41])

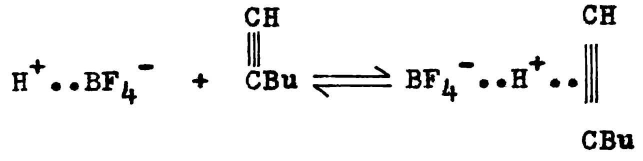
$$HF + BF_3.\text{sulpholane} \rightleftharpoons H^+..BF_4^- + \text{sulpholane} \quad ...(1)$$

If this exchange were fast on the nmr time scale the signal would represent the average fluorine environment. Thus although a more extensive study (with more concentrated solutions, variable temperature measurements, etc) is desirable the nmr evidence here can be used to support Whiting's proposal. On the other hand of course the broadening may simply be due to a quadrupole effect.

The first conductivity experiment gives the expected result; the strong acid HBF_4 is the best conductor.

The second experiment was carried out when it was found that the conductivity of HPF_6 dropped on addition of isomer (see section 4.6); the effect found here however is the opposite.

A possible explanation is that a loose complex with HBF_4 is formed



$$H^+..BF_4^- + \begin{matrix} CH \\ ||| \\ CBu \end{matrix} \rightleftharpoons BF_4^-..H^+..\begin{matrix} CH \\ ||| \\ CBu \end{matrix} \quad ...(2)$$

Such a complex would bind the ionic species to some extent, and would thus tend to lower the conductivity of the solution. However, if Whiting's value (0.41 litre.mole^{-1}) for the equilibrium constant of reaction (1) is correct then only 3.7% association of HF and BF_3 occurs in a 0.1 M "HBF_4" solution.

If the complex were formed to a greater extent the conductivity of the solution may thus rise, even though each individual complex formed would contribute less to the overall value than each free $H^+..BF_4^-$ entity.

Presumably the interaction between the acid and 1-hexyne occurs at the π electron system of the isomer as shown in reaction (2) above; thus n-hexane is not expected to change the conductivity of the solution, as was in fact found.

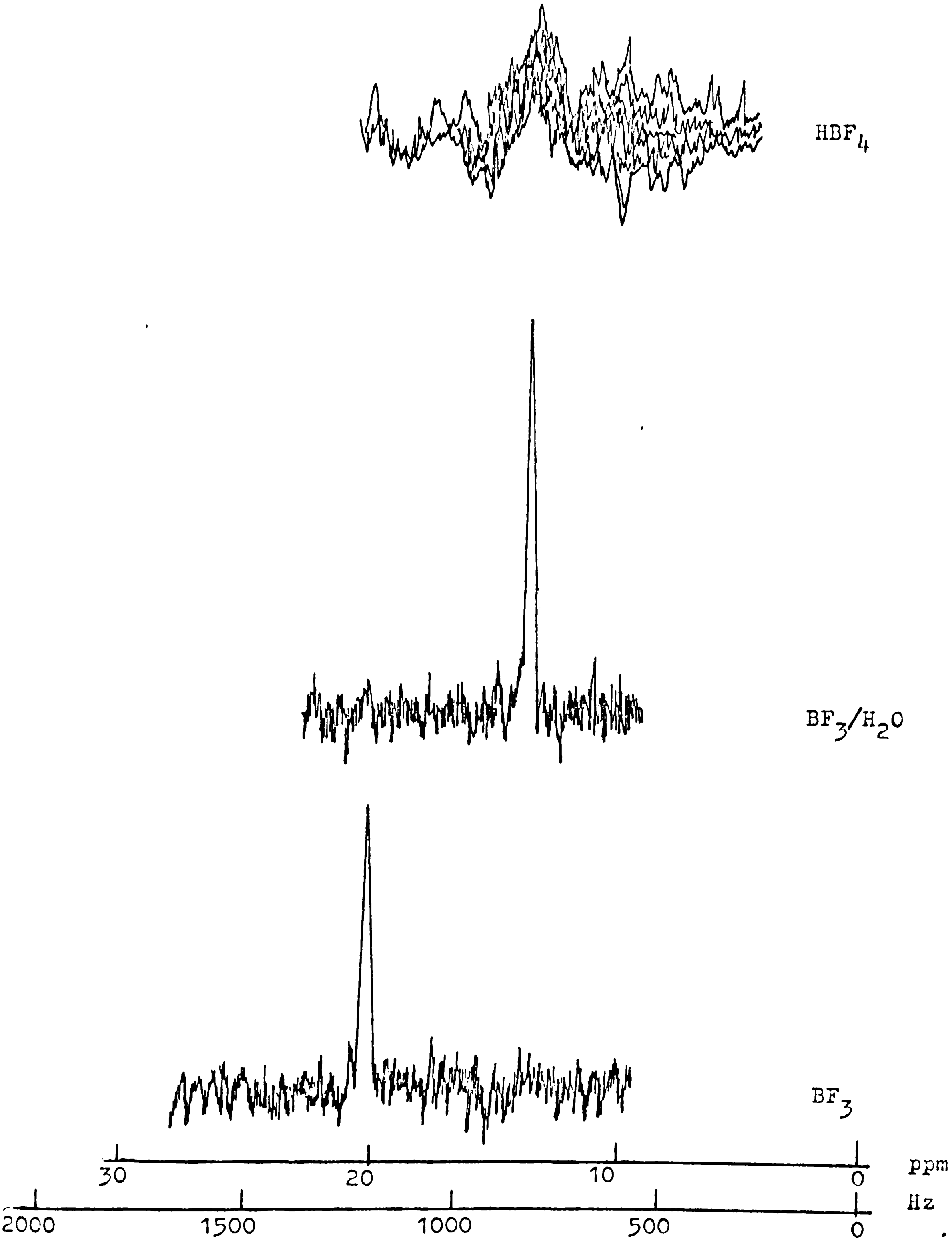


Fig. 3.6 ^{19}F nmr spectra of sulpholane solutions of BF$_3$, BF$_3$/H$_2$O, and HBF$_4$

3.8 THERMODYNAMIC CONSIDERATIONS

When, as is the case with the present reactions, it is not possible to attain an equilibrium mixture of a set of compounds the only method of gaining knowledge of the relative stabilities of those compounds is to use kinetic data.

Thus, previous workers in this group have compared their kinetic results with the published thermodynamic data on the pentyne-pentadiene system[12]; this data (for the gas phase) yields the following values for the standard free energy changes at 25°C:

$$\begin{tikzcd}
\text{1-pentyne} \arrow[r, "-1.07"] & \text{1,2-pentadiene} \arrow[r, "-0.53"] & \text{2,3-pentadiene} \arrow[d, "-1.08"] \\
& & \text{2-pentyne}
\end{tikzcd}$$

It was found that, despite this order, 1,2-hexadiene reacted much faster than 1-hexyne (a similar effect being found for the base catalysed isomerisations[11]).

However, the relative stabilities of these two compounds can be assessed not by comparing overall rates but by comparing the rate of reaction of 1-hexyne to 1,2-hexadiene with the rate of the reverse of this reaction. The overall rate of 1,2-hexadiene isomerisation includes reaction to 2-hexyne (which predominates over reaction to 1-hexyne by approximately 30:1) which is of no relevance to the relative stabilities of 1-hexyne and 1,2-hexadiene.

An equilibrium constant for the reaction between 1-hexyne and 1,2-hexadiene can be calculated if the relative rates of the forward and reverse reactions are known. Similarly, equilibrium constants for the other reactions can be calculated if the rates of the appropriate reactions are known; i.e. if the rate constants can be assessed.

Treatment of data

The method outlined under this heading in section 3.5 was used to calculate relative values of all eight rate constants in the simple pseudo first order system. Equilibrium constants were then calculated from the rate constants as shown below:

$k_1 = 2.5$ $k_2 = 3$; i.e. for 1-hexyne $\rightleftharpoons$ 1,2-hexadiene, $K = 0.8$

$k_3 = 65$ $k_4 = 0.3$; i.e. for 1,2-hexadiene $\rightleftharpoons$ 2-hexyne, $K = 200$

$k_5 = 1$ $k_6 = 20$; i.e. for 2-hexyne $\rightleftharpoons$ 2,3-hexadiene, $K = 0.05$

$k_7 = 13$ $k_8 = 2$; i.e. for 2,3-hexadiene $\rightleftharpoons$ 3-hexyne, $K = 7$

These values are of course subject to large errors due to the approximate nature of the method. This applies especially to k_1 since the isomerisation of 1-hexyne is accompanied by an unknown amount of addition reaction (in this instance it was assumed that the proportion of addition reaction was similar to the proportion in the 3-hexyne reaction).

Discussion

Despite the uncertainties the following order of stability may be deduced with some confidence:

1-hexyne $\sim$ 1,2-hexadiene $<$ 2,3-hexadiene $<$ 3-hexyne $<$ 2-hexyne

Thus the kinetic data yields an order which is in fact in good agreement with the published data.

It must be realised that relative stabilities in the gas phase may well differ from the relative stabilities in solution (especially if complexing such as proposed in section 3.7 occurs). Thus exact correspondence would not be expected even if the calculation of more accurate rate constants was possible.

3.9 AN APPARENTLY ANOMALOUS RESULT

Beale[13] reports as much as 20% 1,2-hexadiene in the 1-hexyne isomerisation. This was a very large amount considering the rate of isomerisation of 1,2-hexadiene and was explained on the basis of the third order kinetics (see section 1.1).

Experimental

1-Hexyne (10 μl) was reacted with HBF_4 (0.1 M, 1 ml) at 25°C for 30 minutes. The result is here compared with the earlier result.

	product composition %		
	1-	1,2-	2-
This Work	80.2	16.5	3.2
Beale	80.1	17.2	2.7

After one hour Beale found 21.1% 1,2-hexadiene.

Discussion

The present result confirms the large build up of 1,2-hexadiene in the reaction mixture.

However, the figures given above for the proportion of 1-hexyne may be misleading due to the possible formation of 2,2-difluorohexane which co-chromatographs with 1-hexyne. If there is a similar extent of addition as in the 3-hexyne isomerisation (e.g. at 34% reaction of 3-hexyne, 17% 3,3-difluorohexane is formed, see section 3.2) the figures above of 80% for 1-hexyne should be split into 60% 1-hexyne and 20% 2,2-difluorohexane (i.e., 1-hexyne may react considerably faster than is at first apparent). This is the basis on which the rate constants were calculated in the last section.

When those rate constants (i.e. $k_1 = 3$, $k_2 = 2.5$, $k_3 = 65$, and $k_4 = 0.3$) are substituted into the appropriate kinetic equations it is found that the maximum proportion of 1,2-hexadiene is only 4%; to obtain a value of approximately 20%, k_1 needs to be increased to 25 (with the others kept constant).

If this is the true value of k_1 a fast reaction is proceeding and the major product is 2,2-difluorohexane. This hypothesis has the advantage of explaining the very slow fall in the proportion of 1,2-hexadiene (Beale found 21% 1,2-hexadiene after 1 hour, 19% after 4.25 hours, 13% after 12 hours, and 6% after 21 hours); the formation of 2,2-difluorohexane requires consumption of HF and therefore lowers the catalyst concentration. In addition, the values $k_1 = 25$ and $k_2 = 2.5$ give $K = 10$ for

$$\text{1-hexyne} \rightleftharpoons \text{1,2-hexadiene}$$

This corresponds to $\Delta G = -1.4$ kcal.mole^{-1} which compares favourably with the value of -1.07 kcal.mole^{-1} for the reaction

$$\text{1-pentyne} \rightleftharpoons \text{1,2-pentadiene}$$

as given in the literature[12].

Definite information on the value of k_1 would require the use of a glc column which could adequately separate the isomers and the addition products; such a column was not used in this study. However the evidence mentioned above indicates that a considerable amount of 2,2-difluorohexane may well be produced in the isomerisation of 1-hexyne.

CHAPTER FOUR

HEXAFLUOROPHOSPHORIC ACID AS A CATALYST

4.1 INTRODUCTION

The catalyst HBF_4 has proved to have several disadvantages. These are

a) addition products are formed preventing equilibration of the isomers and resulting in a decrease in catalyst concentration,

b) product destruction occurs, preventing equilibration and affecting the kinetics,

c) the acid system HF/BF_3/sulpholane appears to be complex[36]; this may affect the kinetics and also be the cause of the addition reactions since HF may be available.

Whiting[36] reported that hexafluorophosphoric acid (HPF_6) in sulpholane is a stronger acid than HBF_4/sulpholane; it can thus be expected to be a more efficient catalyst. It was also reported that the reaction of HF and PF_5 to ion paired $H^+..PF_6^-$ appeared to be complete in sulpholane; thus any problems due to the complexity of the HF/BF_3/sulpholane system should be minimised.

Solutions of HPF_6 in sulpholane were therefore prepared (see appendix 1.10) and the isomerisations were studied with this new catalyst. No other solvent was used in any of the reactions.

4.2 OCTENE ISOMERISATIONS

Isomerisation of the seven straight chain octenes (i.e. 1-, cis- and trans-2-, cis- and trans-3-, and cis- and trans-4-octene) with HBF_4/sulpholane/bromomethane as catalyst has been reported[54]. A brief study was carried out here to check that the stronger acid HPF_6 also catalysed the reaction.

Experimental

Samples of 1- and 2-octene (purchased from B.D.H.) were chromatographed at 100° on the column used for the hexynes and hexadienes (see section 2.2).

1-Octene gave one major peak (with a small impurity which proved to be unaffected by the acid). 2-Octene gave two major peaks (in a 60:40 ratio) which are presumably cis- and trans-2-octene.

Seven peaks were found in the chromatograms of the isomerisation products. These were the starting isomers and four peaks labelled A, B, C and D. 1-Octene appeared as a shoulder on peak D but the others were adequately separated.

isomer	retention time min
1-octene	23.5
2-octene	26.2
	27.6
A	18.0
B	19.2
C	20.4
D	24.2

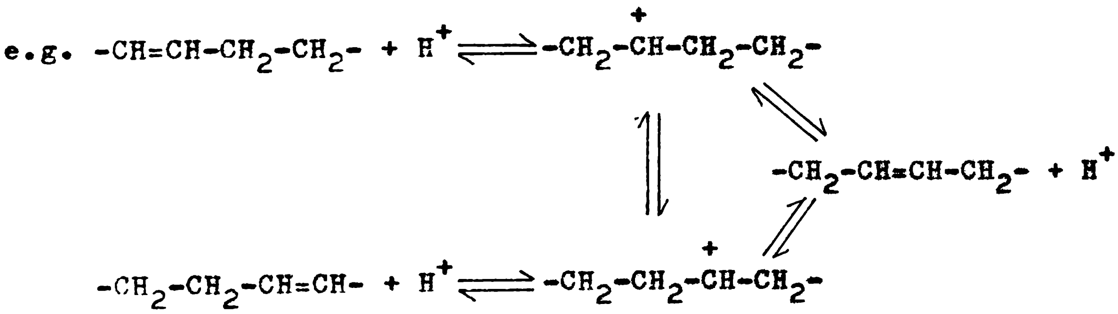
All response factors were taken arbitrarily to be one.

The starting material (10 μl) was reacted with HPF_6 (0.1 M, 1 ml) at 25°C.

Starting material	time min.	% product composition							% recovery
		1-	2-		A	B	C	D	
1-octene	15	trace	8.2	27.5	1.1	1.3	34.8	27.1	47
2-octene	15	trace	8.2	28.0	0.5	1.1	34.8	27.4	49
1-octene	34	trace	6.2	21.7	1.2	1.7	47.5	21.6	33

Discussion

Both starting materials are isomerised extensively. The most probable mechanism is protonation-deprotonation accompanied by hydride shifts, as has been found for the HBF_4 catalysed isomerisation[54].



$$\begin{tikzcd}
\text{e.g. } -CH{=}CH{-}CH_2{-}CH_2{-} + H^+ \arrow[r, shift left] & -CH_2{-}\overset{+}{C}H{-}CH_2{-}CH_2{-} \arrow[l, shift left] \arrow[d, shift left] \arrow[dr, shift left] & \\
& & -CH_2{-}CH{=}CH{-}CH_2{-} + H^+ \arrow[ul, shift left] \arrow[dl, shift left] \\
-CH_2{-}CH_2{-}CH{=}CH{-} + H^+ \arrow[r, shift left] & -CH_2{-}CH_2{-}\overset{+}{C}H{-}CH_2{-} \arrow[l, shift left] \arrow[u, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

After 15 minutes isomerisation 1- and 2-octene give essentially the same product mixture; at 34 minutes isomerisation compound C becomes more dominant while the other compounds remain very similar in proportion to each other.

Considerable product destruction occurs, a phenomenon not found for the HBF_4 catalysed isomerisation[55].

The 2-octene isomer formed predominantly is the less abundant isomer in the 2-octene starting material. Assuming that this isomerisation, like the HBF_4 catalysed reaction, gives predominantly the trans- form, this compound may be identified as trans-2-octene; thus the starting material consists of 40% trans- and 60% cis-2-octene.

The most stable isomers are the trans- forms; thus the two most prominent unknown peaks C and D are probably trans-3- and -4-octene (not necessarily respectively). The remaining two peaks A and B must therefore be cis-3- and -4-octene (again not necessarily respectively).

4.3 ACETYLENE-ALLENE ISOMERISATIONS

Experimental

In experiments 1-5 below, the starting material (10 μl) was reacted with HPF_6 (0.1 M, 1 ml) at 25°

1) 1-hexyne Fig. 4.1

time min.	product composition %				% recovery
	1-	1,2-	2-	2-one	
0	100				100
0.33	94.6	2.3	2.2	1.0	43
1	89.4	4.7	3.5	2.4	39
12.25	83.4	8.4	5.9	2.3	37
30	75.6	11.9	9.2	3.2	42
76.5	65.4	10.6	22.6	1.4	26
134	53.5	9.5	34.3	2.7	31

2) 1,2-hexadiene Fig. 4.2

time sec.	product composition %						% recovery
	1-	1,2-	2-	2,3-	2-one	3-one	
0	5.1	94.9					100
5	5.6	42.7	50.8		0.9	0.1	64
10	6.5	29.3	63.0		1.0	0.1	64
30	4.8	10.4	81.5		2.0	1.3	56
60	3.7	6.0	87.9	1.2	1.0	0.2	50

3) 2-hexyne Fig. 4.3

time min.	product composition %								% recovery
	1-	1,2-	2-	2,3-	3-	X	2-one	3-one	
0			96.2		3.8				100
0.33		0.1	92.4	1.2	5.9		0.2	0.2	80
1		0.2	91.6	1.3	6.3		0.3	0.4	88
12.25		0.4	89.0	3.1	6.5		0.4	0.6	92
30		0.3	87.3	2.3	9.2		0.4	0.5	64
60	0.4	0.4	84.5	2.9	10.8	0.2	0.4	0.5	50
160	1.1	0.6	78.4	3.5	13.6	1.2	0.8	0.9	47

4) 2,3-hexadiene Fig. 4.4

time sec.	product composition %					% recovery
	2-	2,3-	3-	2-one	3-one	
0		100				100
6	19.1	67.5	12.6		0.8	76
10	25.0	56.7	16.9		1.4	76
30	34.8	38.9	24.4		1.9	61
60	41.9	29.5	26.6		2.0	63
120	44.7	24.4	30.0	0.1	0.9	52

5) 3-hexyne Fig. 4.5

time min.	product composition %					% recovery
	2-	2,3-	3-	X	3-one	
0	1.1	0.7	98.2			100
0.16	1.2	3.9	94.9			66
1	1.4	5.1	92.7		0.9	66
5	2.2	8.4	87.9		1.6	67
15	3.6	9.6	85.2		1.5	50
30	5.9	11.7	80.2	0.2	2.1	(not)
60	11.4	10.3	75.8	0.4	2.1	(measured)

6) 2,3-Hexadiene (25 μl) was reacted with HPF_6 (0.1 M, 1 ml) at 25°C. The results are graphed in Fig. 4.4

time. hr.	product composition %							% recovery
	1-	2-	2,3-	3-	X	2-one	3-one	
0			100					100
0.5		43.4	22.6	33.0		0.1	0.8	74
1		50.6	11.2	37.3		0.1	0.8	61
3.6		59.8	5.2	33.8	0.3	0.05	0.9	46
7.4		64.6	4.0	27.4	0.8	0.7	2.5	41
23.2	2.3	68.7	2.5	12.2	4.2	2.4	7.9	21

7) 3-Hexyne (10 μl) was reacted with HPF_6 (0.12 M, 1ml) at 25°C

time min.	product composition %					% recovery
	2-	2,3-	3-	X	3-one	
0	1.1	0.7	98.2			100
1	0.8	6.5	92.3		0.4	71
5	2.2	8.0	88.8	0.4	0.5	55
15	5.4	11.5	81.5	0.9	0.7	53
30	9.5	12.1	76.1	1.5	0.8	43

8) 3-Hexyne (10 μl) was reacted with a mixture of solutions of HF (0.18 M, 0.75 ml) and PF_5 (0.35 M, 0.25 ml) at 25°C.

time min.	product composition %					% recovery
	2-	2,3-	3-	X	3-one	
0	1.1	0.7	98.2			100
1	0.7	4.5	94.6		0.2	81
10	0.9	6.7	91.0		1.4	78
30	4.8	9.8	83.6	0.2	1.7	71
60	10.3	8.7	78.7	0.7	1.6	61

In all the reactions darkening of the solutions occurred.

The two hexanones were identified by their retention times on the glc.

General Observations

a) 1-hexyne isomerisation: The initial products are 1,2-hexadiene and 2-hexyne. 1,2-Hexadiene is formed more rapidly at first and passes through a maximum proportion while the proportion of 2-hexyne increases steadily. No addition products can be distinguished. A small amount of 2-hexanone is formed. Considerable product destruction occurs, especially in the first 20 seconds of reaction.

b) 1,2-hexadiene isomerisation: This is the fastest reaction; the first analysis is carried out after 5 seconds, the minimum time for the reaction procedure (see section 2.1). The major product is 2-hexyne. 1-Hexyne is formed much more slowly and is always in a lower concentration than 1,2-hexadiene; in the course of the reaction it passes through a maximum proportion. 2,3-Hexadiene is formed after a considerable amount of 2-hexyne has built up. No addition products can be distinguished. Both 2- and 3-hexanone are formed with the former predominating. Considerable product destruction occurs.

c) 2-hexyne isomerisation: This is the slowest reaction. The two allenes are formed in low proportions and no definite drop can be seen at long reaction times. 3-Hexyne is formed at a steady rate throughout the reaction. Small amounts of 1-hexyne and 3,3-difluorohexane appear after 1 hour, the former at a greater proportion than 1,2-hexadiene. Both 2- and 3-hexanone are formed, with the latter predominating slightly. Considerable product destruction occurs.

d) 2,3-hexadiene isomerisation: The reaction is slower than for 1,2-hexadiene but faster than for the acetylenes. The main products are 2- and 3-hexyne with the former predominating; the reaction with a larger volume of 2,3-hexadiene shows that the proportion of 3-hexyne drops at high percentage reaction. 3-Hexanone is formed throughout the reaction; 2-hexanone is formed in smaller amounts after approximately 75% reaction. 1-Hexyne and 3,3-difluorohexane are formed after 95% reaction. Considerable product destruction occurs.

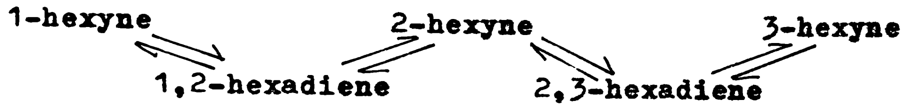
e) 3-hexyne isomerisation: The initial products are 2,3-hexadiene and 2-hexyne. 2,3-Hexadiene is formed more rapidly at first and passes through a maximum proportion while the proportion of 2-hexyne increases steadily. Small amounts of 3,3-difluorohexane and 3-hexanone are formed. Considerable product destruction occurs. The reaction is similar with the stronger acid (experiment 7) and with an excess of HF (experiment 8) although in the latter case product destruction is less at comparable percentage reaction.

Discussion

The evidence summarised above leads to the conclusion that the isomerisation proceeds by the stepwise pathway found for the

H_2SO_4 and HBF_4 catalysed reactions[10,13]:

i.e.



Such a reaction is best explained by the same vinyl cation mechanism postulated for the previous reactions:

i.e. $-C\ C-CH_2- + H^+ \rightleftharpoons -CH{=}\overset{+}{C}-CH_2- \rightleftharpoons -CH{=}C{=}CH- + H^+$

(see section 1.1 for the complete scheme)

Only small amounts of the addition product 3,3-difluorohexane are formed. It may be assumed that production of 2,2-difluorohexane, which is masked by 1-hexyne on the chromatograms, is correspondingly low. The compound labelled "1-" in the 2-hexyne isomerisation appears approximately at the same time and to the same extent as 3,3-difluorohexane; considering that [1,2-hexadiene] is very low, in fact less than ["1-"], in this reaction and that in the 1,2-hexadiene isomerisation 1-hexyne was produced very slowly and was always at a lower concentration than 1,2-hexadiene, the compound "1-" may well be 2,2-difluorohexane.

The production of the addition products is much lower than with the HBF_4 catalyst; this is probably linked to the differing natures of the catalyst solutions[36]. A hypothesis to account for the much lower production will be advanced in section 4.6.

The formation of 3,3-difluorohexane is consistent with the vinyl cation mechanism since it is formed in solutions in which vinyl cations with charge at C-3 would be generated.

An interesting aspect of the reactions is that [3-hexyne] passes through a maximum in the 2,3-hexadiene isomerisation and (less clearly) there is a similar effect for [1-hexyne] in the 1,2-hexadiene isomerisation. This is probably due to kinetic control, 3- and 1-hexyne being initially formed at rates higher than would be expected from their thermodynamic stabilities.

The relative rates of the five isomerisations i.e. 1,2-hexadiene < 2,3-hexadiene < 1-hexyne < 3-hexyne < 2-hexyne is the same as for the HBF_4 and H_2SO_4 catalysed reactions. The relationships between kinetic data and thermodynamic stability will be discussed in section 4.9 and the kinetic order in section 4.8.

HPF_6 is similar to H_2SO_4 but different from HBF_4 in that it leads to the formation of the ketones 2- and 3-hexanone. The pattern of production is the same as with H_2SO_4 for which a convincing mechanism was proposed (see section 1.1). However the analogous mechanism to account for the present results requires that stable vinyl cations be formed; such cations have never been observed[31,32]. An alternative mechanism will be discussed later (in section 4.7).

The product destruction which occurs with the present catalyst is greater than with HBF_4. This may be a reflection of the greater acidity of HPF_6[36].

A comparison may now be made between sulpholane solutions of H_2SO_4, HBF_4 and HPF_6 as catalysts for this reaction.

The present catalyst is superior in that difluorohexane and ketone formation is minimal and will therefore affect the overall reaction very little. However it suffers from the disadvantage that product destruction is somewhat greater. This prevents equilibration of the isomers and enormously complicates the kinetic schemes, as it does with the other two catalysts.

Thus HPF_6 is far from being an ideal catalyst.

Fig. 4.1 The isomerisation of 1-hexyne

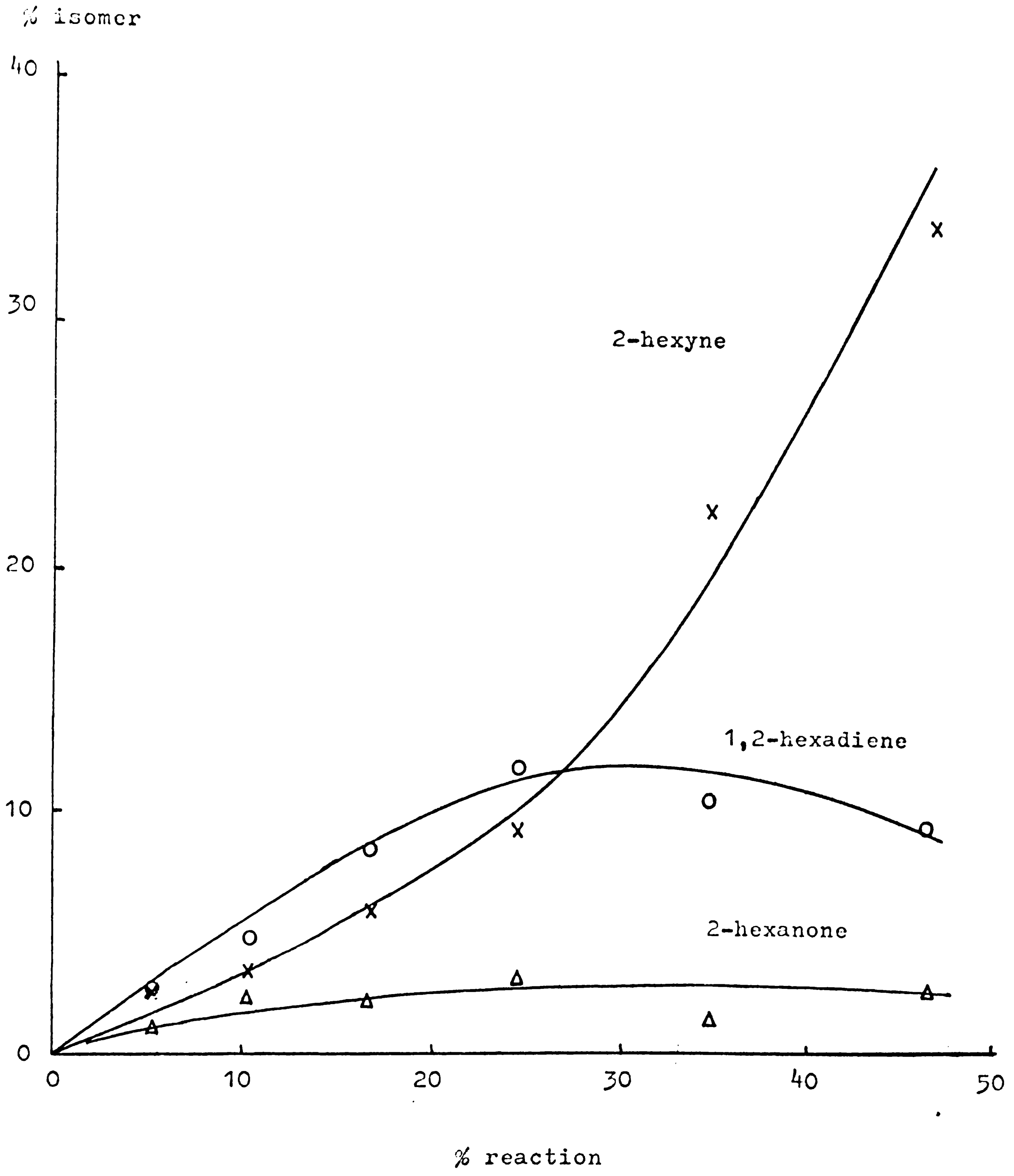
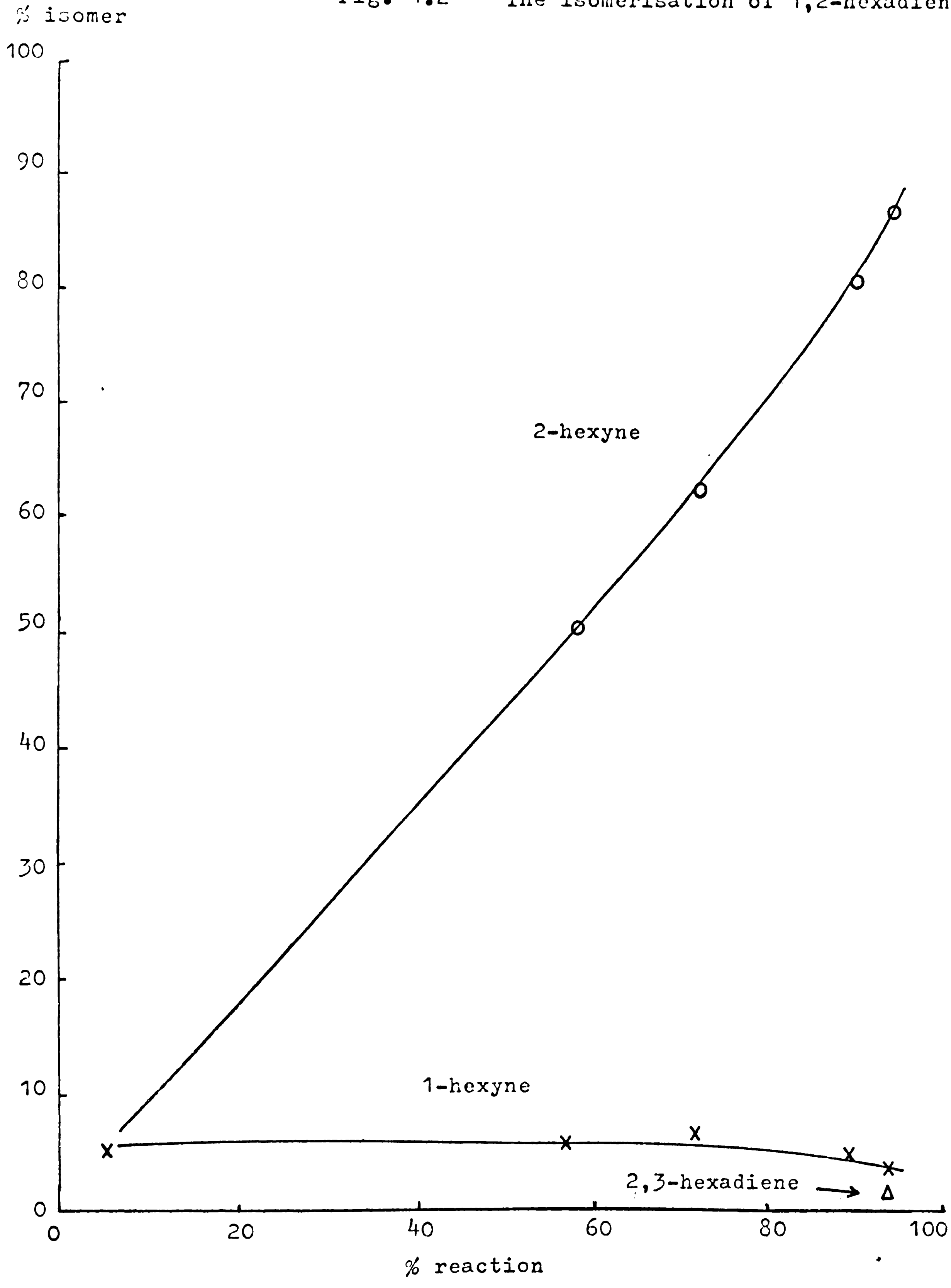
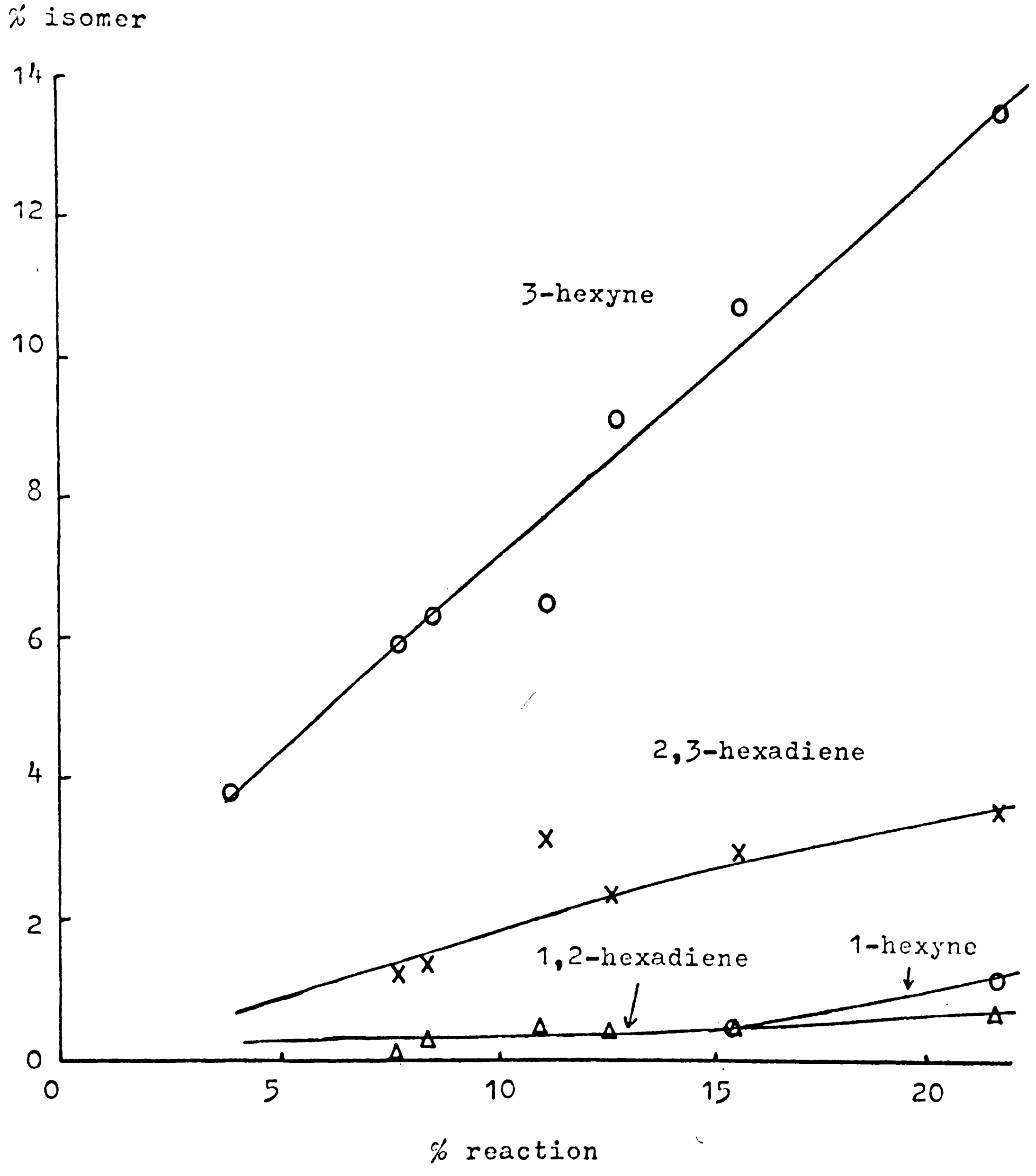


Fig. 4.2 The isomerisation of 1,2-hexadiene



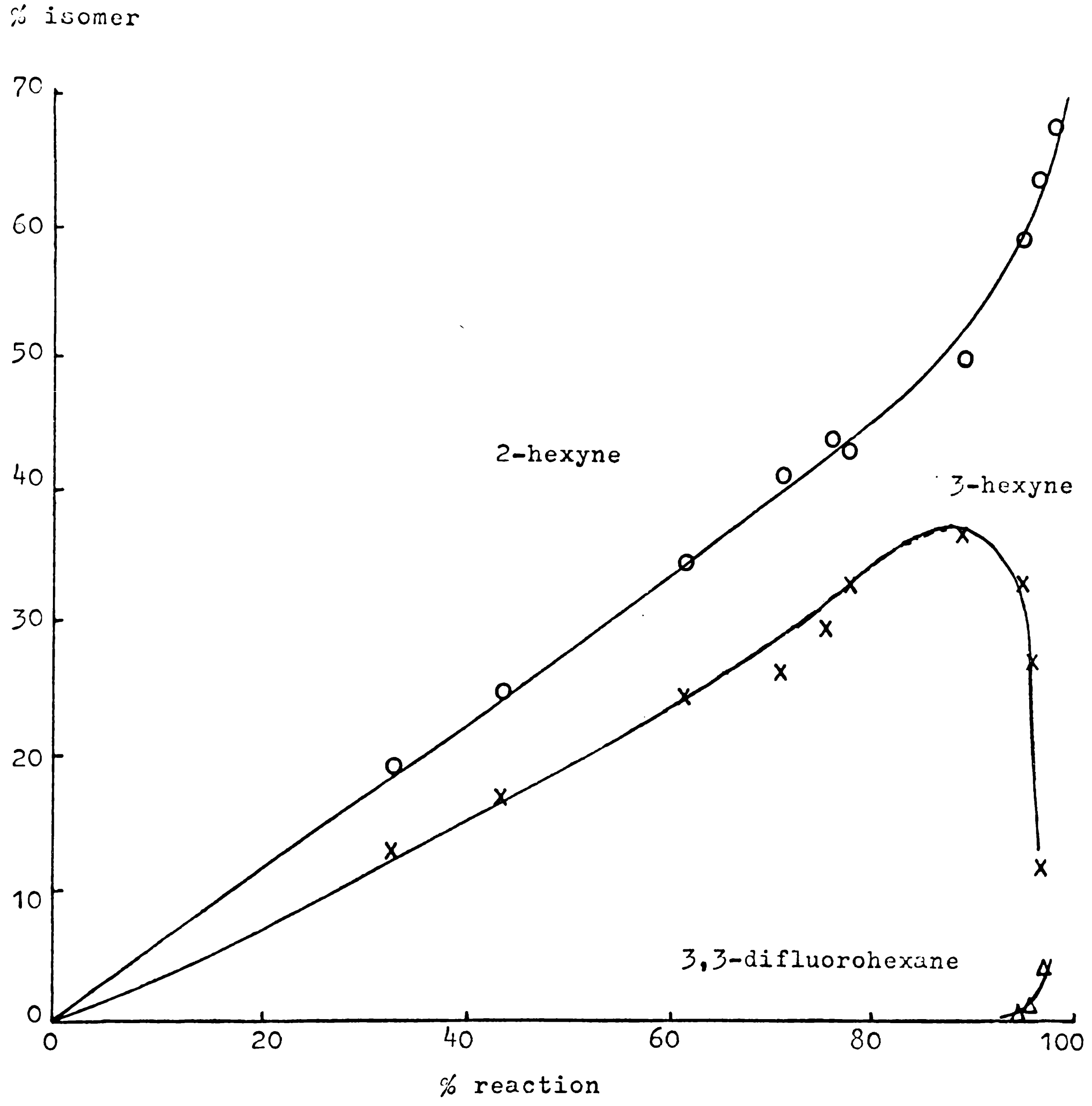
The amounts of both 2- and 3-hexanone are too low to be shown clearly on this graph.

Fig. 4.3 The isomerisation of 2-hexyne



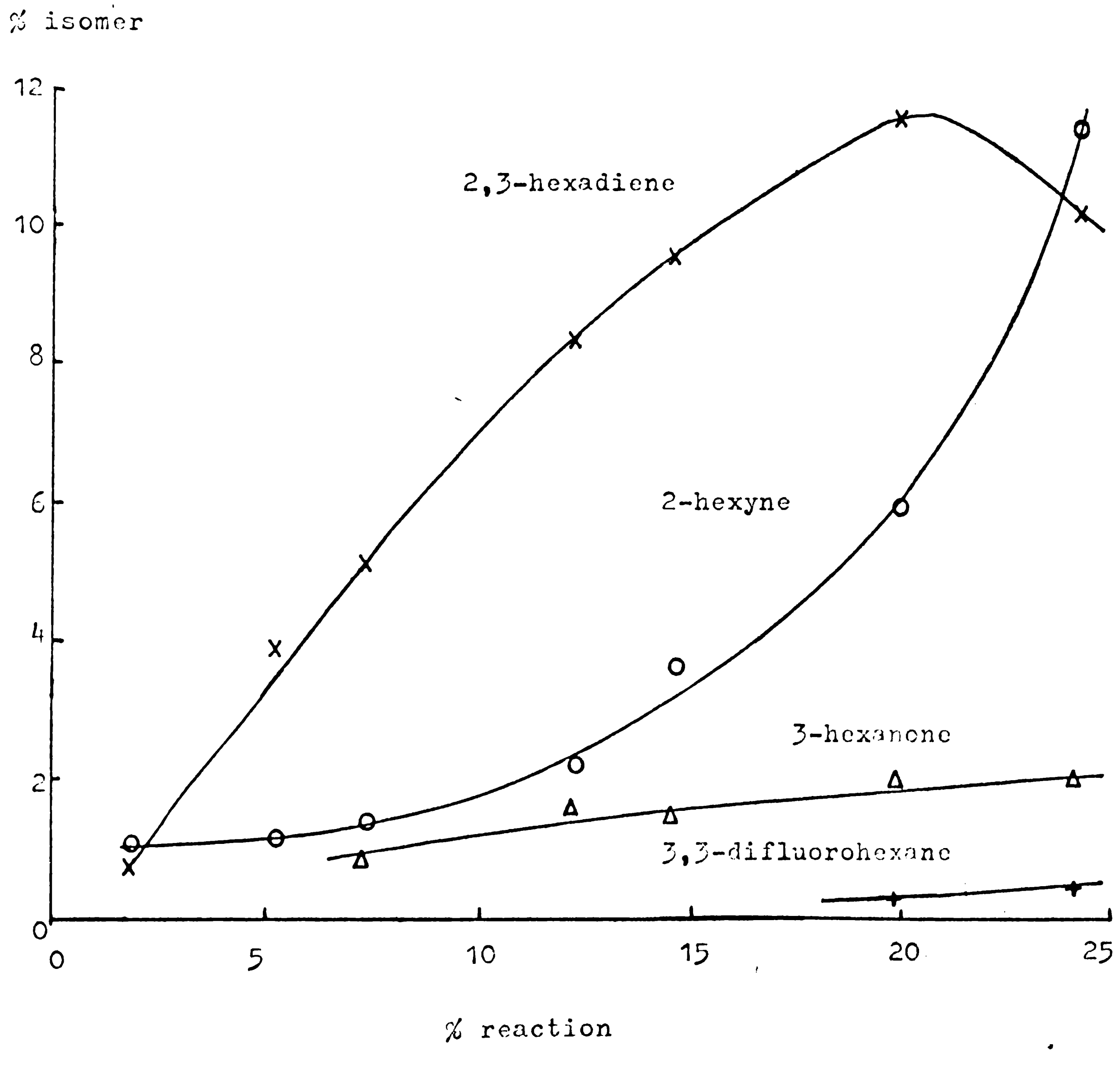
The amounts of 3,3-difluorohexane and of 2- and 3-hexanone are too low to be shown clearly on this graph.

Fig. 4.4 The isomerisation of 2,3-hexadiene



The amounts of 2- and 3-hexanone are too low to be shown clearly on this graph.

Fig. 4.5 The isomerisation of 3-hexyne



4.4 THE REACTION WITH CONJUGATED DIENES

As with the reactions with HBF_4 conjugated dienes may be formed via allyl cations. Conjugated dienes were absent from the chromatograms of the reactions with HPF_6 however, but the stability of these compounds under the reaction conditions needed investigation.

Experimental

2,4-Hexadiene (10 μl) was reacted with HPF_6 (0.1 M, 1 ml) for both 1 and 30 minutes at 25°.

In both cases there was no product recovery.

Discussion

This result is the same as was obtained with HBF_4 and the remarks made in section 3.4 may equally be applied here; i.e. possible mechanisms for product destruction may be based on the formation of allyl cations.

The only positive conclusion is that generation of allyl cations in the acetylene-allene isomerisations would not lead to the formation of conjugated dienes.

4.5 ISOMERISATIONS WITH PHOSPHORUS PENTAFLUORIDE AND PHOSPHORUS PENTAFLUORIDE/WATER

It has already been shown (see section 3.6) that a sulpholane solution of the Lewis acid BF_3 catalyses the acetylene-allene isomerisation. Accordingly the reaction with PF_5/sulpholane was carried out to test whether or not it also catalyses the reaction.

The acids HBF_4 and HPF_6 consist of

$$\{HF + \text{Lewis acid}\}$$

(as do HSO_3F and $HAsF_6$, see chapter 5) whereas H_2SO_4 consists of $\{H_2O + \text{Lewis acid}\}$.
Consequently, it was decided to test the $\{H_2O + PF_5\}$ system for catalytic power; it has already been shown that an equimolar sulpholane solution of H_2O and BF_3 does not catalyse the reaction (see section 3.6).

Experimental

In all the reactions described below sulpholane was used as the solvent.

1) 3-Hexyne (10 μl) was reacted with PF_5 (0.35 M, 1 ml) at 25°C.

time min.	product composition %				% recovery
	2-	2,3-	3-	3-one	
0	1.1	0.7	98.2		100
0.13	0.4	5.3	94.2		68
32	10.0	19.0	68.6	2.4	60
50	15.5	12.1	68.6	3.8	38

2) 2,3-Hexadiene and 3-hexyne (in the volumes shown below) were reacted with PF_5 (0.23 M) for 30 minutes at 25°C

reactant	volume µl	product composition %				% recovery
		2-	2,3-	3-	3-one	
3-hexyne	10	9.6	20.5	63.2	6.7	42
2,3-hexadiene	10	47.1	12.3	36.9	3.6	31
2,3-hexadiene	50	34.0	30.2	34.9	0.8	64

3) The reactions detailed below were carried out for 30 minutes at 25°C. In each case the amount of water shown was added to the PF_5 solution (1 ml) with a microsyringe before the addition of the reactant isomer.

reactant	$[PF_5]$	vol H_2O µl	product composition %					% recovery
			2-	2,3-	3-	X	3-one	
3-hexyne (10 µl)	0.35	5	9.0	14.0	74.7	2.9	0.5	68
3-hexyne (10 µl)	0.23	4	5.4	12.3	78.1	0.1	4.1	46
2,3-hexadiene (10 µl)	0.23	4	53.3	8.4	36.2		2.1	53
2,3-hexadiene (50 µl)	0.23	5	12.1	78.2	9.6		0.2	67

4) 2,3-Hexadiene (10 µl) was reacted with

a) PF_5 (0.23 M, 1 ml) + 0 µl H_2O

b) PF_5 (0.23 M, 1 ml) + 2 µl H_2O

for 5 minutes at 25°C.

	product composition %				% recovery
	2-	2,3-	3-	3-one	
a	51.3	8.2	37.6	2.9	59
b	52.5	9.6	35.5	2.5	67

5) An equimolar solution of PF_5, H_2O and HF was made up in the following sequence:

i) H_2O (4 μl) was added to PF_5 (0.23 M, 1 ml)

ii) HF (0.18 M, 0.56 ml) was added to a sample of this solution (0.44 ml).

With the resulting solution 0.6% isomerisation of 3-hexyne occurred in 30 minutes at 25°C.

6) 2,4-Hexadiene (10 μl) was reacted with PF_5 (0.35 M, 1 ml) for 1 minute at 25°C. Yellow fumes were evolved immediately upon addition of the diene.

No products were recovered.

Discussion

During this discussion the two catalytic systems will be referred to as PF_5 and PF_5/H_2O although solvent sulpholane is always present.

The evidence above shows that both PF_5 and PF_5/H_2O catalyse the isomerisation reaction.

From the point of view of both product patterns and rates of reaction the two catalysts act in a very similar manner; this contrasts sharply with the comparison between the BF_3 and BF_3/H_2O systems. The main differences between the present two catalysts are that 3,3-difluorohexane is formed in the reaction with PF_5/H_2O only, and that product destruction is greater with PF_5.

There are several direct parallels between the isomerisations promoted by these two catalysts and by HPF_6. These are as follows: i) in the 3-hexyne isomerisation, 2,3-hexadiene is the initial product, experiment 1 showing that it passes through a maximum proportion (about twice as large as in the HPF_6 reactions) to be followed by an increase in the proportion of 2-hexyne; ii) the 2,3-hexadiene reactions give 2- and 3-hexyne as the major products; iii) 3-hexanone is produced in the two reactions studied (in somewhat larger quantities); iv) 3,3-difluorohexane is produced in the reaction of 3-hexyne with PF_5/H_2O; v) product destruction occurs to a comparable extent.

Thus any proposed mechanism for these reactions must explain the same type of sequential reaction as found for all other catalysts (see section 1.1) and the same side products found for the HPF_6 catalysed reaction.

There are some aspects of the data which indicate that the reaction kinetics are complicated. The proportion of 3-hexyne in experiment 1 does not change from 32 to 50 minutes while that of 2-hexyne increases and of 2,3-hexadiene decreases. 3-Hexyne reacts to a slightly greater extent after 30 minutes in the less concentrated PF_5 solution, with the proportion of 3-hexanone being almost trebled. The product patterns for the 2,3-hexadiene reaction with PF_5 at 5 minutes (experiment 4a) and 30 minutes (experiment 2) are similar (although product destruction is greater at the longer time), and a similar effect is found for the wet PF_5 solutions (experiments 3 and 4b).

Although this data does show some inconsistencies it appears that the reactions slow down considerably in their later stages.

In addition it appears that the reaction rates are about the same with and without the addition of water provided there is no more than a 1:1 molar ratio of $H_2O:PF_5$ (i.e. 1 ml 0.23 M PF_5 + 4 μl H_2O). For instance, while 2,3-hexadiene reacts to about the same extent with 0:1 and 0.5:1 (experiment 4) and 0:1 and 1:1 (experiments 2 and 3) molar ratios of $H_2O:PF_5$, the two reactions with 50 μl 2,3-hexadiene (experiments 2 and 3) show that with an excess of water the reaction is considerably slower.

If a mechanism is to be proposed for the PF_5 catalysed reaction the problem that must be faced, as with the BF_3 catalysed reaction, is the lack of a source of protons.

In the BF_3 catalysed reaction the possibility of traces of water acting as a co-catalyst was considered. Such a possibility must also be considered here since it is generally accepted that a co-catalyst is required in Lewis acid catalysed reactions(see section 1.3) and also since the procedure for drying the PF_5 was not exhaustive (see appendix 1.10).

According to Heslop and Robinson[56] hydrolysis of the group V pentahalides occurs in two steps:

$$PX_5 + H_2O \longrightarrow POX_3 + HX \qquad \ldots \text{ i}$$

$$POX_3 + 3H_2O \longrightarrow H_3PO_4 + 3HX \qquad \ldots \text{ ii}$$

It is therefore expected that with traces of water POF_3 and HF would be formed. A solution of HF in sulpholane is known not to catalyse the isomerisation (see appendix 1.9) and catalysis by POF_3 poses the same type of problem as with PF_5. As will be described in the next section neither conductivity nor nmr evidence support a reaction scheme such as that above, but point to the possibility that the reaction in sulpholane is analogous to that of BF_3 and H_2O:

$$PF_5 + H_2O \longrightarrow H^+(PF_5OH^-)$$

This reaction is in accord with the experimental evidence above. The result of experiment 5 is explained if addition of HF to $H^+(PF_5OH^-)$ results in the displacement of OH^- by F^- to form the stable PF_6^- ion:

$$H^+(PF_5OH^-) + HF \longrightarrow H_3O^+(PF_6^-)$$

Thus a species with a hydrated proton is formed and consequently the isomerisation would not be catalysed. It has also been shown (experiment 3) that an excess of water retards the reaction; this is intelligible in terms of the present proposal since once again a hydrated proton would result:

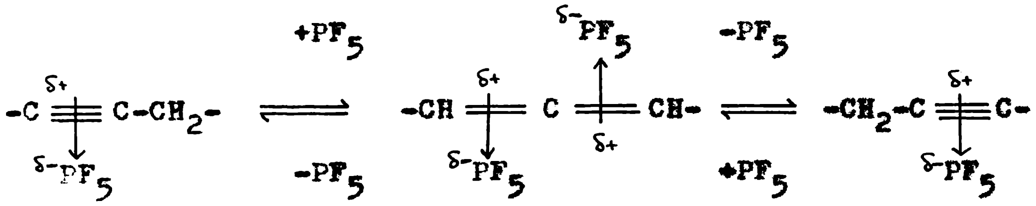
$$H_2O + H^+(PF_5OH^-) \longrightarrow H_3O^+(PF_5OH^-)$$

$H^+(PF_5OH^-)$ should catalyse the reaction in a manner similar to HPF_6, i.e. via formation of vinyl cations, so that formation of other isomers in the usual stepwise pattern and of the side products is only to be expected; this is the most likely explanation of the reactions.

However, there is some evidence that co-catalyst water is not required in the PF_5 catalysed reactions. Although the results above may be complicated by the slowing of the reactions in their later stages it seems that there is little or no variation in reaction rate as the amount of water in the catalyst system is increased from zero to equimolar (see discussion above). It is usual in Lewis acid catalysed reactions that a maximum reaction rate occurs at some optimum value of $[H_2O]:[\text{Lewis acid}]$ (see section 1.3). In addition, it will be shown in the next section that PF_5 forms a complex with 3-hexyne (and presumably the other isomers) and a mechanism may possibly be based on this.

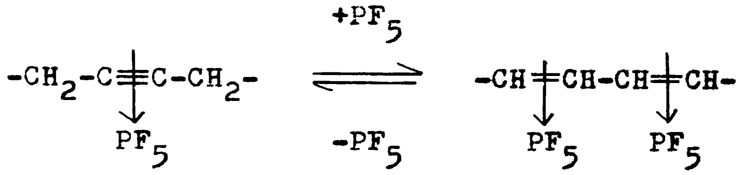
Thus it is worth while to consider some possible mechanisms, especially since the evidence that BF_3 requires a co-catalyst is also not clear cut.

If PF_5 and the isomers form a complex in which the vacant p orbital on the phosphorus atom interacts with the π electron system of the isomer a mechanism involving 1,3-hydride shifts would account for the reaction:

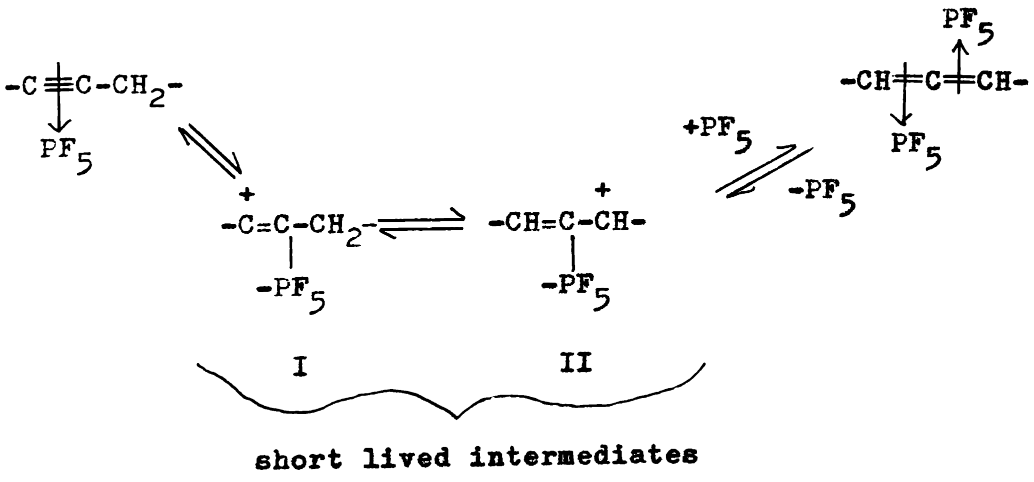


(addition of water to quench the reaction would destroy the complexes). Compared to 1,2-hydride shifts, 1,3-hydride shifts in acyclic systems are rare[57] but convincing evidence has been found for them in some cases[58]. In this case it should be noted that a 1,2-shift would not lead to a stable product:

However, simultaneous 1,2-shifts could lead to conjugated dienes:



Hydride shifts are generally postulated to occur in species with a fully developed positive charge. Such a species for the present case could be an extreme form of the PF_5- isomer complex in which the P atom forms a covalent bond to complete its electron shell and carries a negative charge (cf $PF_5 + F^- \longrightarrow PF_6^-$; also, the stable anions $CH_3PF_5^-$ and $C_6H_5PF_5^-$ have been prepared and characterised[59]). Thus the complete mechanism for an acetylene-allene interconversion would be:

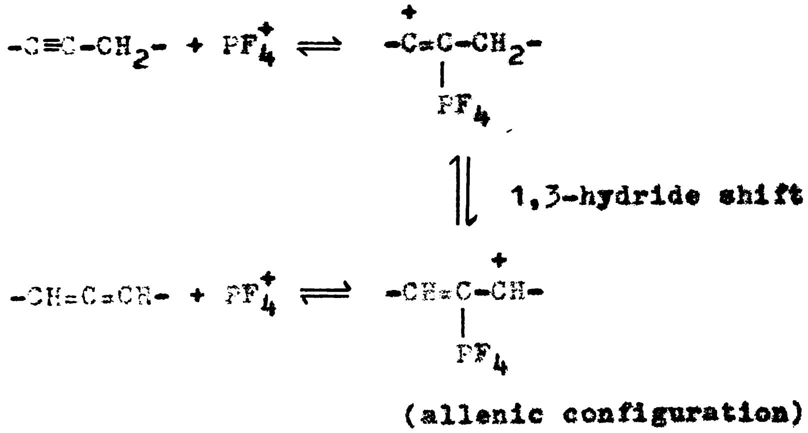


In this mechanism the ion II would be in the allenic configuration; if it adopted the configuration required for resonance stabilisation (cf the protonation of allenes, section 1.2) the reverse reaction to I would be unlikely to occur.

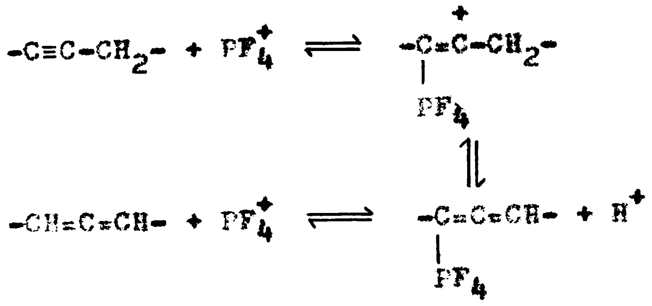
This mechanism could equally well be applied to BF_3 catalysed reactions. However, the formation of the BF_3-isomer complex would be in competition with the formation of the BF_3-sulpholane complex[41]; this provides a rationale for the very much faster reaction with PF_5 than with BF_3.

Possible mechanisms for the PF_5 but not the BF_3 catalysed reactions can be based on the theory that PF_5 dissociates into PF_4^+ and PF_6^- in sulpholane solution (for simplicity, in the mechanisms a and b below the PF_5'-isomer complexes are not shown):

a)



b)



However these two mechanisms are unlikely on the basis of evidence presented in the next section.

Thus mechanisms for the isomerisation catalysed by Lewis acids without co-catalysts may be envisaged. It would be desirable for the PF_5/sulpholane catalyst to be used on a substrate which gives a cleaner reaction (i.e. no product destruction or other side reactions) than the hexynes and hexadienes if the mechanism of its action as a catalyst is to be properly elucidated.

Finally, the reaction with conjugated dienes gives the same result as with the other catalysts; complete product destruction occurs, the reaction in this case being more violent. Once more the only conclusion that may be drawn is that the non-formation of conjugated dienes in the isomerisation reactions cannot be taken as evidence that the intermediates that theoretically would lead to their production are not formed.

4.6 THE NATURE OF THE CATALYST SOLUTIONS

The properties of the catalyst solutions PF_5, PF_5/H_2O and PF_5/HF (all as sulpholane solutions) were studied with and without the addition of isomers. The techniques used were ^{19}F nmr, conductivity measurements and petroleum spirits extraction.

Experimental

1) ^{19}F nmr. All chemical shifts recorded here were determined with respect to C_6F_6. All samples were solutions in sulpholane.

a) Spectra of the three catalysts mentioned above were run both with and without added isomer with the following results:

Sample	Description of spectrum	δ ppm	J_{P-F} Hz
HPF_6 (0.1 M)	sharp doublet	-91.4	770
PF_5 (0.23 M)	broad doublet	-96	780
PF_5/3-hexyne (equimolar)	two sharp doublets	i) -91.3	770
		ii) -81.4	1075
PF_5/H_2O (equimolar)	sharp doublet	-91.5	770

Addition of 3-hexyne to HPF_6 and PF_5/H_2O did not change the spectra.

The spectra of HPF_6, PF_5, and PF_5/H_2O are shown in Fig. 4.6, that of PF_5/3-hexyne not being shown as it is virtually identical to that of HPF_6.

Because of the low signal to noise ratio the spectrum of PF_5 was scanned about five times to confirm the existence of the doublet (cf. the spectrum of HBF_4, see section 3.7).

The PF_5/H_2O and PF_5/3-hexyne spectra did not change over a period of several hours.

None of the signals showed fine structure when expanded up to ten times.

A search for signals due to the PF_4-C group was made about 20 ppm downfield from the HPF_6 region (since, e.g., $C_6H_5CH{=}CHPF_4$ resonates at -118 ppm ($CFCl_3$)[53]). No signals were found.

b) The spectra of the PF_5 and PF_5/3-hexyne solutions were integrated with the results shown in Fig. 4.7.

c) Spectra of PF_5 were run at room temperature, 50°, 95° and 148°C (Fig. 4.8).

2) Conductivity measurements. These were carried out as described in section 3.7. All conductivities quoted here are relative to that of HF (0.18 M) being one; the absolute conductivity of this solution was in the order of $10^{-6}\Omega^{-1}\ cm^{-1}$.

a) The conductivities of HPF_6 and PF_5 were measured and are here tabulated with the results for HBF_4, BF_3, and HF (see section 3.7):

sample	relative conductivity
HPF_6 (0.12 M)	440
HBF_4 (0.1 M)	75
PF_5 (0.35 M)	295
BF_3 (0.22 M)	7
HF (0.18 M)	1

b) The variation in the conductivities of PF_5 and HPF_6 on addition of water was studied.

i) Varying amounts of water were added to PF_5 (0.35 M, 1 ml) at room temperature and the conductivities measured, with the following results (see Fig. 4.9a):

Volume H_2O added μl	relative conductivity
0	295
0.5	465
1	635
2	800
5	840,895
7.5	895
10	925
20	830
30	780

There was no noticeable tendency for these readings to change over times up to approximately one minute.

ii) Varying amounts of water were added to HPF_6 (0.12 M, 1 ml) at room temperature and the conductivities measured, with the following results (see Fig. 4.9b):

Volume H_2O Added μl	Relative Conductivity
0	440
0.2	460
0.4	475
0.6	425
0.8	425
1	405
1.4	385
2.0	370
2.5	360
3	355

There was no noticeable tendency for these readings to change over times up to approximately one minute.

Results with a similar general trend (i.e. passing through a maximum for the addition of ca. 0.5 μl H_2O) were found when an equivalent experiment was carried out on solutions in which the HF:PF_5 molar ratios were 1.2 and 1.45.

c) The isomers 1-, 2- and 3-hexyne and 1,2-hexadiene (7 μl) were added to HPF_6 (0.07 M, 1 ml) and the change in conductivity followed:

time min.	relative conductivity			
	1-	1,2-	2-	3-
0	170	170	170	170
0.25	135	135	130	140
0.5	130	130	125	140
1	125	125	125	135
1.5	120	125	125	135
2	120	125	125	135
3	120	120	120	135
4	120	120	120	130
5	115	120	120	130
34				125

The 3-hexyne sample which had been left in the conductivity cell for 34 minutes was analysed; a separate sample of 3-hexyne was isomerised for the same time but in the usual reaction tube:

	product composition %			% recovery
	2-	2,3-	3-	
conductivity cell	3.8	8.2	88.1	38
usual tube	3.9	7.1	89.1	45

It was also found that the addition of n-hexane (10 μl) to HPF_6 (0.07 M, 1 ml) resulted in no change in the conductivity of the solution.

3) Petroleum spirits extractions. The detailed procedure for these experiments is as follows. A given amount of isomer was added to the acid catalyst solution (1 ml) and shaken to ensure mixing. Petroleum spirits (1 ml, dried over anhydrous $MgSO_4$) was added as soon as

possible and the mixture again shaken, to extract the isomer. A sample of the hydrocarbon layer (2 μl) was taken with a microsyringe for glc analysis. If desired, water (ca. 0.5 ml) was then added to the mixture so that a comparison of the extraction with and without water could be made.

The whole process was carried out as quickly as possible, 15-20 seconds usually being required to complete the extraction and sampling with petroleum spirits alone.

a) 3-Hexyne (10 μl) was extracted from pure sulpholane with petroleum spirits alone.

Complete extraction occurred.

b) 3-Hexyne (10 μl) was extracted from various acid solutions with petroleum spirits alone with the following results:

acid	% extraction
HF (0.18 M)	37,68
HPF_6 (0.1 M)	41
PF_5 (0.35 M)	6
HBF_4 (0.1 M)	56
BF_3 (0.22 M)	85

c) 1-, 2- and 3-hexyne (10 μl of each) were added to HPF_6 (0.1 M) and were extracted with petroleum spirits alone with the following results:

isomer	% extraction
1-hexyne	40
2-hexyne	38
3-hexyne	41

d) Varying amounts of 3-hexyne were added to HPF_6 (0.07 M) and were extracted first with petroleum spirits alone and then with both petroleum spirits and water (for procedure, see above).

The % extraction with petroleum spirits alone was divided by the % extraction with petroleum spirits/water to give the fraction extracted with petroleum spirits alone. This procedure was carried out since, in the 10-20 seconds required for the petroleum spirits extraction, product destruction occurs (see section 4.3 for extent). The amount of isomer extracted at that time should be compared with the amount actually present at that time, not with the amount added.

The amount of isomer actually present (including the 2,3-hexadiene and 2-hexyne formed in the reaction which takes place) is calculated from the percentage recovery in the petroleum spirits/water extractions. Thus, when 6 μl of 3-hexyne is added and 83% recovery occurs, the amount present is listed in the table below as 5.0 μl.

volume of 3-hexyne added μl	amount of isomer present μl	fraction extracted with petroleum spirits alone
3	2.6,3.1	0.16,0.20
5	4.6,4.8	0.30,0.35
6	5.0	0.45
7	4.7,4.7,5.7	0.59,0.56,0.61
8	5.8	0.64
10	6.8,6.9,7.1,7.2	0.70,0.72,0.85,0.64
12.5	7.8,8.6	0.88,0.73
15	10.1	0.85
20	15.2	0.80
7	4.4	0.57

The last row of the table gives the result of an experiment in which the extraction with petroleum spirits alone was not performed until one minute after the addition of the 3-hexyne.

These results are graphed in Fig. 4.10.

Discussion

The sulpholane solution of HPF_6 gives the expected qualitative result in the nmr experiment; i.e. a sharp doublet which can be ascribed to P-F splitting in a species with identical fluorine nuclei bonded to a single phosphorus atom.

In the table below, the data found here for HPF_6 is compared with literature data for HPF_6 and PF_6^-:

sample	δ ppm	J_{P-F} Hz	reference
HPF_6, sulpholane solution	-91	770	this work
HPF_6, aqueous solution	-92(TFA)	713	60
KPF_6, aqueous solution	-94(TFA)	705	60
PF_6^-, aqueous solution	-98(TFA)	710	61
$Bu_4N^+PF_6^-$, CH_2Cl_2 solution	-92($CFCl_3$)	711	62

The chemical shift found here agrees well with the literature figure but the coupling constant is significantly higher than any of the literature figures for either HPF_6 or PF_6^-. This constitutes evidence that the nature of HPF_6 in sulpholane is different from that in aqueous solution.

PF_5/sulpholane gives a broad doublet, the same result as found by Brownstein[42] for PF_5 solutions in CH_2Cl_2, in contrast with the sharp doublet found for neat PF_5[60,61].

In the following table, the data found here for PF_5 is compared with literature data:

sample	δ ppm	J_{P-F} Hz	reference
PF_5, sulpholane solution	-96	770	this work
PF_5, sulpholane solution	-101($CFCl_3$)	-	41
PF_5, CH_2Cl_2 solution	-97($CFCl_3$)	947	62
PF_5, neat	-91(TFA)	929	60
PF_5, neat	-91(TFA)	916	61

The value of δ found here is closer to the literature values in solutions in which fluorine exchange has been postulated[41,62] than to the values in the neat PF_5 samples[60,61]. In addition the J_{P-F} value is lower than in any of the three literature examples in which PF_5 gives a doublet[60,61,62].

Tebbe and Muetterties[45] have explained the collapse of the PF_5 doublet to a singlet at 80° in acetonitrile as being due to fluorine exchange between PF_6^- impurity and the PF_5. Such a hypothesis could also explain the broad doublet found here except that it is unlikely for two reasons.

Firstly, when two species giving nmr signals are exchanging rapidly the chemical shift of the coalesced signal is given by

$$\delta = p_1\delta_1 + p_2\delta_2$$

where p_1 and p_2 are the mole fractions, and δ_1 and δ_2 are the chemical shifts of each form[63]. Thus the chemical shift from the exchanging species is always in between δ_1 and δ_2. Using the figures $\delta_1 = -98$ ppm for PF_6^- and $\delta_2 = -91$ ppm for PF_5, the value of $\delta = -96$ ppm found here will only occur if the solution contains about 75% PF_6^- (i.e. $p_1 = 0.75$); furthermore the chemical shift of -101 ppm found by Jones[41] for PF_5 in sulpholane is outside the possible range based on the figures above.

Secondly, it is unlikely that the preparative procedure (see appendix 1.10) would lead to the formation of PF_6^-.

Therefore the PF_5 spectrum observed here is most unlikely to be due to exchange with PF_6^- impurity.

The broadening is best explained by intermolecular fluorine exchange via an autoionisation process:

i.e. $2PF_5 \rightleftharpoons PF_4^+ + PF_6^-$

or, in the poorly solvating solvent sulpholane, perhaps an ion paired species, $PF_4^+..PF_6^-$.

Raising the sample temperature causes the doublet to coalesce into one signal which narrows as the temperature is further increased (experiment 1c, Fig. 4.8); this can be explained as being due to an increase in the rate of fluorine exchange at the higher temperatures so that the exchange lifetime of any individual fluorine nucleus decreases. Jones[41] observed a broad singlet for PF_5 in sulpholane; however, his solutions contained up to 50% of the amount of PF_5 required to form a 1:1 complex with sulpholane, whereas the solutions used in this study contained only about 4 % of that amount. The exchange lifetime of a fluorine nucleus is, on the autoionisation theory, expected to decrease as the concentration is raised and collisions between PF_5 molecules become more frequent; thus the doublet is expected to coalesce.

Sulpholane solutions of PF_5/H_2O and PF_5/3-hexyne give identical doublets to that from HPF_6 (with another doublet, see below, in the PF_5/H_2O spectrum). This indicates i) that the intermolecular fluorine exchange occurring in the PF_5 solutions is suppressed, and ii) that the species formed in the other three solutions are identical, i.e. PF_6^-. However there is evidence against the latter conclusion.

The logical reaction to produce PF_6^- in the PF_5/H_2O system is:

$$6PF_5 \ + \ 4H_2O \longrightarrow 5(H^+..PF_6^-) \ + \ H_3PO_4$$

By this reaction the solution produced from equimolar amounts of 0.23 M PF_5 and water would contain non-hydrated HPF_6 with a minimum concentration of 0.15 $mole.litre^{-1}$; this solution should catalyse the isomerisation considerably faster than 0.1 M HPF_6 but such was found not to occur (see section 4.5). Also, the addition of HF to the equimolar PF_5/H_2O solution gave a solution which did not catalyse the isomerisation (also see section 4.5); this should not be the case if HF were added to a mixture of HPF_6 and H_3PO_4.

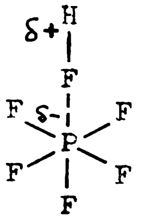
The stoichiometry of a reaction between PF_5 and 3-hexyne leading to the formation of PF_6^- would be as follows:

$$6PF_5 \ + \ n(3\text{-hexyne}) \longrightarrow 5PF_6^- \ + \ P(3\text{-hexyne})_n^{5+}$$

The integration of the spectrum (Fig. 4.7) shows that, as far as can be determined because of the low signal to noise ratio, all the PF_5 is converted to "PF_6^-" in an equimolar mixture, so that n would have to be approximately six. A compound with the empirical formula $P(3\text{-hexyne})_6^{5+}$ (or with n being any other value) is extremely difficult to visualise. Also, the result of this integration and of the search for signals due to $PF_4-\overset{|}{\underset{|}{C}}-$ indicates that $H^+..PF_6^-$ and species such as $-C(PF_4)=C=CH-$ (see mechanistic schemes for the PF_5 catalysed reaction, section 4.5) are not formed.

The simplest explanation of these three spectra is that the vacant p orbital in PF_5 interacts with an electron donor (such as HF, H_2O or the π electron system of the hexyne) to form a complex, so that the nmr signal is due to fluorine attached to an octahedrally coordinated phosphorus atom:

i.e.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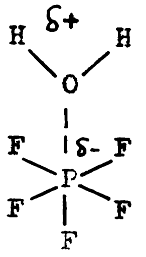
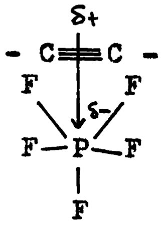
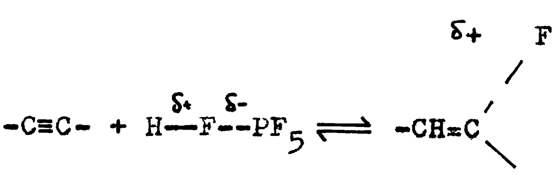

, and



The complexes with HF and H_2O could act as protonic acids since they could each release a proton in the presence of a suitable base. The complexes themselves can be regarded as being very similar to ion paired species such as $H^+..PF_6^-$ and $H^+..PF_5OH^-$, and would act in an identical manner;

e.g. compare $-C{\equiv}C- + H^+..PF_6^- \rightleftharpoons -CH{=}\overset{+}{C}\ ..PF_6^-$

with



$$-C{\equiv}C- + \overset{\delta+}{H}\text{—}\overset{\delta-}{F}\text{--}PF_5 \rightleftharpoons -CH{=}\overset{\delta+}{C}{<}^{\overset{\delta-}{F}\text{--}PF_5}$$

(see below)

The comparatively high value of J_{P-F} in the HPF_6 solution is expected if such complexes are formed; the P-F bonding would retain some of the character of the P-F bonding in PF_5 which has a higher J_{P-F} value than PF_6^-.

The species giving rise to the minor doublet in the PF_5/H_2O spectrum must now be considered. One possibility is that POF_3 is formed via the reaction described by Heslop and Robinson[56]. However, it has been shown that POF_3, although it gives rise to a doublet with approximately the same coupling constant (1058 Hz), resonates about 11 ppm upfield from the minor doublet[60]. A more likely identification is that the doublet is due to some other hydrolysis product, e.g. a dihydrate complex.

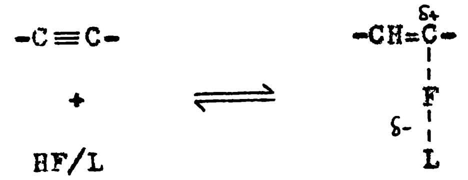
If complexes such as those proposed above are formed in the PF_5/HF system, then presumably similar complexes are formed in the BF_3/HF system. The literature evidence combined with this observation, which is not incompatible with the nmr evidence presented in section 3.7, leads then to the following description of the BF_3/HF system (all species solvated):

$$BF_3\text{-sulpholane} + HF \rightleftharpoons \overset{\delta+}{H}\text{--}F\text{--}\overset{\delta-}{BF_3} + \text{sulpholane}$$

As with the $HF\text{-}PF_5$ complex, the $HF\text{-}BF_3$ complex can be considered as very similar to the corresponding ion paired species $H^+..BF_4^-$, and will act as a protonic acid.

Polarisable charged transition states are more solvated in dipolar aprotic solvents than in protic solvents[33,64]. Thus the isomerisation reaction intermediates may well be of a similar nature to the complexes above:

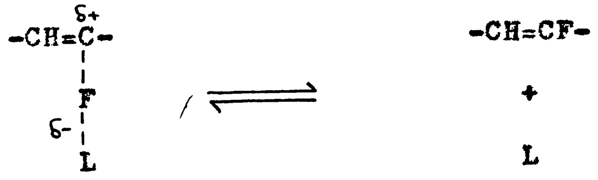
i.e.



$$\begin{array}{c}\text{-C}\equiv\text{C-}\\ +\\ \text{HF/L}\end{array} \rightleftharpoons \begin{array}{c}\text{-CH=}\overset{\delta+}{\text{C}}\text{-}\\ \vdots\\ \text{F}\\ \delta- \vdots\\ \text{L}\end{array}$$

(L = Lewis acid)

Such a complex could exist in equilibrium with a fluoroalkene thus:



$$\begin{array}{c}\text{-CH=}\overset{\delta+}{\text{C}}\text{-}\\ \vdots\\ \text{F}\\ \delta- \vdots\\ \text{L}\end{array} \rightleftharpoons \begin{array}{c}\text{-CH=CF-}\\ +\\ \text{L}\end{array}$$

The equilibrium would lie further to the right with $L=BF_3$ than with $L=PF_5$ because of the formation of the stable BF_3-sulpholane complex; this would explain the greater extent of formation of the difluorohexanes in the HF/BF_3 system since they could be formed by a similar reaction from the fluoro-alkenes.

The results of the conductivity measurements on the acid solutions reflect Whiting's[36] finding that HPF_6 is a stronger acid than HBF_4; as expected with a stronger acid the conductivity is higher. (For a table comparing the conductivities and H_o values of sulpholane solutions of HPF_6, HBF_4, $HClO_4$, H_2SO_4 and HSO_3F, see appendix 4).

The conductivity of PF_5/sulpholane is very much higher than that of BF_3/sulpholane and correlates with the proposed ionic nature (see above) of the PF_5/sulpholane solutions. There is however an alternative explanation of this phenomenon; the curve of conductivity against volume of water added to PF_5/sulpholane (experiment 2bi, Fig. 4.9a) has a very steep initial rise; thus the high conductivity may be at least partly due to the presence of traces of water in the solution.

The increase in conductivity as water is added to the PF_5 solution is expected if a protonic acid such as the PF_5-H_2O complex proposed above is formed; the reaction proposed by Heslop and Robinson[56] (formation of POF_3 and HF) would lead to a drop in the conductivity.

The maximum conductivity of the sulpholane solution of PF_5 and water occurred at $[H_2O] = [PF_5]$. Further, as water was added to the HPF_6 solution the conductivity rose initially (experiment 2bii, Fig. 4.9b); this effect was not due to a small excess of PF_5 since the same behaviour was found when water was added to solutions containing an excess of HF. In both these cases the explanations would have to be able to distinguish between the conductivities of different ionic species rather than between ionic and covalent species as in the PF_5 case; the prediction of such effects would require a much more detailed theoretical approach than is possible here.

Just as nmr provided evidence for complex formation between PF_5 and the isomers, so conductivity (experiment 2c) provides evidence for complex formation between HPF_6 and the isomers (as it did, see section 3.7, for complex formation between the isomers and HBF_4); upon the addition of the four isomers tested a fast initial fall in conductivity is followed by a very slow decrease. This is intelligible if an acid-isomer complex similar to that proposed for HBF_4 (see section 3.7) is formed quickly. The formation of such a complex would bind the ionic acid species to some extent and hence would lower the conductivity of the solution (cf. the rise in conductivity found when an isomer is added to HBF_4, see section 3.7).

The two experiments associated with these measurements show firstly that the saturated straight chain hydrocarbon n-hexane does not affect the conductivity of the HPF_6

solution and secondly that the conductivity measurements do not affect the reaction which is proceeding.

The petroleum spirits extractions were initially performed in an attempt to study the formation of hexanones in the HPF_6 catalysed isomerisations (as for the H_2SO_4 catalysed reaction, see section 5.5).

The results were subject to considerable experimental uncertainty due to such factors as the difficulty of performing the extractions at exactly the same time in each experiment, the occurrence of reaction in the approximately five seconds between sampling the petroleum spirits layer and quenching the reaction with water, the likelihood that in some cases the extractions were not performed as efficiently as possible because of the requirement for speed (see, e.g., the extraction from HF/sulpholane in experiment 3b), and the uncertainty associated with the measurement of percentage recovery (see section 2.2). Thus the deductions to be made from these results are at best qualitative.

Despite these drawbacks however the data definitely shows that whereas petroleum spirits alone extracts 3-hexyne completely from pure sulpholane (experiment 3a), it does not do so from any of the acid solutions tested (experiment 3b), the same effect being found for all three hexynes when extracted from HPF_6/sulpholane, (experiment 3c). The simplest explanation is that a complex is formed between the acid and the isomer and that this complex is either more soluble in sulpholane or less soluble in petroleum spirits (or both) than the free isomer. Thus these experiments support the evidence described above for complex formation in sulpholane solutions of the acids used in this study.

Experiment 3d was an attempt to gain quantitative data on the extraction process. The spread of results apparent from the table of data illustrates the above mentioned difficulties in obtaining significant results. However, the plot of fractional recovery against the amount of isomer present (Fig. 4.10) does show recognisable trends.

The values of fractional extraction are in fact slightly high since some product destruction occurs between sampling the petroleum spirits layer and adding water (see above). Inspection of the figures in the table reveals that the greatest proportion of product destruction occurs with the larger amounts of added isomer; thus these figures will be proportionately higher than the 'true' values than will be the figures for the smaller amounts of added isomer.

In addition, although dried petroleum spirits was used some traces of water may have been present and this would have the effect of (as the results above show) increasing the amount of isomer extracted.

Also plotted in Fig. 4.10 is the curve resulting from a mathematical analysis (see appendix 5) of the system

$$I_p \rightleftharpoons I_s \qquad K_1 = 0.025$$

$$I_s + \text{acid} \rightleftharpoons \text{complex} \qquad K_2 = 4000$$

where I_p = isomer in the petroleum spirits layer

I_s = isomer in the sulpholane layer

(These equilibrium constants correspond to 97% extraction of free isomer from the sulpholane layer, and to 94% formation of the complex when total [isomer] and [acid] are both 0.07 mole.litre^{-1}).

Although the theoretical curve shows a similar trend it does not give a reasonable fit to the experimental results unless the factors mentioned above that would lower the fractional extraction are bigger than expected. Other values of the equilibrium constants were tried but a better fit at one end of the curve was only obtained at the expense of a worse fit at the other end.

Thus it seems that the simple model proposed above is not correct. Various refinements to the model are possible, such as the presence of petroleum spirits causing decomposition of the complex, some extraction of the complex directly into the petroleum spirits layer and so on; however, these were not incorporated into any mathematical analysis.

The last result of experiment 3d shows that the effect persists after some reaction has taken place and is not merely associated with the initial reaction.

To summarise therefore, these experiments have provided further evidence that the isomers and acids are associated in some way in sulpholane solution. Unfortunately however the experimental results will not fit the simple easily analysed model tested here.

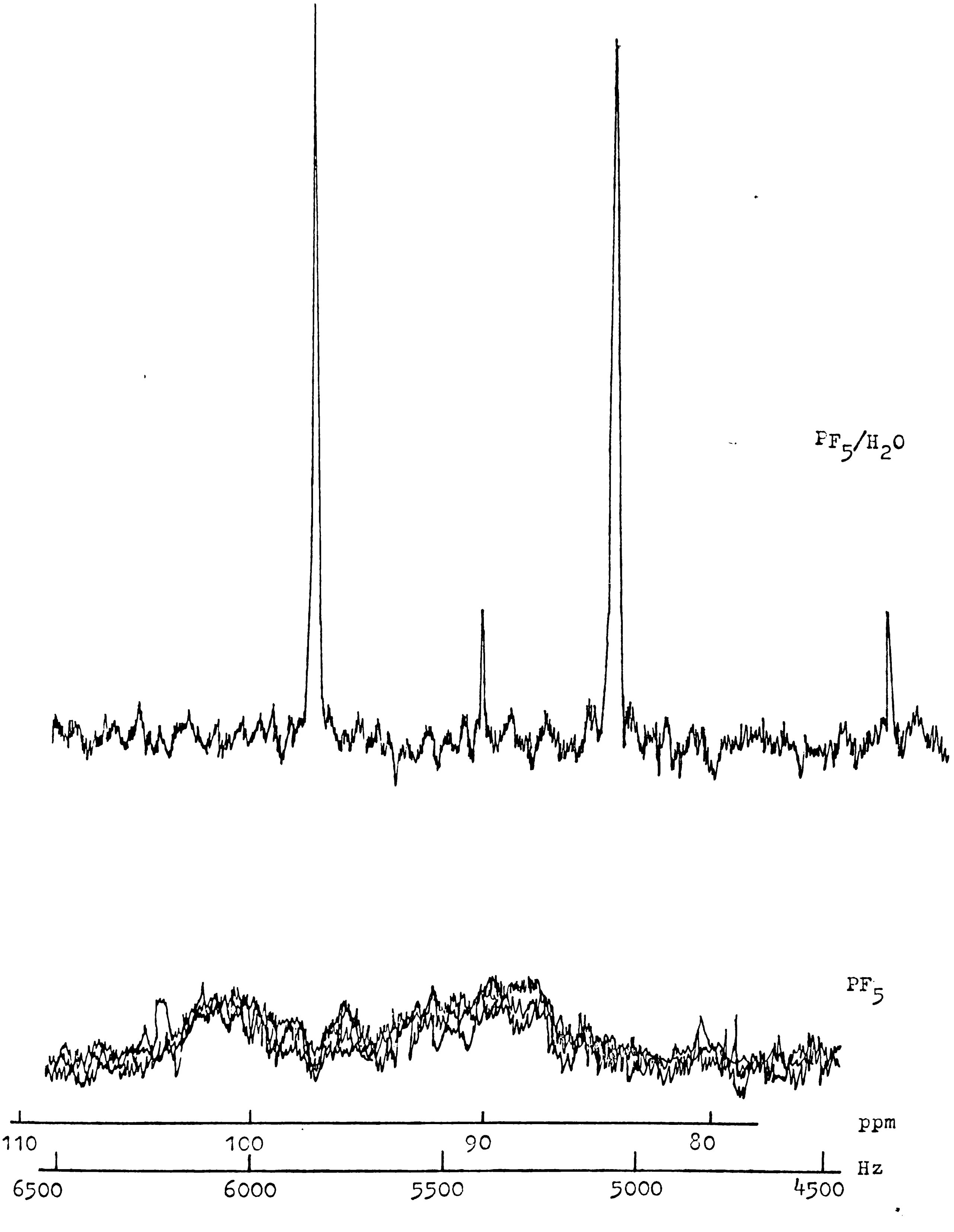


Fig. 4.6a ^{19}F nmr spectra of sulpholane solutions of PF_5 and PF_5/H_2O

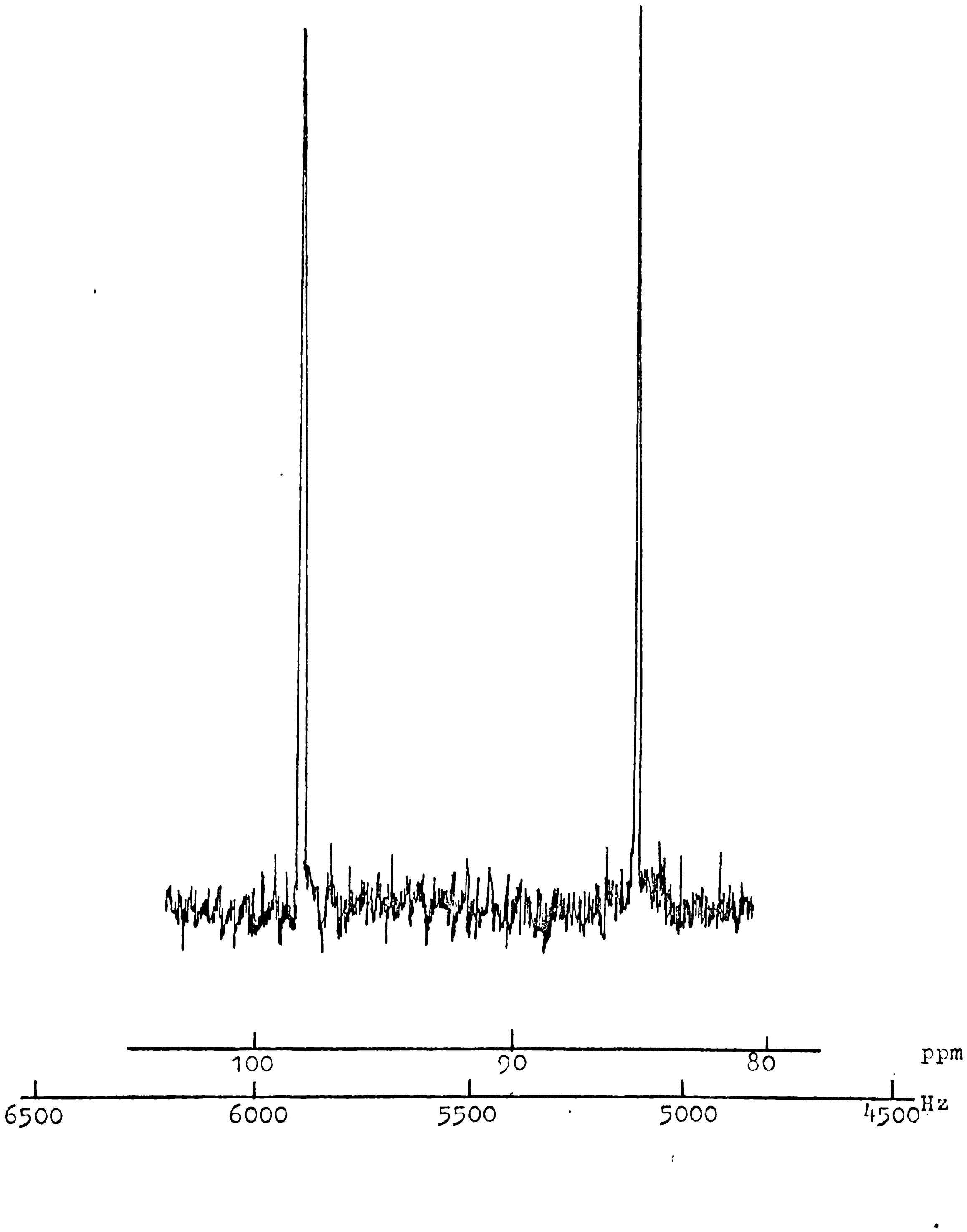


Fig 4.6b ^{19}F spectrum of HPF_6/sulpholane

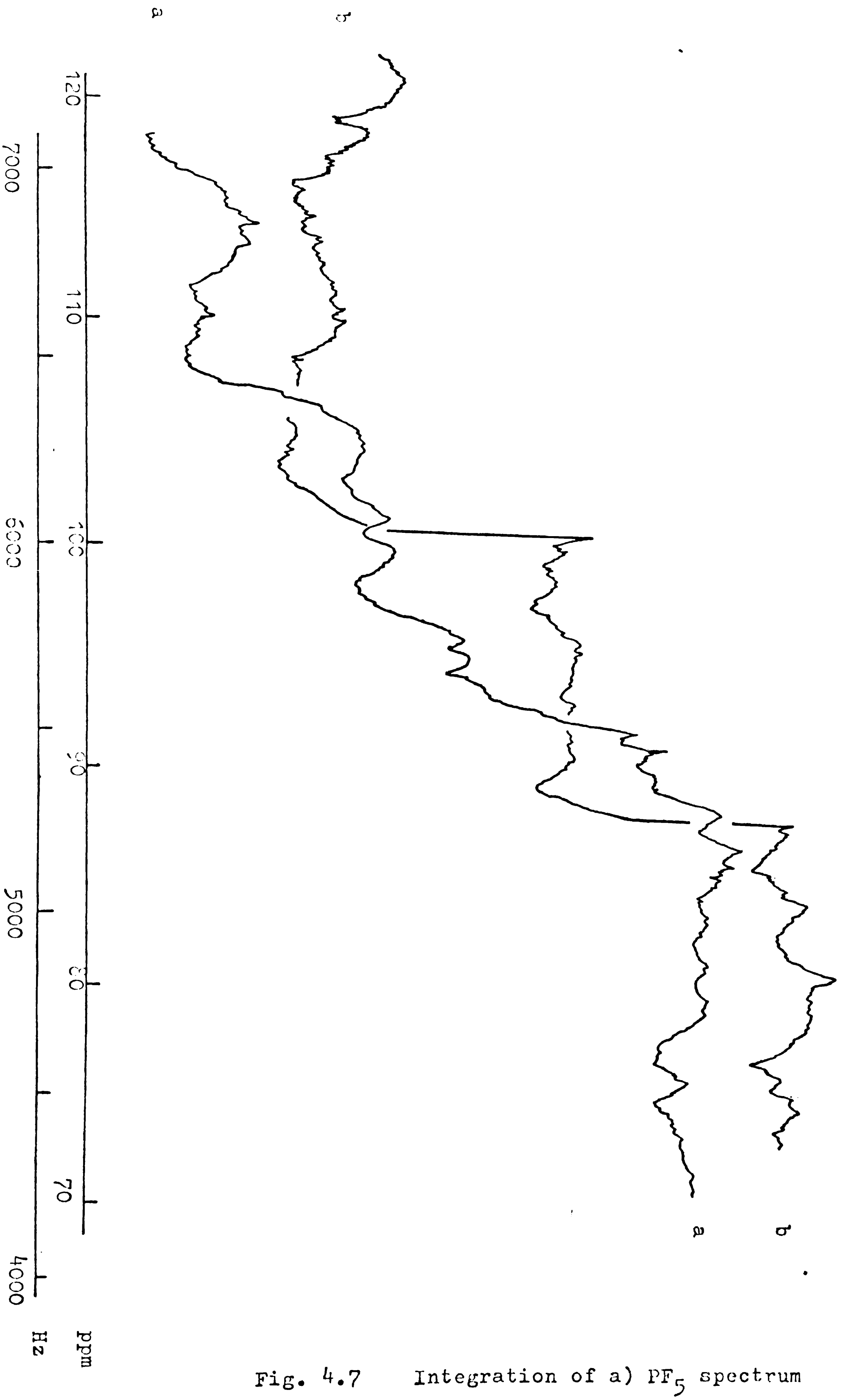


Fig. 4.7 Integration of a) PF_5 spectrum

b) PF_5/3-hexyne spectrum

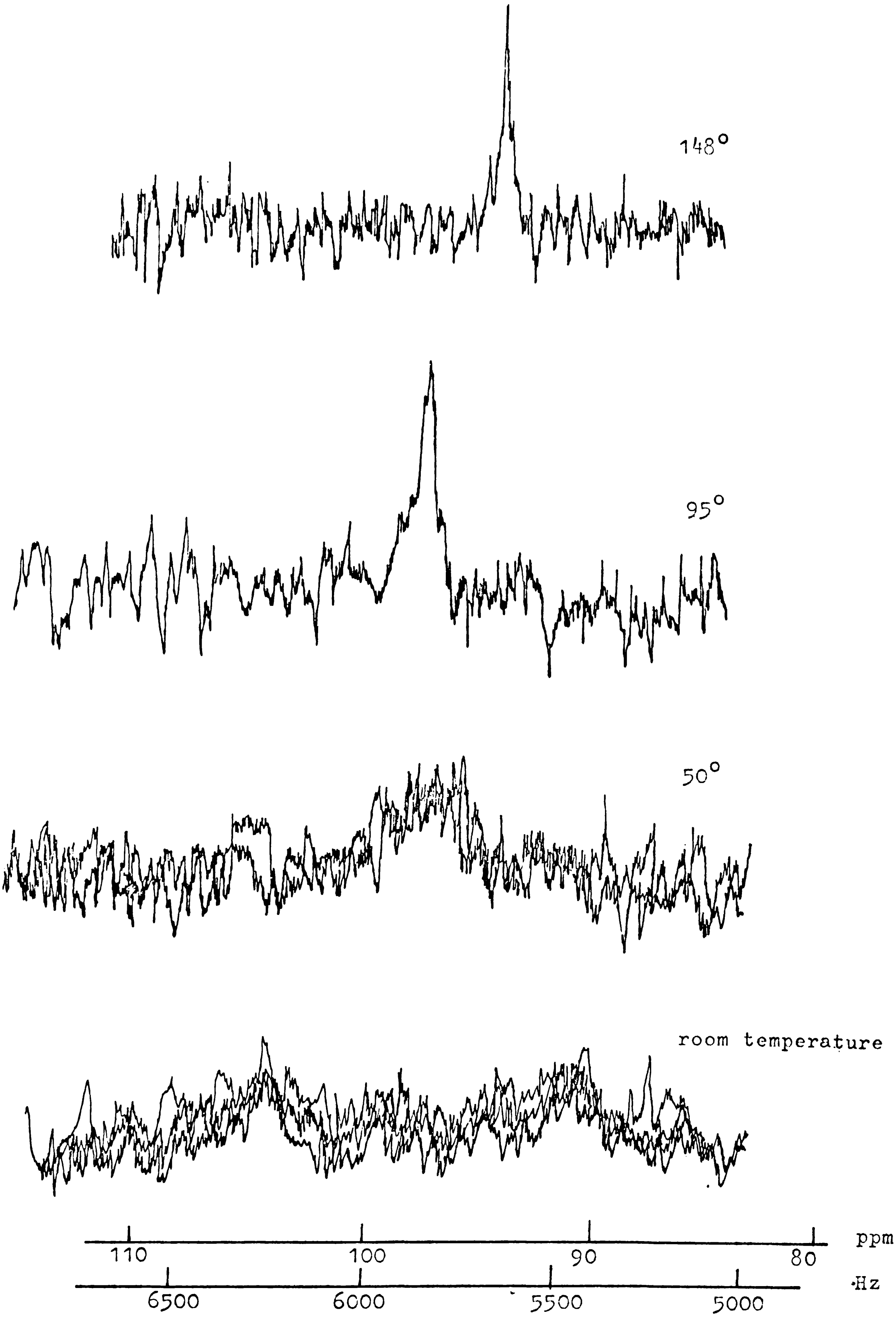


Fig. 4.8 Variation of the ^{19}F nmr spectrum of PF_5/sulpholane with temperature

Fig. 4.9a

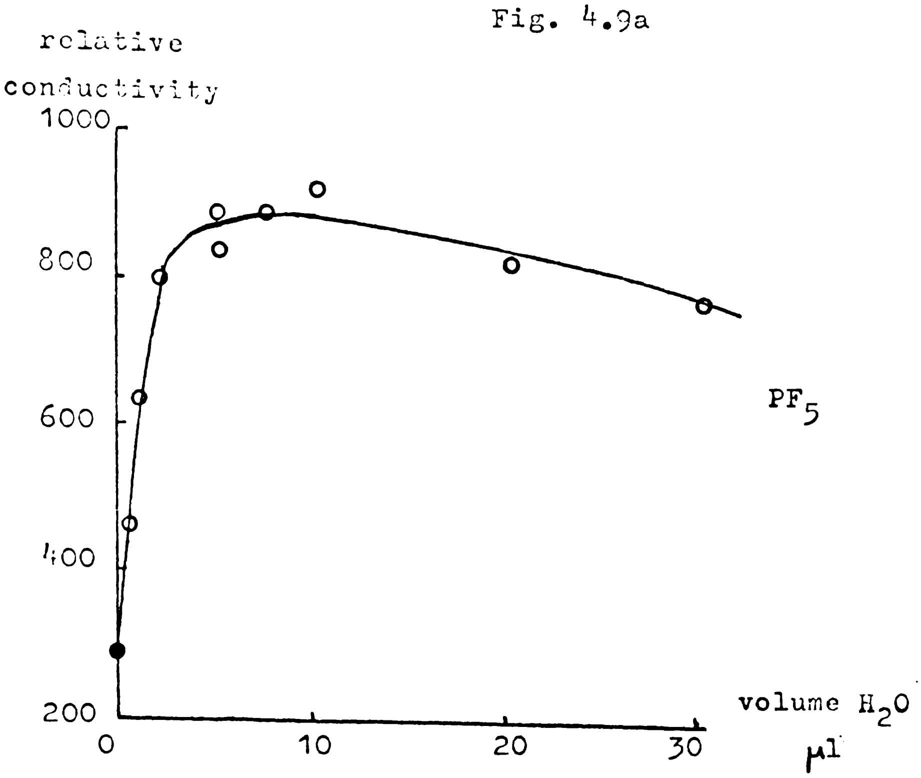
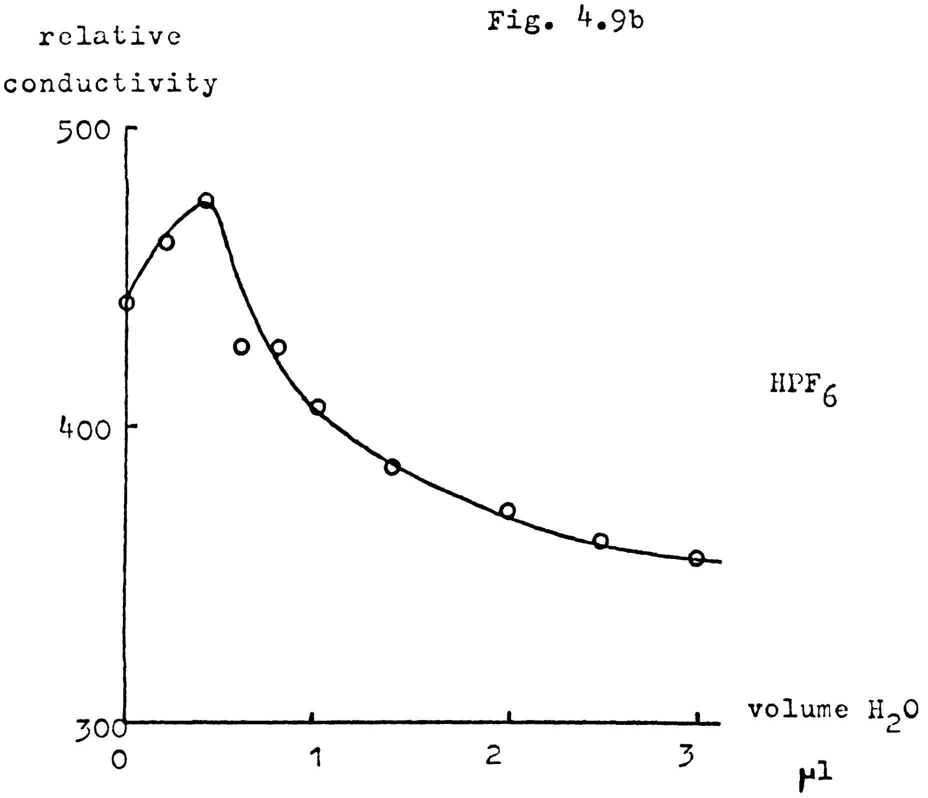


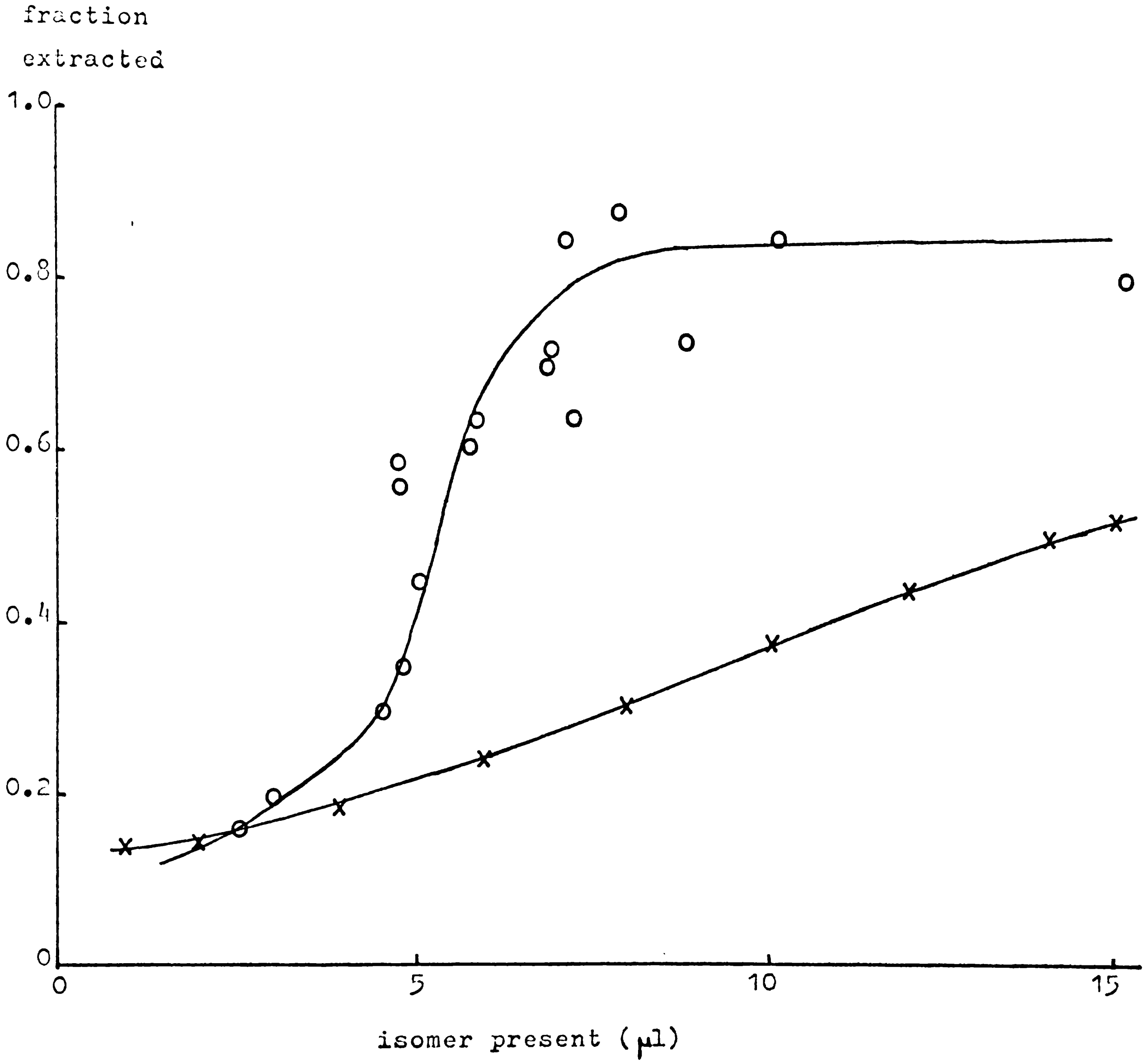
Fig. 4.9b



Variation of conductivity with added water

Fig. 4.10

Extraction of 3-hexyne from HPF_6/sulpholane with petroleum spirits alone



O observed

X theoretical

4.7 THE FORMATION OF HEXANONES

Results show that 2- and 3-hexanone are produced in low proportions in the isomerisations with HPF_6, PF_5 and PF_5/H_2O (large amounts of these two compounds were generated in the isomerisations with H_2SO_4 but none with HBF_4).

The pattern of production of the hexanones in the HPF_6 catalysed reactions is very similar to that found for H_2SO_4 (see section 1.1). Both 1-hexyne and 1,2-hexadiene give 2-hexanone exclusively, 2-hexyne gives approximately equal amounts of 2- and 3-hexanone, 2,3-hexadiene gives 3-hexanone with a small amount of 2-hexanone at high percentage reaction, and 3-hexyne gives exclusively 3-hexanone.

Acetylenes and allenes require the addition of an H_2O entity to form a ketone, presumably via the formation of an enol which subsequently tautomerises. Two sources of the H_2O entity are possible; traces of water in the catalyst solutions, and the water used to quench the reaction. It had been hoped to distinguish between these possibilities by extracting the reaction products before the reaction was quenched; if the hexanones had been produced from contaminant water they would have been detectable in the glc analysis. However, the lower efficiency of extraction under these conditions (see the last section) made the results very difficult to interpret since only small amounts of the ketones are formed. Hence this type of experiment was not used for this section of the work.

The experiments which were carried out involved the addition of water to HPF_6 solutions; if the ketones were formed from contaminating water a considerable increase in the amount formed would result.

Experimental

3-Hexyne (10 μl) was reacted with HPF_6 (0.12 M, 1 ml) containing added water, the molar ratio of acid to water being 4:1, at 25°C.

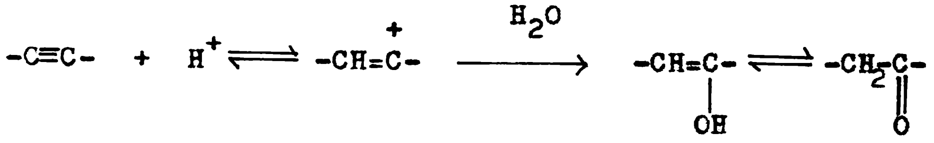
time min.	product composition %					%
	2-	2,3-	3-	X	3-one	recovery
1	0.3	5.8	93.4		0.4	90
5	1.0	7.7	90.8		0.5	69
15	4.2	12.0	82.9	0.2	0.7	71
30	7.7	10.3	80.2	1.0	0.7	54

Discussion

The expected increase, if contaminant water is the cause of the ketone formation, in the amount of 3-hexanone produced does not occur. In fact, comparison of the results with those for HPF_6 (see section 4.3) reveals that adding water merely slows the reaction, leaving the reaction pattern virtually unchanged.

This result can be explained if the addition of water to HPF_6 simply results in the formation of H_3O^+ which is not a sufficiently strong acid to form a cationic species with the isomers.

Thus it seems that the two ketones are formed when water is added to quench the reaction. A reaction mechanism analogous to that proposed for the H_2SO_4 catalysed reaction is as follows[10]:



$$-C\equiv C- \; + \; H^+ \rightleftharpoons -CH=\overset{+}{C}- \xrightarrow{H_2O} -CH=\underset{\overset{|}{OH}}{C}- \rightleftharpoons -CH_2-\underset{\overset{\|}{O}}{C}-$$

I

(The intermediate I may not have the positive charge fully developed on the C atom, see section 4.6). Because of the extent of ketone formation this mechanism implies that at least 1% association of isomer and acid takes place. This in its turn implies that I has a stability greater than the literature evidence suggests since no vinyl cations have been prepared in a long lived form[31,32]. Thus the mechanism is an unlikely one.

The ketone formation is in fact probably connected with the formation of complexes in the acid solution (see section 4.6). It may be that, in competition with destroying the complex by decomposition to the free isomer, reaction takes place between the water and the complex. It is worth noting that evidence exists for a strong complex in the PF_5 solutions (also see section 4.6) and in this medium the ketones are formed to a greater extent (up to 3%) than in the HPF_6 solution.

This hypothesis is tentative but with the present evidence cannot be improved; the small extent of formation of the two ketones and the drop in the efficiency of extraction when water is not added to the reaction mixture combine to make any study very difficult.

4.8 THE KINETICS OF THE ISOMERISATION

The comparative absence of addition products in the HPF_6 catalysed reactions should result in simplified kinetics compared with the HBF_4 catalysed reactions. However, the occurrence of considerable product destruction will prevent a detailed analysis of the reaction order along the lines attempted in section 3.5.

Treatment of data

The tabulations of the results of the acetylene-allene isomerisations (see section 4.3) give percentages of recovered products only. This data was treated as before (see section 3.5) to give relative concentrations.

All the reactions below were carried out with 0.1 M HPF_6 (i.e. experiments 1 to 5 of section 4.3).

1) 1-hexyne

time min.	[1-]
0	100
0.33	41
1	35
12.25	33
30	29
76.5	22
134	14

2) 1,2-hexadiene

time sec.	[1,2-]
0	95
5	27
10	19
30	6
60	3

3) 2-hexyne

time min.	[2-]
0	96
0.33	85
1	81
12.25	68
30	56
60	42
160	35

4) 2,3-hexadiene

time sec.	[2,3-]
0	100
6	54
10	43
30	26
60	17
120	13

5) 3-hexyne

time min.	[3-]
0	98
0.17	76
1	60
5	52
15	43

Discussion

These results reveal that all the reactions are of a higher order than one. Third order plots for 2,3-hexadiene and 2-hexyne are shown as examples (Fig. 4.11); the 2,3-hexadiene reaction fits the third order plot (cf the HBF_4 catalysed reaction) while the 2-hexyne reaction is of higher order again.

In general, the results are characterised by an initial reaction which is considerably faster than the subsequent reaction; this same general pattern was found for the PF_5 and PF_5/H_2O catalysed reactions. Two methods of producing this effect are product destruction and complex formation.

Inspection of the results in section 4.3 shows that product destruction is initially very fast. The change from a fast to a slow isomerisation is expected in such a situation since the isomer concentrations are decreased by product destruction. The catalyst concentration could also decrease since the product destruction reaction may involve its consumption in some manner and this would further slow the later stages of the reaction.

If complexes between the isomers and acids are formed the isomers are stabilised with respect to the reactive intermediates. As a consequence, if complex formation is not instantaneous the rate constants for the isomerisation will decrease over some (unknown) period of time. Therefore complex formation can lead to an initially fast reaction slowing down when complex formation reaches an advanced stage (the conductivity and petroleum spirits extraction results, see section 4.6, indicate that complex formation is essentially complete after 10 - 15 seconds, no information being available for shorter times).

Either or both of these effects might account for the high order kinetics and no firm conclusions about the isomerisation reaction itself may be drawn. This further highlights the fact that a catalyst causing no product destruction is essential to elucidate the kinetics of a complicated system such as the four consecutive reversible reactions under study here.

Fig. 4.11a

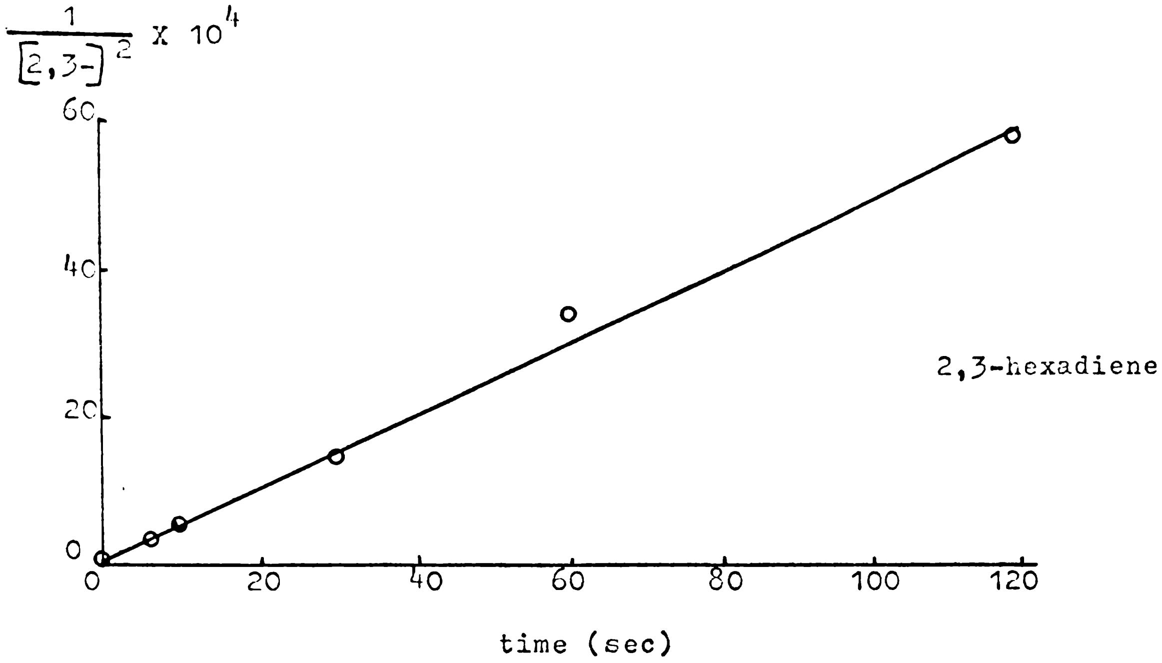
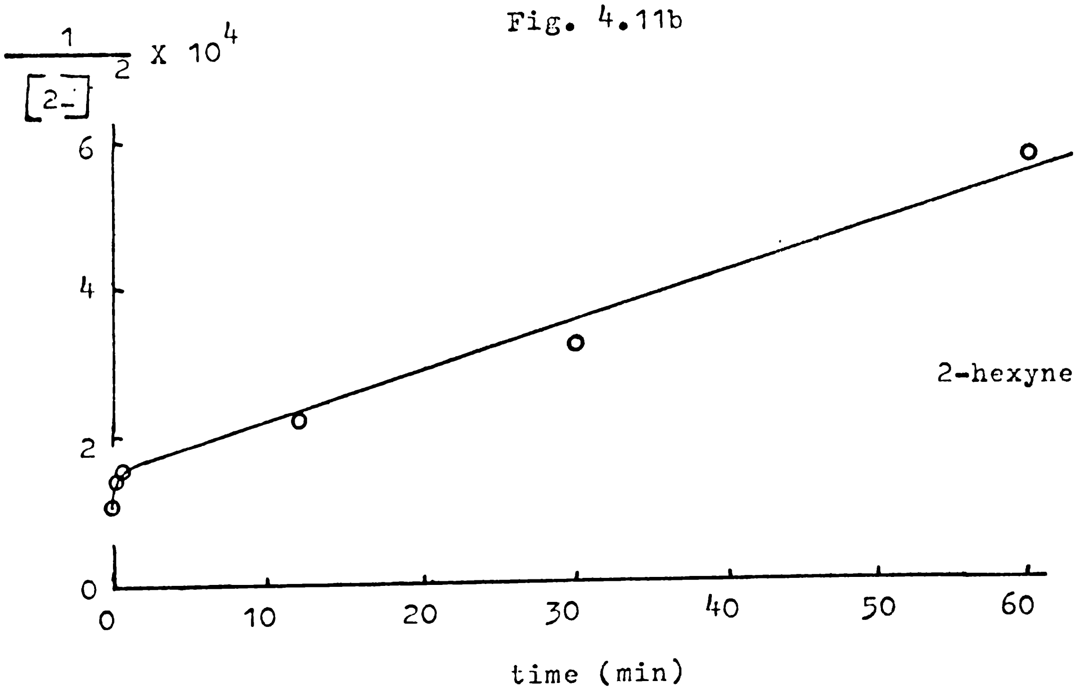


Fig. 4.11b



Third order plots for HPF_6/sulpholane catalysed isomerisations

4.9 THERMODYNAMIC CONSIDERATIONS

It was pointed out in section 3.8 that the correct method of comparing the kinetics of the present system with published thermodynamic data is to assess values of each rate constant in the complete isomerisation sequence, not simply to use overall rates of reaction. It was then found that there existed a good parallel between the kinetics of the HBF_4 catalysed isomerisations and the expected sequence of thermodynamic stabilities.

The kinetic data from the HPF_6 catalysed isomerisations was analysed to find whether or not a similar parallel exists. It must be emphasised that the methods used are very approximate and no firm quantitative results can be expected.

Treatment of data

The results of section 4.3 were treated in the manner outlined in section 3.5 to yield the following rate (relative to $k_5 = 1$) and equilibrium constants:

$k_1 = 40$ $k_2 = 50$; i.e. for 1-hexyne $\rightleftharpoons$ 1,2-hexadiene $K = 0.8$

$k_3 = 2500$ $k_4 = 0.033$; i.e. for 1,2-hexadiene $\rightleftharpoons$ 2-hexyne $K = 75000$

$k_5 = 1$ $k_6 = 750$; i.e. for 2-hexyne $\rightleftharpoons$ 2,3-hexadiene $K = 0.0013$

$k_7 = 500$ $k_8 = 10$; i.e. for 2,3-hexadiene $\rightleftharpoons$ 3-hexyne $K = 50$

Discussion

From the above results the following order of stability may be postulated:

1-hexyne $\sim$ 1,2-hexadiene $<$ 2,3-hexadiene $<$ 3-hexyne $<$ 2-hexyne.

It should be noted that in the 1,2-hexadiene reaction, the proportion of 1-hexyne is always less than that of 1,2-hexadiene, even at very high percentage reaction. This implies that 1-hexyne is less stable than 1,2-hexadiene yet the values derived for k_1 and k_2 imply that 1-hexyne is slightly more stable. This discrepancy may be due either to the approximate nature of the method or to the production of 2,2-difluorohexane (cf section 3.9). Whatever the explanation it does illustrate the point made above that quantitative data cannot be expected from this analysis. However the remaining pairs of rate constants are so different that the above order of stability may be postulated with some confidence.

The order is the same as was found for the HBF_4 catalysed reactions. As in that case this method gives a much closer parallel to the published thermodynamic data (see section 3.8) than does a comparison based on the overall reaction rates.

CHAPTER FIVE

OTHER ACID CATALYSTS

5.1 INTRODUCTION

The use of HPF_6 as a catalyst has only partly solved the problems associated with H_2SO_4 and HBF_4, and as well has raised some of its own. Further catalyst systems were therefore studied and this chapter describes some preliminary work with sulpholane solutions of $HClO_4$, HSO_3F, $HAsF_6$ and H_3PO_4.

Also described are some experiments aimed at further elucidating the mechanism of the formation of hexanones in the H_2SO_4 catalysed reactions.

5.2 PERCHLORIC ACID AS A CATALYST

It has been shown that sulpholane solutions of $HClO_4$ are of comparable acidity to solutions of HBF_4 and HPF_6[36]. Therefore this acid would be expected to catalyse the isomerisation.

Experimental

A solution of $HClO_4$ (1.17 M) in 1,2-dichloroethane was made up as described in appendix 1.14 (where some experiments aimed at making bromomethane solutions of the acid are also described). A 0.12 M $HClO_4$ solution was then prepared by mixing sulpholane and the 1,2-dichloroethane solution in a 9:1 ratio by volume.

3-Hexyne (10 μl) was reacted with both the 1,2-dichloroethane solution and with the sulpholane diluted solution at 25°C with the following results:

[acid] mole.litre^{-1}	time min.	product composition %			% recovery
		2-	2,3-	3-	
0.12	10	1.3	8.8	89.9	35
1.17	20		20	80	1

A sputtering sound was heard when the isomer was added to the 1,2-dichloroethane solution. With both solutions, darkening occurred as the reaction proceeded.

Note

In both reactions the product recovery was larger than the above figures would indicate since large amounts (ca. 20% in the dilute $HClO_4$ solution, ca. 40% in the concentrated solution) of some unknown compounds with retention times in the hexanone region were found. Analysis showed that these compounds were not present in the 1,2-dichloroethane $HClO_4$ solution.

Discussion

The two reactions show that isomerisation does indeed take place.

Because of the very low product recovery from the reaction in the 1,2-dichloroethane solution little can be surmised from its result. However the product pattern in the reaction with the dilute solution is typical of other acids tested and indicates that a similar mechanism is involved.

No attempt was made to identify the unknown compounds since their mere presence made this catalyst unsuitable for studying the acetylene-allene isomerisation. Therefore the study of $HClO_4$ was not extended.

5.3 FLUOROSULPHURIC ACID AND SULPHUR TRIOXIDE AS CATALYSTS

Literature data suggests that sulpholane solutions of HSO_3F are of comparable acidity to HPF_6, HBF_4 and $HClO_4$ solutions[36]. These three acids have been found to catalyse the isomerisation so HSO_3F was tested also.

Some Lewis acids which form protonic acids with HF and/or H_2O (i.e. BF_3, PF_5) have been found to catalyse the isomerisation. Accordingly, the Lewis acid SO_3, which forms the protonic acids HSO_3F and H_2SO_4 with HF and H_2O respectively, was tested.

Experimental

1) A sulpholane solution of HSO_3F was prepared as described in appendix 1.13.

3-Hexyne (10 µl) was reacted with HSO_3F (0.13 M, 1 ml) at 25°C with the following results:

time min.	product composition %			% recovery
	2-	2,3-	3-	
30	0.7	11.6	87.8	10
30		7.2	94.8	13
60	0.4	3.9	95.7	17
60		4.4	95.6	14
90		10	90	2

An aqueous extract from one of the 30 minute reactions was treated with NaOH (ca 1 M); the petroleum spirits extract from this solution was analysed for hexanones but none were found.

2) 2,4-Hexadiene (10 μl, containing ca. 20% 1,3-hexadiene) was reacted with HSO_3F (0.13 M, 1 ml) for 1 minute at 25°C.

Complete product destruction occurred.

3) A sulpholane solution of SO_3 was prepared as described in appendix 1.13.

3-Hexyne (10 μl) was reacted with SO_3 (0.49 M, 1 ml) for 30 minutes at 25°C.

No isomerisation occurred but the product recovery was only 25%.

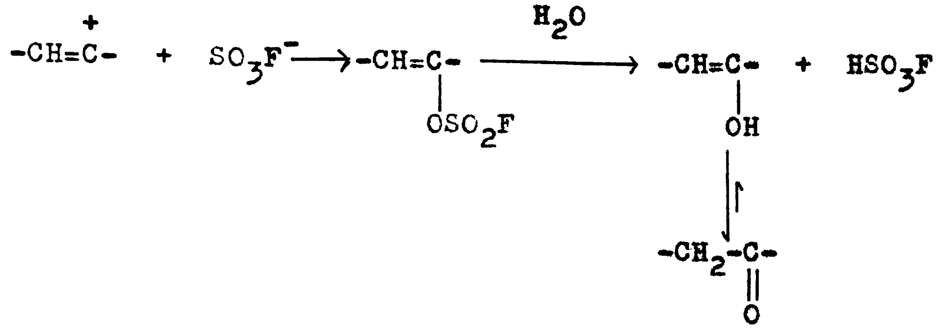
Discussion

Although the results of experiment 1 are somewhat inconsistent it can be seen that isomerisation does take place. No side products were noted on the chromatograms but extensive product destruction occurred. This feature of the reaction made HSO_3F unsuitable for use as a catalyst in this study.

The product pattern is not easily explained but may be due to the low recovery. If product destruction occurs at different rates for the different isomers an unusual pattern might well result.

It is puzzling that 3-hexanone is not formed since, by analogy with the results for H_2SO_4 as the catalyst, a vinyl ester which can subsequently react with water is likely to be formed in competition with deprotonation of the vinyl cations.

i.e.



$$-CH=\overset{+}{C}- + SO_3F^- \longrightarrow -CH=\underset{OSO_2F}{C}- \xrightarrow{H_2O} -CH=\underset{OH}{C}- + HSO_3F$$

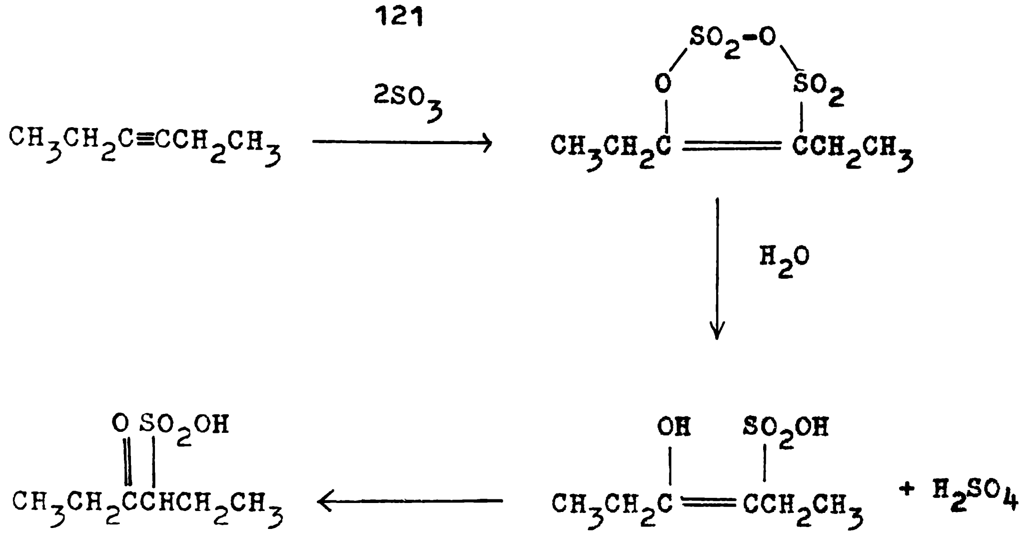
$$-CH=\underset{OH}{C}- \rightleftharpoons -CH_2-\underset{\overset{\|}{O}}{C}-$$

Either the ester is not formed at all or it is formed but does not react with water. The extract from one of the reactions was treated with NaOH in an attempt to catalyse the formation of the enol but still no ketone was found. Thus it is probable that the ester is not formed. The group OSO_2F^- should be less nucleophilic than OSO_2OH^- since the electronegative fluorine atom would withdraw negative charge from the reactive centre; it should be noted however that HSO_3F does form an ester with, for example, ethylene[65a].

The reaction with conjugated dienes gives the same result as with the other acids tested and the same conclusions may be drawn (see sections 3.4, 4.4 and 4.5).

The Lewis acid SO_3 does not catalyse the isomerisation but the low recovery indicates that it does catalyse polymerisation or whatever reaction is responsible for product destruction. One possibility is that a reaction similar to that between SO_3/dioxane and acetylene or phenylacetylene occurs[65b]:

i.e.



It is likely that the α-ketosulphonate would not be detected on the glc by reason of a long retention time on the polar column used.

5.4 ARSENIC PENTAFLUORIDE SYSTEMS AND ORTHOPHOSPHORIC ACID AS CATALYSTS

Gillespie[66] has shown that in HSO_3F solutions AsF_5 and mixtures of AsF_5 and SO_3 are more acidic than PF_5. Thus, sulpholane solutions of these species might be expected to catalyse the isomerisation more efficiently than PF_5 solutions. In addition AsF_5, being a stronger electron pair acceptor than PF_5, should more readily accept a fluoride ion from HF and could thus form a protonic acid, $HAsF_6$, which is stronger than HPF_6. Accordingly it was decided to test sulpholane solutions of these systems.

In addition, a sulpholane solution of H_3PO_4 was prepared and tested; this has implications for the PF_5/H_2O catalysed reactions, as shown below.

Experimental

1) Preparation of a sulpholane solution of AsF_5 proved difficult (see appendix 1.15) and only a very dilute solution was prepared.

Mixtures of AsF_5 (0.083 M) and HF (0.18 M) were made up in the following ratios by volume (AsF_5:HF):

0.6:0.4 0.7:0.3 0.8:0.2 0.9:0.1 1.0:0

3-Hexyne (10 μl) was reacted with each of these solutions (1 ml) for 1 hour at 25°C. The extent of reaction increased as the proportion of AsF_5 in the solutions increased but even with pure AsF_5 solution no more than 3% reaction occurred. About 1% 3-hexanone was produced and about 20% product destruction occurred with the pure AsF_5 solution.

3-Hexyne (10 μl) was reacted with a mixture of AsF_5 (0.083 M, 0.9 ml) and SO_3 (0.49 M, 0.1 ml) for 1 hour at 25°C with the following result:

product composition %				%
2-	2,3-	3-	3-one	recovery
1.7	7.7	87.4	3.2	20

2) A sulpholane solution of H_3PO_4 was prepared as described in appendix 1.16.

3-Hexyne (10 μl) was reacted with H_3PO_4 (1M, 1ml) for 2½ hours at 25°C. No isomerisation occurred, product recovery was 70%.

Discussion

Such little isomerisation occurs with the AsF_5 and the AsF_5/HF solutions that no useful conclusions may be drawn. However, the addition of SO_3 to AsF_5 results in a system of increased catalytic activity. Product destruction is extensive and this makes the catalyst unsuitable for further use. However, it is apparent that the initial isomerisation product is 2,3-hexadiene and this is in line with results with previous catalysts. The increased catalytic activity correlates with Gillespie's[66] finding that AsF_5 reacts with SO_3 to produce $AsF_4(SO_3F)$ which is a stronger acid than AsF_5 itself.

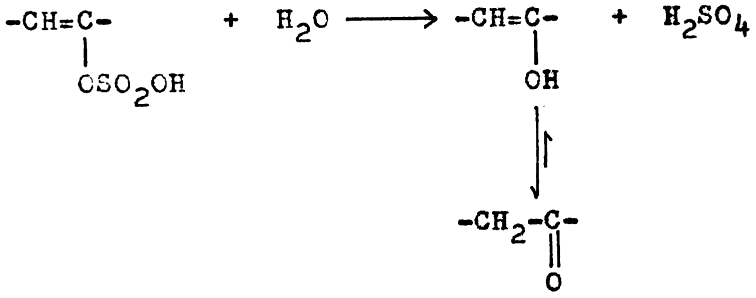
No isomerisation but some product destruction was caused by H_3PO_4. This acid is a possible product of the reaction between PF_5 and water (see section 4.6) and the present result shows that no contribution to reaction rates would result from its formation.

Neither acid tested here gave encouraging results and no further work was carried out.

5.5 HEXANONE FORMATION WITH SULPHURIC ACID/SULPHOLANE

Hei[10] proposed (see section 1.1) that hexanones were formed in the H_2SO_4 catalysed isomerisations when water, which was added to quench the reactions, reacted with vinyl sulphate esters:

i.e.



However no direct test of this hypothesis was made.

A simple test would be to extract the reaction products with petroleum spirits alone. If the proposed mechanism were correct no hexanones would be formed since the ester would stay dissolved in sulpholane; subsequent addition of water should liberate the hexanones.

Experimental

An H_2SO_4 solution in sulpholane was prepared as described in appendix 1.12.

1) 2-Hexyne (10 µl) was reacted with H_2SO_4 (1 M, 1 ml) for 66 hours at 25°C with the following result:

product composition %					% recovery
2-	2,3-	3-	2-one	3-one	
38.1	0.1	12.0	22.4	27.3	49

2) 3-Hexyne (50 μl) was reacted with H_2SO_4 (1M, 1ml) for 42½ hours at 25°C. The products were extracted first with petroleum spirits (dried over anhydrous $MgSO_4$) alone, and a sample was taken for analysis; water was then added and after shaking another sample was taken for analysis (cf. section 4.6, experiment 3d).

	product composition %				% recovery
	2-	2,3-	3-	3-one	
petroleum spirits extraction	4.3	1.2	42.4	52.1	16
petroleum spirits/H_2O extraction	3.9	1.0	37.2	57.9	26

3) 3-Hexyne (50 μl) was reacted with a mixture of H_2SO_4 (1 M, 0.8 ml) and SO_3 (0.49 M, 0.2 ml) for 23 hours at 25°C. The reaction products were extracted as in experiment 2 above.

	product composition %				% recovery
	2-	2,3	3-	3-one	
petroleum spirits extraction	4.7	3.7	69.1	22.5	18
petroleum spirits/H_2O extraction	2.1	2.3	80.7	14.9	44

Discussion

Experiment 1 was carried out to compare the present catalyst solution with that used by Hei[10].

The isomerisation is much faster than was found in the previous work (in the reaction of 2-hexyne with 0.96 M H_2SO_4 only about 12% reaction had occurred after the same time). There are two possible reasons for this. Firstly, it was found by Hei that the reaction rate is very sensitive to $[H_2SO_4]$; the present solution was made up to be approximately 1 mole.litre^{-1} only and so may have been of a slightly higher concentration. Secondly, the previous solutions may have been contaminated by water.

Whatever the reason for the rate difference the fact that the product pattern is very similar to that found by Hei indicates that the present system catalyses the isomerisation in a similar way; thus the conclusions drawn here will apply to the earlier work as well.

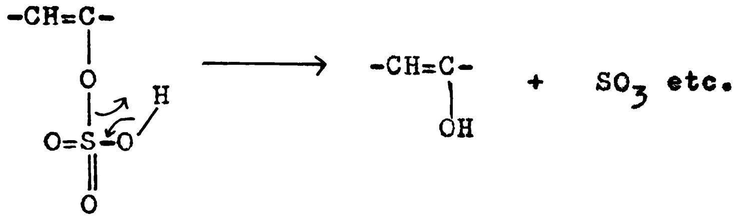
The result of the petroleum spirits extraction in experiment 2 shows that 3-hexanone is formed before the reaction is quenched with water.

To eliminate the possibility that 3-hexanone is formed from contaminating water the reaction was also carried out with a solution containing excess SO_3 sufficient to eliminate water present to the extent of 12% in the H_2SO_4 solution (experiment 3).

3-Hexanone was again formed before quenching water is added.

Thus at least some of the 3-hexanone formed in the reactions is generated concurrently with the isomerisation products. The most likely mechanism for the reaction is the elimination of a SO_3 molecule from the vinyl ester intermediate:

e.g.



Rigorous establishment of a mechanism such as this would require a very much more extensive study than was undertaken here.

CHAPTER SIX

FURTHER WORK

The results of the work described in this thesis provide convincing evidence that acid catalysed acetylene-allene isomerisations occur via vinyl cations; the pattern of production not only of the isomers but also of the other identifiable reaction products are consistent with this view. It is unlikely that further work along the lines of the present study would result in any useful information. All the catalysts used have promoted side reactions which render the calculation of accurate quantitative data virtually impossible. In particular, the side reactions prevent a) equilibration studies, which would enable the relative stabilities of the isomers to be calculated, and b) the calculation of accurate rate constants, which would yield information on the stabilities of the reaction intermediates. Only a completely different approach would yield more significant results.

There are however some aspects of the work not primarily concerned with acetylene-allene isomerisations which could well warrant further study.

Much could be done to elucidate the nature of the acid species in sulpholane and the nature of the interactions between those acids and unsaturated hydrocarbons.

The production of 3-hexanone in the reaction of 3-hexyne with H_2SO_4 / sulpholane in the absence of water is very puzzling. Further work in this direction, possibly with alkenes also, should prove interesting.

A fruitful line of research could be to utilise the catalysts used in the present study for other reactions. In organic reaction studies sulpholane has, to the author's knowledge, been used as a solvent for HBF_4, H_2SO_4 and BF_3 only of the catalysts used here[37]. This is despite the large rate enhancements possible over solutions in protic solvents.

There is no coherent body of theory of the catalysis of organic reactions by Lewis acids as there is for catalysis by protonic acids. If a clean reaction (i.e. no side reactions) could be found, sulpholane solutions of, e.g., PF_5 could be used in a study of such topics as the required proportion of co-catalysts and the identification of the reactive intermediates.

Finally, some implications for other work are worth noting. Not all those who have studied reactions in which vinyl cations are formed have made it clear that the possibility of deprotonation was adequately investigated. To take an example involving the isomers used here, Peterson and Duddy[67] studied the addition of trifluoroacetic acid to 1-, 2- and 3-hexyne and implicated vinyl cations in the reaction mechanism. The reaction kinetics were followed by monitoring the alkyne concentration by glc; however, no information on the column used, retention times etc., was given so it is not possible to tell if the three isomers could be distinguished. It may well be that deprotonation does occur in this and similar reactions and recognition of this fact may be vital to the proposed reaction mechanism.

APPENDIX 1

PREPARATION OF REAGENTS

1.1 1-Hexyne

Liquid ammonia suspensions of sodium amide and sodium acetylide were prepared by the standard methods[68].

1-Hexyne was then prepared by the following reaction as described by Reid[9]:

$$CH_3CH_2CH_2CH_2Br \; + \; NaC{\equiv}CH \longrightarrow CH_3CH_2CH_2CH_2C{\equiv}CH \; + \; NaBr$$

1-Bromobutane (1 mole) was added to sodium acetylide (1 mole) in liquid ammonia (1.5 litre). On completion of the addition the mixture was stirred for a further three hours. A small amount of water was then added and the ammonia left to evaporate overnight. A large excess of water was then added and the oily product recovered, dried with calcium chloride and distilled through a spinning band column.

1-Hexyne was recovered in a 10% yield, b.p. 70.5 - 71.0°C at atmospheric pressure (cf. 71.2°C at 760 Torr[69]), and purity $>$ 99.5%.

1.2 1,2-Hexadiene

1,2-Hexadiene was prepared by the following reaction, as outlined by Gaudemar[70]:

$$BrCH_2C{\equiv}CH \xrightarrow[\text{ether}]{CH_3CH_2CH_2MgBr} \begin{array}{c} CH_3CH_2CH_2CH_2C{\equiv}CH \\ + \\ CH_3CH_2CH_2CH{=}C{=}CH_2 \end{array}$$

The Grignard reagent 1-propyl magnesiumbromide (1 mole) was prepared in a nitrogen atmosphere by the standard method[71a]. The ether solution was then cooled to ca. -10°C and 3-bromo-1-propyne (1 mole) added slowly, still in the nitrogen atmosphere. On completion of the addition the mixture was allowed to stand for several hours before water was added carefully to hydrolyse the reaction products. The oily layer was separated, dried with anhydrous $MgSO_4$, and distilled through the spinning band column.

1,2-Hexadiene was recovered in a 50% yield, containing ca. 5% 1-hexyne.

1.3 2-Hexyne

A successful method of preparing dialkyl acetylenes has been described by Bried and Hennion[72]. The preparation proceeds through the following sequence:

$$CH_3CH_2CH_2Br + NaC{\equiv}CH \longrightarrow CH_3CH_2CH_2C{\equiv}CH + NaBr$$

$$CH_3CH_2CH_2C{\equiv}CH + NaNH_2 \longrightarrow CH_3CH_2CH_2C{\equiv}CNa + NH_3$$

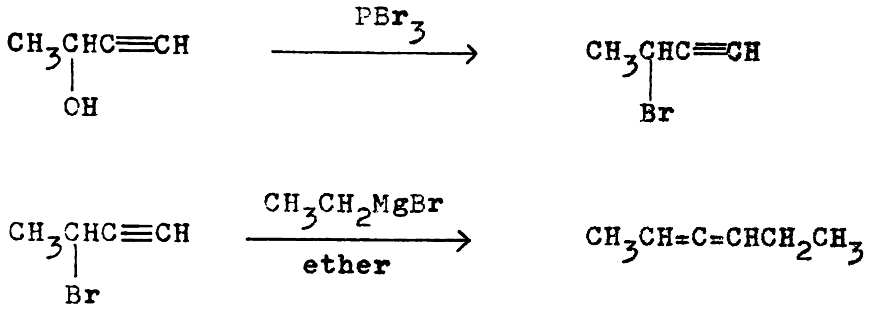
$$CH_3CH_2CH_2C{\equiv}CNa + CH_3Br \longrightarrow CH_3CH_2CH_2C{\equiv}CCH_3 + NaBr$$

Sodium acetylide (1 mole) in liquid ammonia (1.5 litre) was prepared in the usual manner[68], and 1-bromopropane (1 mole) was added dropwise with stirring. After three hours stirring sodium amide (1.3 mole) in liquid ammonia (300 ml) was carefully added. On completion of the addition a dry ice condenser was fitted to the reaction vessel. A large excess of bromomethane (2 mole) was added at a fast rate. The oily layer which separated immediately was washed successively with water, dilute HCl, sodium carbonate, and finally water. After drying over calcium chloride 2-hexyne was distilled through the spinning band column.

2-Hexyne was recovered in a 12% yield, containing 4.3 3-hexyne.

1.4 2,3-Hexadiene

2,3-Hexadiene was prepared by the following reaction sequence, as outlined by Reid[9]:



$$CH_3\underset{OH}{CH}C\equiv CH \xrightarrow{PBr_3} CH_3\underset{Br}{CH}C\equiv CH$$

$$CH_3\underset{Br}{CH}C\equiv CH \xrightarrow[\text{ether}]{CH_3CH_2MgBr} CH_3CH{=}C{=}CHCH_2CH_3$$

Phosphorus tribromide (0.5 mole) containing dry pyridine (ca. 1 ml) was slowly added to 1-butyn-3-ol (1.5 mole) in a dry nitrogen atmosphere at -10°C. On completion of the addition the reaction mixture was allowed to stand for several hours. A large excess of water was then added, the oily layer separated, and distilled through the spinning band column to give 99% pure 3-bromo-1-butyne in a 16% yield.

Ethyl magnesium bromide (0.25 mole) was prepared by the usual method[71a]. Treatment of this with 3-bromo-1-butyne (0.25 mole) at -10°C was followed after several hours by the addition of an excess of water. The hydrocarbon layer was separated and distilled through the spinning band column.

2,3-Hexadiene was recovered in a 50% yield, at a greater than 99.5% purity.

1.5 3-hexyne

3-Hexyne was prepared by the same method as was used for 2-hexyne; i.e. by the following reaction sequence:

$$CH_3CH_2Br + NaC{\equiv}CH \longrightarrow CH_3CH_2C{\equiv}CH + NaBr$$

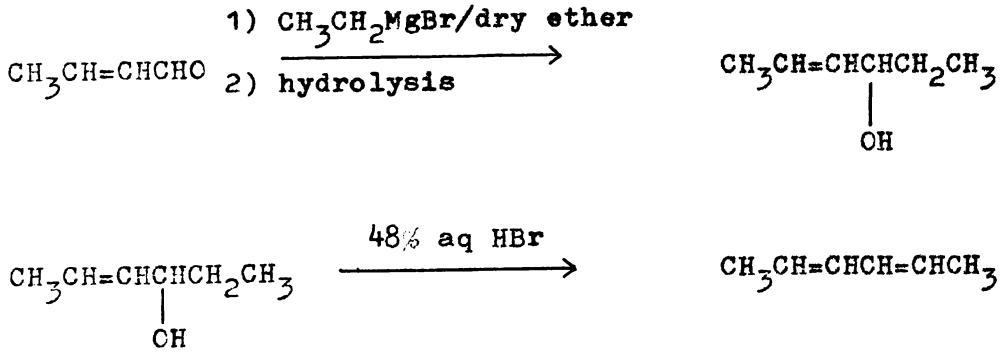
$$CH_3CH_2C{\equiv}CH + NaNH_2 \longrightarrow CH_3CH_2C{\equiv}CNa + NH_3$$

$$CH_3CH_2C{\equiv}CNa + CH_3CH_2Br \longrightarrow CH_3CH_2C{\equiv}CCH_2CH_3 + NaBr$$

3-Hexyne was recovered in an 11% yield, containing 1.1% 2-hexyne and 0.7% 2,3-hexadiene.

1.6 2,4-Hexadiene

Synthesis of 2,4-hexadiene was accomplished by the following reaction sequence[73]:



$$CH_3CH{=}CHCHO \xrightarrow[\text{2) hydrolysis}]{\text{1) }CH_3CH_2MgBr/\text{dry ether}} CH_3CH{=}CH\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$$

$$CH_3CH{=}CH\underset{\displaystyle CH}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{48\%\text{ aq HBr}} CH_3CH{=}CHCH{=}CHCH_3$$

Crotonaldehyde (1 mole) was added dropwise to a solution of ethylmagnesium bromide (prepared by the standard method[71a], 1 mole) in dry ether. The reaction mixture was vigorously stirred and the temperature maintained at 15-20°C by controlling the addition and cooling the reaction in an ice bath. The reaction mixture was then hydrolysed with cold NH_4Cl solution. The ether layer was separated and worked up in the usual manner to obtain hex-2-en-4-ol in 45% yield.

Hex-2-en-4-ol (0.25 mole) was then dehydrated by treatment with 48% aqueous HBr. The hydrocarbon layer was then separated, washed with sodium carbonate solution, and dried with calcium chloride.

2,4-Hexadiene containing 1,3-hexadiene was obtained in a 40% yield.

The product gave four peaks on analysis by glc as shown below (the proportions are calculated on the basis of all response factors being one):

peak	retention time min.	proportion %
a	34.2	14
b	46.3	42
c	51.1	41
d	55.2	3

Gan[11] identified b, c and d as the three geometrical isomers of 2,4-hexadiene and a as one of the two 1,3-hexadiene isomers. The peaks b and c were tentatively identified as *trans, trans*- and *cis,trans*-2,4-hexadiene (not necessarily respectively), thus identifying d as *cis,cis*-2,4-hexadiene by elimination. Gan also synthesised 1,3-hexadiene and found a mixture containing 80% of isomer a and 10% of another isomer (plus 10% benzene); he made no attempt to further identify the two isomers. However, Alder and Voght^{74a} synthesised 2,4-hexadiene by a similar method to the one used here ($KHSO_4$ was used as the dehydrating agent instead of HBr^{74b}) and found about 20% of *trans*-1,3-hexadiene. Hence isomer a is probably *trans*-1,3-hexadiene.

1.7 Purification of petroleum spirits

Commercial petroleum spirits (boiling range at least 90% between 30° and 40°C) was distilled through the spinning band column. The fraction boiling at less than 37° was collected. A chromatograph of this fraction revealed no components with retention times similar to those of the hexynes and hexadienes.

1.8 Purification of Sulpholane (tetrahydrothiophene-1,1-dioxide)

Sulpholane (100 ml) was added to crushed ice (100 g) and $KMnO_4$ (5 g) mixed with concentrated sulphuric acid (5 ml). The resulting solution was stirred for three hours and enough sodium bisulphite added to destroy the manganese dioxide formed. The solution was filtered and the sulpholane extracted with dichloromethane (3 x 50 ml). After drying with anhydrous magnesium sulphate, the dichloromethane was removed with a rotary evaporator. The remaining product was treated with P_2O_5 (1 g) to remove the last traces of water. The purified sulpholane was subsequently distilled under vacuum. B.p. 108-110° at ca. 1.5 mm.

1.9 Hydrofluoric acid

Anhydrous HF was prepared by the following reaction, as outlined by Beale[13].

$$KHF_2 \xrightarrow{\text{heat}} KF + HF$$

Potassium hydrogen fluoride (ca. 30 g) was placed in a copper U-tube of one inch diameter which was plugged at one end, and led to a vertical spiral condenser of quarter inch copper tubing at the other. This condenser was contained in a jacket of iced water. The bottom of the U-tube was heated to red heat and the hydrogen fluoride produced was trapped in a 30 ml polythene bottle immersed in iced water.

If required in the synthesis of the difluorohexanes (see appendix 1.17) the HF was used in this form.

If required for making a sulpholane solution, $SOCl_2$ (0.2 ml) was added to this fraction. The $SOCl_2$ reacts to form SOF_2 which hydrolyses instantaneously in HF containing a trace of water[75]:

$$SOCl_2 + 2HF \longrightarrow 2HCl + SOF_2$$

$$SOF_2 + H_2O \longrightarrow SO_2 + 2HF$$

Thus the HF is dried; dry nitrogen was then flushed through to remove the HCl, SO_2 and the excess SOF_2 (all more volatile than HF). The HF was then redistilled through a vertical spiral condenser of polythene ($\frac{3}{16}$" i.d.), cooled in ice/water and collected in a polythene flask containing sulpholane.

Weight of flask + sulpholane + HF	:	118.47 g
Weight of flask + sulpholane	:	116.49 g
Weight of flask	:	81.44 g

$\therefore$ Weight of Sulpholane : 35.05 g

Weight of HF : 1.98 g

Then, assuming no volume change and taking the density of sulpholane as 1.26 $g.ml^{-1}$ as shown on the reagent bottle,

$$[HF] = \frac{1.98}{20} \times \frac{1.26}{35.05} \times 10^3$$

$$= 3.56 \text{ mole.litre}^{-1}$$

This solution was diluted approximately seventeen times and the resulting solution was titrated with a 0.050 M NaOH solution standardised with potassium hydrogen phthalate.

A few drops of phenolphthalein and ca. 5 ml of water were added to HF/sulpholane (5 ml) and successive titration figures were 18.02, 18.04, 18.26, 18.18, 18.02 and 18.06 ml. Taking the mean of these figures gave

$$[HF] = 0.181 \text{ mole.litre}^{-1}.$$

This figure is somewhat lower than expected, possibly due to such factors as loss of the volatile acid and the difficulty of completely transferring from one vessel to another the viscous liquid sulpholane.

An attempt was made to isomerise each of the three hexynes with the strong HF solution but there was no reaction.

1.10 Phosphorus pentafluoride and hexafluorophosphoric acid

Phosphorus pentafluoride was prepared by the decomposition of benzenediazonium hexafluorophosphate, as described by Rutherford et. al[76]:

$$PhN_2PF_6 \xrightarrow{heat} PhF + N_2 + PF_5$$

Aniline (10 ml) was diazotised by the standard method[71b]. A voluminous precipitate of benzenediazonium hexafluorophosphate was then formed by quickly adding a 20% excess of aqueous HPF_6. After cooling to ca. 5° the precipitate was filtered, washed with cold water, and finally washed with a large volume of 80:20 ether:methanol. The salt was then powdered and dried in vacuo overnight.

Ondina oil (ca. 50 ml) was placed in a three necked 250 ml flask. Attached to a flask via a bent delivery tube was a 50 ml flask containing the diazonium salt; by rotating the delivery tube the salt could be poured into the oil. The oil was heated over an oil bath to ca. 100° and the salt added to it in small portions. The gases evolved were passed through a double surface condenser and a cold trap immersed in an ice/salt bath before being led into a flask of sulpholane. Any gas which passed through the sulpholane was then vented to the atmosphere through a drying tower of $CaCl_2$. A stream of dry nitrogen was maintained through the apparatus during the entire procedure.

In a typical experiment the following results were obtained:

Weight of flask + sulpholane + PF_5	:	244.38 g
Weight of flask + sulpholane	:	241.30 g
Weight of flask	:	108.15 g

$$\therefore \boxed{PF_5} = \frac{3.08}{126} \times \frac{1.26 \times 1000}{133.15}$$

$$= 0.23 \text{ mole.litre}^{-1}$$

This result represents a 10% yield only of PF_5; considerable amounts of cloudy fumes issued from the drying tower during the preparation indicating that the PF_5 did not dissolve readily. Jones[41] prepared a solution of PF_5 in sulpholane approximately twelve times more concentrated than this (see section 4.6); to do this he used a cylinder as his source of PF_5 and was thus able to obtain and maintain a high pressure during the solution process.

Sulpholane solutions of HPF_6 were then prepared by mixing solutions of PF_5 and HF. For example, HPF_6 (0.1 M, 30 ml) was prepared by mixing PF_5 (0.23 M, 16.8 ml) and HF (0.18 M, 13.2 ml).

1.11 Boron trifluoride and tetrafluoroboric acid

Boron trifluoride was prepared by heating boron trifluoride diethyletherate, as outlined by Beale[13].

Boron trifluoride diethyletherate (30 g) was added to warm concentrated H_2SO_4 (50 g) through a dropping funnel. The gas which was liberated (BF_3, and perhaps a small amount of ether which had not dissolved in the H_2SO_4) was bubbled through a flask containing concentrated H_2SO_4 (to remove the excess ether) and then passed over molten sulpholane which was gently shaken until a known amount of BF_3 had been absorbed. A small sample of the solution obtained was diluted with water, extracted with petroleum spirits, and analysed by glc. No trace of diethyl ether was found although as little as 0.1% could have been easily detected by this method.

By this method 12.71 g of BF_3 were dissolved in 124.70 g of sulpholane. Assuming no volume change this gives

$$[BF_3] = \frac{12.71}{67.81} \times \frac{1.26 \times 1000}{124.70}$$

$$= 1.89 \text{ mole.litre}^{-1}$$

This solution was diluted as required.

Solutions of HBF_4 were then prepared by mixing solutions of BF_3 and HF. For example, HBF_4 (0.1 M, 50 ml) was prepared by mixing BF_3 (0.22 M, 22.5 ml) and HF (0.18 M, 27.5 ml).

1.12 Sulphuric acid

A sulpholane solution of H_2SO_4 (ca. 1 M) was prepared by adding concentrated H_2SO_4 (0.5 ml) to sulpholane (10 ml).

1.13 Sulphur trioxide and fluorosulphuric acid

Sulphur trioxide was generated from oleum by the method outlined by Herber[77].

Oleum (20%, 20 g) containing $K_2S_2O_8$ (ca. 1 g) to oxidise any SO_2 present was warmed gently until the oxide (bp 44.8°) was evolved. The SO_3 passed through a condenser with no water flowing and the liquid so formed was passed into a receiver cooled in ice/water where it condensed to a white solid (3.98 g). The outlet to the atmosphere led through a drying tower of P_2O_5. Sulpholane (ca. 100 ml) was added and the SO_3 dissolved after vigorous stirring.

A sample of this solution (5 ml) was mixed with distilled water (to form H_2SO_4) and titrated with 0.100 M NaOH to give

$$[SO_3] = 0.490 \text{ mole.litre}^{-1}$$

A solution of HSO_3F (0.13 M, 50 ml) was then prepared by mixing HF (0.18 M, 36.5 ml) and SO_3 (0.49 M, 13.5 ml).

1.14 Perchloric acid

An anhydrous solution of $HClO_4$ in 1,2-dichloroethane was prepared by the method of Klages and Hegenberg[79].

Aqueous $HClO_4$ (70%, 5 ml) was added to the oleum (20%, 25 ml) and 1,2-dichloroethane (25 ml), and shaken vigorously in a separating funnel (the ground glass joints of which were not greased). The 1,2-dichloroethane layer containing dissolved $HClO_4$ was then separated. Water was added to a 5 ml portion of this layer and titrated with 0.100 M NaOH to give

$$[HClO_4] = 1.168 \text{ mole.litre}^{-1}$$

According to Klages and Hegenberg[79] only small amounts of H_2SO_4 are dissolved in the 1,2-dichloroethane (the molar ratio $H_2SO_4:HClO_4$ being 0.004:1); in addition, the solution is completely dry since traces of water immediately precipitate the insoluble hydrate $HClO_4.H_2O$.

This solution was mixed with sulpholane to form a catalyst (see section 5.2), the possible effect on the isomerisation of the 1,2-dichloroethane not being studied. Since bromomethane has been found to be inert when used as a co-solvent in HBF_4/sulpholane[54] it was thought that it could be more suitable than 1,2-dichloroethane.

When the preparation was carried out using bromomethane rather than 1,2-dichloroethane the organic layer turned brown and the space above the solution in the reagent bottle contained a brown vapour. On testing it was found that the solution bleached both red and blue litmus and that on addition of $Ca(OCl)_2$ and 1-octene it turned colourless. These facts suggested that bromine had been formed.

Bromomethane and bromoethane were then tested with four acid solutions with the results shown in the table:

acid solution	effect of added halide	
	CH_3Br	CH_3CH_2Br
70% aq. $HClO_4$	nil	nil
1.17 M $HClO_4$/1,2-dichloroethane	brown layer produced after 1 day	
conc. H_2SO_4	nil	nil
20% oleum	brown layer formed	brown layer formed slowly; very dark after 2 days

These results indicate that the bromide radical is oxidised by both oleum and anhydrous $HClO_4$. Under these conditions it was decided not to proceed with the attempt to make $HClO_4$ in any solvent other than 1,2-dichloroethane.

1.15 Arsenic pentafluoride

Attempts were made, using the method described in appendix 1.10, to prepare AsF_5/sulpholane by the decomposition of m-nitrobenzene diazonium hexafluoroarsenate[80]. White fumes were vented to the atmosphere throughout the procedure and, as is noted in section 5.4, only a dilute solution (0.083 M) could be prepared. In all likelihood a stronger solution could be prepared only by dissolving the AsF_5 in sulpholane under pressure, as was done by Jones[41] for PF_5.

1.16 Orthophosphoric acid

Orthophosphoric acid (ca. 100%, 0.5 g) was dissolved in sulpholane (ca. 5 ml).

1.17 2,2- and 3,3-Difluorohexane

These compounds were prepared by the method of Grosse and Linn[14].

1-Hexyne (1 ml) was added slowly to anhydrous HF (1 ml, see appendix 1.9) in a polythene bottle cooled in an ice/water bath. Sputtering sounds were heard as the addition proceeded. The bottle was left standing with occasional shaking for a half hour. Sodium carbonate solution was added to neutralise excess HF and the dark brown organic layer was separated and distilled through a small scale condenser to give 2,2-difluorohexane.

3,3-Difluorohexane was prepared in a similar manner from either 3-hexyne or 2,3-hexadiene.

APPENDIX 2

NUCLEAR MAGNETIC RESONANCE

The spectra described in sections 3.3, 3.7 and 4.6 were run at 56.4 MHz and 14092 gauss on a Jeol C60HL spectrometer operating on external lock.

Samples (ca. 0.75 ml) were pipetted into standard sample tubes which were stoppered with plastic caps; because the tubes did not exactly fit the instrument some difficulty was met in maintaining constant high spinning rates.

The internal standard C_6F_6 was added to the samples so that its concentration was approximately equal to that of the sample.

As a typical example of the spectra of the sulpholane solutions (see sections 3.7 and 4.6), for PF_5/H_2O (Fig. 4.6a) the offset was + 25 ppm, the sweep time was 100 seconds, and the sweep width was 90 ppm.

Some initial work was carried out at 15 MHz by courtesy of Chemistry Division, D.S.I.R., Gracefield; the results obtained were confirmed and extended by the work at 56.4 MHz described above.

APPENDIX 3

KINETIC EQUATIONS

3.1 Consecutive reversible reactions

Consider the following system:

$$A \underset{k_b}{\overset{k_a}{\rightleftharpoons}} B \underset{k_d}{\overset{k_c}{\rightleftharpoons}} C$$

General solutions of the kinetics of such systems are given along the following lines by Matsen and Franklin[81] and by Zwolinski and Eyring[82].

Using the operator notation, i.e. $\frac{d}{dt} = D$, the basic equations are

$$D[A] = -k_a[A] + k_b[B] \qquad \ldots(1)$$

$$D[B] = k_a[A] - (k_b + k_c)[B] + k_d[C] \qquad \ldots(2)$$

$$D[C] = k_c[B] - k_d[C] \qquad \ldots(3)$$

Treating these as simultaneous equations, rearranging, and solving for $[B]$, it is found that

$$D\left\{D^2 + D(k_a+k_b+k_c+k_d) + (k_ak_c+k_ak_d+k_bk_d)\right\}[B] = 0$$

i.e. $D(D-m)(D-n)[B] = 0$

where m and n are the solutions of the quadratic equation. The solutions for $[A]$ and $[C]$ are exactly similar.

Thus the general solutions are of the form:

$$[A] = A_1e^{nt} + A_2e^{mt} + A_3 \qquad \ldots(4)$$

$$[B] = B_1e^{nt} + B_2e^{mt} + B_3 \qquad \ldots(5)$$

$$[C] = C_1e^{nt} + C_2e^{mt} + C_3 \qquad \ldots(6)$$

where the A_i, B_i and C_i are constants.

Differentiating (4) gives

$$D[A] = nA_1e^{nt} + mA_2e^{mt} \qquad \ldots(7)$$

Substituting (4) and (5) into (1) gives

$$D[A] = k_bB_1e^{nt} + k_bB_2e^{mt} + k_bB_3 - k_aA_1e^{nt} - k_aA_2e^{mt} - k_aA_3 \qquad (8$$

Then, by putting $(7)\equiv(8)$ it is found that

$$B_1 = \frac{n+k_a}{k_b}A_1$$

$$B_2 = \frac{m+k_a}{k_b}A_2$$

$$B_3 = \frac{k_a}{k_b}A_3$$

Values of the A_i in absolute terms are then calculated by substitution of the following conditions:

at $t = 0$, $[A] = [C] = 0$, $[B] = 100$ (arbitrary units)

and at $t = \infty$ $[A] + [B] + [C] = 100$,

$$[B]/[A] = \frac{k_a}{k_b}, \quad [C]/[B] = \frac{k_3}{k_4}.$$

This leads to the following expression for $[B]$:

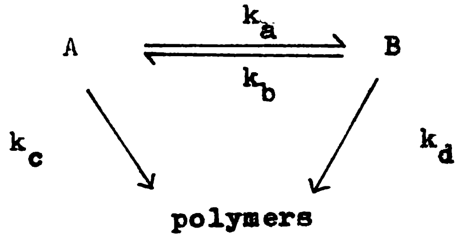
$$[B] = -\frac{100(n+k_a)}{m-n}\left\{1+\frac{mk_d}{k_ak_c+k_ak_d+k_bk_d}\right\}e^{nt}$$

$$+\frac{100(m+k_a)}{m-n}\left\{1+\frac{nk_d}{k_ak_c+k_ak_d+k_bk_d}\right\}e^{mt}$$

$$+\frac{100k_ak_d}{k_ak_c+k_ak_d+k_bk_d}$$

3.2 The effect of product destruction

Consider the following system:



The conditions are: at $t = 0$, $[A] = 100$, $[B] = 0$

at $t = \infty$, $[A] = [B] = 0$

This system was solved by the method described above to give

$$[A] = -\frac{100(k_a+k_c+n)}{m-n}e^{mt} + \frac{100(k_a+k_c+m)}{m-n}e^{nt}$$

where m and n are the solutions of the same quadratic equation as in appendix 3.1 above.

As was pointed out in section 3.5 the system

$$\begin{tikzcd}
A \arrow[r, shift left, harpoon] \arrow[dr] & B \arrow[l, shift left, harpoon] \arrow[r, shift left, harpoon] \arrow[d] & C \arrow[l, shift left, harpoon] \arrow[dl] \\
 & \text{polymers} &
\end{tikzcd}$$

was not analysed. This was partly because of the complexity of the algebra involved in the solution (seven rate constants instead of four as in both the above examples) and partly because little or no information would be obtained. The kinetic curve for $[A]$ in the system

$A \rightleftharpoons B$, initial condition 100% A

is, by appropriate choice of rate constants, virtually identical to that of $[B]$ in

$A \rightleftharpoons B \rightleftharpoons C$, initial condition 100% B.

Since the point of the present calculation is to establish the effect of product destruction on the reaction kinetics it was felt that the simpler system would suffice.

APPENDIX 4

ACIDITY FUNCTIONS AND CONDUCTIVITIES

In the table below the H_o values and the conductivities of sulpholane solutions of acids used in this study are compared. The H_o values are taken from a graph[36]; the conductivities were measured as described in section 3.7 and are relative to that of HF (0.18 M) being one.

acid	relative conductivity	$-H_o$
HPF_6 (0.12 M)	440	8.3
$HClO_4$ (0.12 M)	290	7.3
HBF_4 (0.10 M	75	6.9
HSO_3F (0.13 M)	17	7.0
H_2SO_4 (0.49 M)	31	3.8

There is a good parallel between the two sets of values except for the low value for HSO_3F.

Notes

1) The $HClO_4$ solution contained 10% 1,2-dichloroethane.

2) The H_2SO_4 solution was made up by adding water (9 μl) to a sulpholane solution of SO_3 (0.49 M, 1 ml).

APPENDIX 5

PETROLEUM SPIRITS EXTRACTIONS

Consider the system

$$I_p \rightleftharpoons I_s$$

$$I_s + A \rightleftharpoons C$$

where I_s and I_p are the isomer in the sulpholane and petroleum layers respectively, A is the acid, and C is the complex.

When equilibrium is established

$$K_1 = [I_s]/[I_p] \qquad (1)$$

and $$K_2 = [C]/[I_s][A] \qquad (2)$$

Now, $[A]_{total} = 0.07$ mole.litre^{-1}

$$\therefore \quad [A] + [C] = 0.07 \qquad (3)$$

Let α be $[\text{isomer}]_{total}$

Then $$\alpha = [I_p] + [I_s] + [C] \qquad (4)$$

From (3) and (4), $\alpha = [I_p] + [I_s] + (0.07 - [A])$

From (2) $$K_2 = \frac{0.07-[A]}{[A][I_s]}$$

i.e. $$K_2[A][I_s] = 0.07-[A]$$

$$\therefore [A] = \frac{0.07}{1+K_2[I_s]}$$

From (1) $[I_s] = K_1[I_p]$

$$\therefore \alpha = [I_p] + K_1[I_p] + 0.07 - \frac{0.07}{1+K_1K_2[I_p]}$$

Rearrangement then gives

$$K_1K_2(1+K_1)[I_p]^2 + \left\{1+K_1+K_1K_2(0.07-\alpha)\right\}[I_p] - \alpha = 0$$

A program was written for the Hewlett-Packard 9100A calculator so that this equation could be solved for $[I_p]$ by putting in values of K_1, K_2 and α .

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