NUCLEAR MAGNETIC RESONANCE STUDIES
OF BORON TRIFLUORIDE AND SOME OF
ITS COMPLEXES

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by

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SCOPE AND CONTENTS:

Nuclear magnetic resonance spectroscopy has been used to study donor-acceptor complexes of boron trifluoride with ketones, water, and methanol. Various NMR techniques have been applied which, in certain favourable cases, have yielded information on the stoichiometry, structure, relative stabilities, and reactions of the complexes in solution. A new method is proposed for the detection of BF_3 complexes having low formation constants.

The magnitude and sign of the B-F coupling constant in the tetrafluoroborate anion have been found to be dependent on the solvent. This solvent dependence is interpreted in terms of solvation and association of the ion in solution.

^{19}F spectra of $^{10}BF_3$ over a range of temperatures agree well with line shapes calculated, using Pople's expressions, for coupling of fluorine-19 with boron-10 (I=3) which is undergoing partial quadrupole relaxation.

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CHAPTER I

INTRODUCTION

(A) NUCLEAR MAGNETIC RESONANCE

(i) General

Nuclear magnetic resonance spectroscopy (NMR) has become a major technique of chemistry in recent years and has facilitated the solution of a wide variety of chemical problems. The principles of nuclear magnetism have been outlined by Abragam (1); several reviews of high-resolution NMR are now available (2-4). This thesis describes high-resolution NMR studies which have yielded information on the stoichiometry, structure, relative stabilities, and reactions of some donor-acceptor complexes of boron trifluoride in solution.

Nuclear magnetic resonance spectroscopy depends on the existence of nuclear magnetic moments. A nucleus of spin quantum number I has a magnetic moment μ such that

$$\mu = \frac{\gamma I h}{2\pi} \qquad (1)$$

where γ is the magnetogyric ratio, a parameter characteristic of a given nucleus, and h is Planck's constant. When the nucleus is placed in a magnetic field H it can exist in any of a series of equally spaced energy levels of relative energies

$$E = -\frac{m\mu}{I} H \qquad (2)$$

where m is the magnetic quantum number, which can take the values I, I-1, ...-I. The NMR experiment consists of inducing transitions between the levels, subject to the selection rule

$$\Delta m = \pm 1 \tag{3}$$

so that the energy change in any allowed transition is $\frac{\mu H}{I}$. Thus the frequency which can cause transitions is

$$\nu = \frac{\mu H}{Ih} = \frac{\gamma H}{2\pi} \ . \tag{4}$$

(ii) The Chemical Shift

The magnetic fields at chemically different nuclei differ slightly from one another, and from the applied field H_o, as a result of local magnetic interactions arising from induced orbital motions of the electrons about the nuclei. Thus in the NMR experiment as it is usually performed, in which the irradiating frequency is kept constant and the magnetic field is varied, each chemically distinct group of nuclei comes into resonance at a different applied field H_o as the resultant field H at each group of nuclei becomes the required field to allow transitions at the fixed frequency. The separate resonances due to nonequivalent nuclei, which appear at different values of H_o, can be correlated with the chemical environments of the nuclei, so that in effect the magnetic nucleus is used as a probe to investigate the electronic structure of the molecule.

Since the induced motions of the electrons, and hence the local magnetic interactions, are proportional to the applied field H_o, the magnetic field H at a nucleus can be given by

$$H = H_o (1 - \sigma), \tag{5}$$

where σ is a dimensionless constant known as the screening constant. In practice the magnetic fields at the nuclei are not measured with respect to the applied field but instead with respect to the resultant magnetic field H_r corresponding to a screening constant σ_r of a reference substance. The chemical shift δ with respect to the reference substance is defined as the difference in screening constants:

$$\delta = \sigma - \sigma_r = \frac{H - H_r}{H_r} \quad . \tag{6}$$

It is conveniently expressed in parts per million (p.p.m.), since the local magnetic interactions cause only small changes in the applied field. Tetramethylsilane (TMS) is the usual reference substance for proton spectra. Trichlorofluoromethane is often used as a reference for fluorine spectra.

(iii) Spin-Spin Coupling

The local magnetic field H at a nucleus can be affected by electron-coupled spin interactions with magnetic nuclei elsewhere in the same molecule. The interactions can be transmitted through several bonds but usually attenuate rapidly as the number of intervening bonds increases. The energy of interaction of two magnetic nuclei i and j can be given by

$$E = J_{ij} \left[I_i \cdot I_j \right] \tag{7}$$

where I_i and I_j are the spin angular momentum vectors of nuclei i and j, and J_{ij} is the spin-spin coupling constant. The energy of interaction depends on both the total product and the relative spatial orientation of the nuclear magnets; J_{ij} is defined to be positive if the spin states in which the nuclei have antiparallel spins are lowered in energy, and those in which they have parallel spins are raised in energy, by the interaction. J_{ij} is independent of the applied magnetic field and can be considered qualitatively to be the result of magnetic fields arising within the molecule.

To illustrate the effects of spin-spin interactions the simplest case, consisting of two spin-1/2 nuclei A and X in which the energy of interaction is much less than the energy separations of the spin states, is now considered. Figure 1a shows the four energy levels for the AX system in the absence of spin-spin interactions (i.e., $J_{AX} = 0$). Spin states parallel to the applied field are designated α, those opposed to it are designated β. The two possible transitions of the A nucleus are shown; both are of equal energy since in the absence of spin-spin interactions the A nucleus is unaffected by the spin state of the X nucleus. Simultaneous transitions of both nuclei are rare and can be neglected. Figure 1b shows the effect of a positive coupling constant J_{AX} as defined above. It has been shown that each state is raised or lowered in energy by an amount equal to J/4. It is seen in the Figure that the two transitions of the A nucleus are no longer of equal energy. One has been raised in energy by J/2; the other has been lowered in energy by the same amount. Thus two resonances separated by J are expected. Figure 1c shows the effect of a negative J_{AX}. States with parallel spins are now lowered in energy, while states with antiparallel spins are raised in energy. Thus the resonance of the A nucleus should again be split into a doublet of separation J_{AX}. In practice the absolute sign of J cannot be determined under the usual conditions of high-resolution NMR; it can be determined by a special technique (5). The concept of opposite signs of J will be applied in Chapter X.

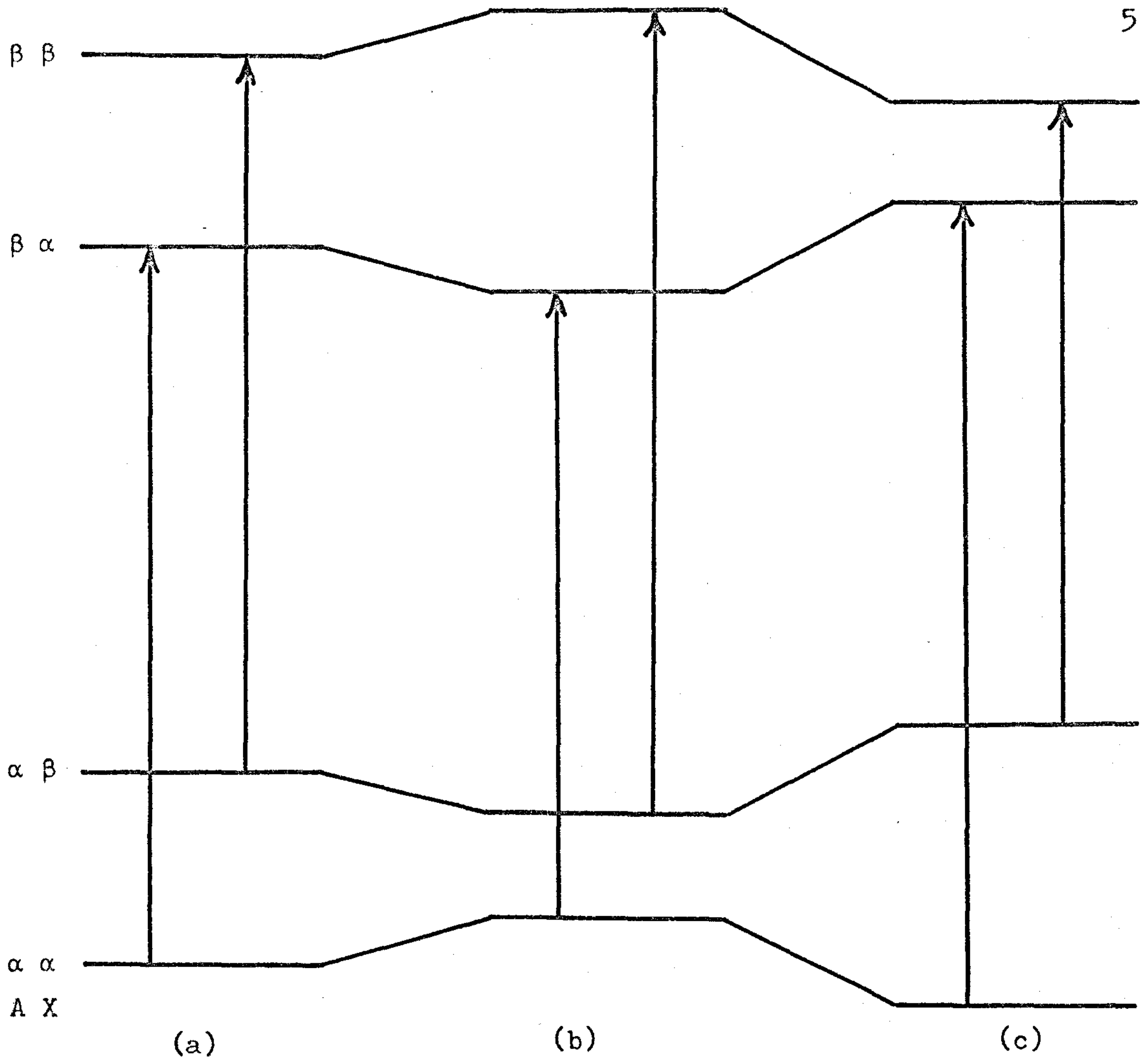


Fig. 1 Spin states of the AX system: (a) $J_{AX} = 0$; (b) J_{AX} positive; (c) J_{AX} negative.

In the AX case described above, each possible value of the spin of the X nucleus produces a different magnetic field at the A nucleus, so that the A resonance is split into a doublet. Similarly, when the A nucleus is coupled to n equivalent X nuclei, the A resonance is split into n+1 lines, corresponding to the n+1 values of the total spin state of the X nuclei. Thus in the AX_3 case the three X nuclei can have the spin states shown in Table I. The total spin states of the three X nuclei have the statistical weights shown in Table I, so that the A nucleus which undergoes a transition has these probabilities of being in the environment of each of these total spin states. Thus the resonance of the A nucleus is split into a 1:3:3:1 quartet; the separation of the components is equal to J_{AX}.

TABLE I

SPIN STATES OF THREE EQUIVALENT SPIN-1/2 NUCLEI

Nucleus			Total Spin State (I_z)	Statistical weight
1	2	3		
α	α	α	3/2	1
α	α	β	1/2	3
α	β	α		
β	α	α		
α	β	β	-1/2	3
β	α	β		
β	β	α		
β	β	β	-3/2	1

(iv) Rates of Exchange by NMR

Chemical shift and spin-spin splitting patterns may be modified if a rate process involving the magnetic nuclei is present. For example, rapid exchange of magnetic nuclei between different environments causes a coalescence of the chemically shifted resonances due to these environments, in accordance with

$$\tau \Delta \nu \approx \frac{1}{2\pi} , \tag{8}$$

where $\Delta \nu$ is the separation of the resonance lines in the absence of the rate process, and τ is the smallest lifetime of a magnetic nucleus in the different environments for which separate resonances can be distinguished. If the mean lifetimes of the nuclei in the different environments are much greater than this, separate signals are obtained, with the chemical shifts and any fine structure that would be observed in the absence of the exchange process. If the mean lifetimes are of the order of magnitude of τ in equation (8), the observed signal shape changes in a regular fashion with exchange rate. As the lifetimes decrease, the separate peaks broaden and their maxima draw closer together until they coalesce to yield a single broad peak in an averaged position. This peak becomes sharper as the mean lifetimes are further decreased, so that for very short lifetimes a single sharp signal is obtained in the averaged position.

In the region of intermediate lifetimes it is possible to determine the mean lifetimes of the species from observed signal shapes. The use of changes in NMR signal shapes to determine lifetimes of species in solution is now a well-established and extensively used technique for the study of rapid rate processes involving no permanent chemical change (6-9). The theory relating line shapes to lifetimes of nuclei in different environments was first given by Gutowsky, McCall and Slichter (10) in 1953, and has since been reviewed (i.e., (1), pp. 447-451, 501-506; (2), Chapter 10; (6); (9)). A line shape expression involving inversion of an nxn matrix is obtained for the general case of exchange of magnetic nuclei among n different sites of populations p_1, p_2.....p_n. Such an expression is applied in Chapter III to exchange among six sites. Lifetimes can be estimated by matching of calculated and observed spectra. In the general case no explicit expressions exist for directly calculating lifetimes from an easily measurable spectral parameter except in the slow exchange limit in which the chemically shifted peaks do not overlap appreciably. In the slow exchange limit the exchange process causes only a broadening of the peaks, and $\mathcal{T}_j$ of the jth species is given by

$$(T_{2j}')^{-1} = T_{2j}^{-1} + \mathcal{T}_j^{-1} \tag{9}$$

where $(T_{2j}')^{-1}$ is equal to the width at half-height of the exchange broadened peak and T_{2j}^{-1} is equal to the width at half-height of the peak in the absence of exchange. Thus the exchange is treated as an additional relaxation process contributing to the line width and allows each $\mathcal{T}_j$ to be obtained independently of all the other $\mathcal{T}$'s. This procedure can be used only if the other contributions to line broadening are negligible or are otherwise known.

Most NMR rate studies utilizing the collapse of chemically shifted peaks have involved only two nonequivalent sites. Explicit line shape expressions, corresponding to the solution of the 2x2 matrix expression, are available for the collapse of two chemically shifted peaks ((2), equations 10-23 to 10-25). As in the more general case of n different sites, lifetimes of magnetic nuclei on the sites can be determined by matching of calculated and observed spectra as is done in Chapter VII of this thesis. In addition, certain approximate expressions have been developed which allow a more convenient determination of lifetimes, but which are valid only when the experimental conditions approximate closely to certain assumed conditions. For example, Gutowsky and Holm (11) developed expressions, used in Chapter VI, for exchange between two sites of equal populations and lifetimes, assuming infinitely sharp peaks in the absence of exchange. It has recently been pointed out by Gutowsky and co-workers (12) that many of the approximate treatments commonly used lead to large systematic errors when applied to systems in which the approximations are not justified, and that many NMR kinetic studies reported in the literature are based on such unjustified approximations. Computer calculations using the full line shape expressions are more reliable since they avoid systematic errors.

The components of a spin multiplet can be collapsed under conditions of rapid exchange of one of the spin-coupled nuclei, even among identical molecules. The explanation is very similar to that given previously to explain the collapse of chemically shifted peaks. For example, in the AX case described previously the position of absorption of the A nucleus is determined by the spin state of the X nucleus. A rapid intermolecular exchange of X nuclei, yielding in any molecule a series of X nuclei with random spin states, causes rapid changes in the environment at the A nucleus, and a consequent collapse of the multiplet components.

The use of NMR in kinetic studies is not limited to determining rates of rapid reversible exchange reactions by variations in signal shapes. It is also becoming important as a device for monitoring the progress of complex reactions by the observation of changes with time in relative peak areas of reactants and products (13).

(v) Effects of Quadrupole Relaxation

In the absence of the effects of chemical exchange, discussed in the previous section, spin-spin multiplets can be collapsed by a rate process involving rapid relaxation, i.e., rapid transitions among spin states, of one of the coupled nuclei. In general, spin-1/2 nuclei do not relax sufficiently rapidly to cause collapse of spin-spin multiplets, although such rapid relaxation can be induced artificially by the technique of double irradiation (14). However, nuclei with spin $I > 1/2$ possess electric quadrupole moments, arising from charge distributions which are not spherically symmetric, which in many cases allow very rapid relaxation of the nuclear spin states through interactions with fluctuating electric field gradients. In such cases a second nucleus of spin $I=1/2$, coupled to the high-spin nucleus, yields a spectrum in which the nuclei appear to be decoupled, i.e., no splittings arising from the coupling can be observed. In other cases quadrupole relaxation of the high-spin nucleus is not as effective, so that partially collapsed multiplets are observed in the spectrum of the spin-1/2 nucleus. An example of this is described in detail in Chapter XI.

The degree of quadrupole relaxation depends on the magnitude of the nuclear quadrupole moment eQ of the nucleus, the electric field gradient eq at the nucleus, and the correlation time τ_q for molecular reorientation, according to the equations of Chapter XI. The electric field gradient at the nucleus is highly dependent on the molecular environment, so that a given species of high-spin nucleus can undergo widely differing degrees of quadrupole relaxation in different environments. A high degree of symmetry about the nucleus results in a low electric field gradient and only a small degree of quadrupole relaxation. Thus the spectrum of a spin-1/2 nucleus coupled to a single nucleus of spin $I > 1/2$ should be dependent on the symmetry about the high-spin nucleus. If the latter is in a highly symmetrical environment, the spectrum of the spin-1/2 nucleus is likely to be split into a spin multiplet consisting of $2I+1$ equally spaced lines of equal intensities. If the high-spin nucleus is in an environment of low symmetry, the spin multiplet structure in the spectrum of the spin-1/2 nucleus is likely to be partially or completely collapsed.

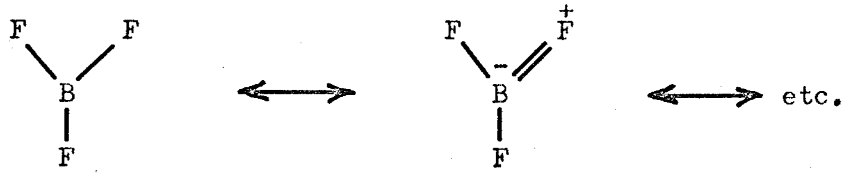
(B) DONOR-ACCEPTOR COMPLEXES OF THE BORON TRIHALIDES

The boron trihalides are electron deficient compounds since the boron atom has an empty orbital in its valence shell. They therefore behave as Lewis acids, or electron-pair acceptors; coordination of an additional electron pair completes the boron octet. The boron trihalides are among the strongest Lewis acids known, and form donor-acceptor complexes with a wide variety of Lewis bases, or electron-pair donors. Donors include many neutral molecules such as ketones, ethers, and water, as well as ions such as the halide ions. All molecules which act as donors have a lone pair of electrons in the valence shell of at least one atom; in other respects the donor molecules can be of widely varying structural types, including for example transition metal hydrides such as dicyclopentadienyl tungsten dihydride (15).

Many reports of reactions of BF_3 with organic species, and of the isolation of crystalline complexes, appeared during the nineteenth century; the early references are given in a review by Martin and Cannon (16). However, few detailed systematic studies were carried out on such complexes before 1945. Since then the application of various physical methods, as outlined by Coyle and Stone (17), Stone (18), and Greenwood and Martin (19), has led to a considerable degree of understanding of the structural types of complexes and of their relative stabilities. Other reviews of boron trihalide complexes are available as well (20,21).

Several independent studies have shown that the relative Lewis acid strengths of the boron trihalides increase in the order

$BF_3 < BCl_3 < BBr_3 < BI_3$. This is contrary to the order expected from either electronegativity or steric considerations and is attributed to pπ-pπ bonding in the free trihalide molecules:



Ia

Ib

This π bonding, which allows some electron density to be present in the formally vacant orbital on boron, should be most effective in BF_3 since the orbitals involved are all in the same principal valence shell. The expectation of greater overlap of orbitals, and hence stronger π bonding, in the case of the trifluoride has been supported by molecular orbital calculations (22). The extra stability arising from π bonding in the free trihalide molecule is lost when a coordinate bond is formed. The stability of the adduct with respect to the free components is therefore decreased; the greatest decrease in relative stability of the adduct occurs in the case of the trifluoride. It is interesting that, although BF_3 is a weaker Lewis acid, many more donor-acceptor complexes of the trifluoride are known than of the other boron trihalides. This is a result of the increasing tendency of the adducts to undergo further intramolecular reactions (23) as the donor-acceptor bond becomes stronger. It appears that increased polarity of the complex favours ionization or the elimination of small molecules, as in the following reaction:

$$ROH + BX_3 \longrightarrow \left[ROH \circ BX_3\right] \longrightarrow HX + ROBX_2 \longrightarrow (RO)_3B \qquad (10)$$

Thus whereas many donor-acceptor complexes of BF_3 with alcohols are known, the corresponding complexes of the other trihalides either have not been reported or are much more prone to decomposition. In cases where further reaction of complexes does not occur readily it is sometimes found that, whereas BF_3 is too weak an acceptor to form a complex, complexes of the other trihalides can be isolated (24).

Orders of relative base strengths towards the boron trihalides have been determined; for example, in series of closely analogous compounds nitrogen has been shown to be a better donor atom than oxygen. However, the effect of the donor atom can be greatly outweighed by the effect of donor substituents in determining base strength. Electron-withdrawing substituents, or bulky substituents which cause steric hindrance at the donor site, can greatly decrease the donor strength. It should be borne in mind that orders of Lewis base strengths, as are discussed in this thesis, refer in the strictest sense only to the reference acid which was used in their determination. However, it seems reasonable that the results could be extrapolated to closely related acids.

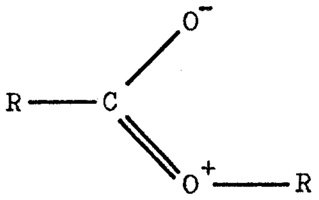
Relative strengths of donor-acceptor bonds are best determined from comparison of the heats of dissociation of the complexes in the gas phase, which gives a direct measure of the enthalpy of the coordinate bond. However, such measurements are often not obtainable since many complexes are completely dissociated in the gas phase. Alternative methods involving displacements and equilibria in solution are more convenient and more generally applicable but give a measure of the free energy difference rather than of the enthalpy difference, so that the results are not strictly comparable. However, it is found that estimates of relative bond strengths obtained in the gas phase and in solution agree well in series of related compounds in which entropy changes on complex formation are similar. Thus in the present work it seems justified to draw conclusions about relative strengths of donor-acceptor bonds from studies of equilibria in solution.

A wide range of stabilities has been encountered in studies of boron trihalide complexes. The most stable complex of a given donor with a given acceptor is usually that with 1:1 proportions of donor and acceptor. Some 1:1 complexes, such as $BrF_3.BF_3$ (25), are completely dissociated at quite low temperatures, while a few, such as pyridine.BF_3, can be distilled unchanged at high temperatures. 1:1 complexes of oxygen donors with BF_3 generally have intermediate stabilities; the coordinate bond is sufficiently weak that there is significant dissociation into the free acid and base at room temperature. The liberated gaseous BF_3 fumes in air as a result of complexation with water vapour. Rapid breaking and re-forming of the weak donor-acceptor bond in the presence of excess BF_3 was shown to occur in complexes of ethers with BF_3 and has been utilized in the separation of the boron isotopes (26).

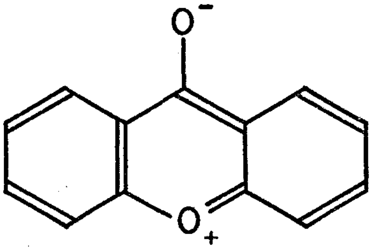
Crystalline complexes of a variety of acid-base ratios other than 1:1 have been reported to exist in a number of cases (16,17). In most cases these were found to be stable only at low temperatures. However, hydroxylic species such as water, alcohols and carboxylic acids form stable crystalline 2:1 complexes $(donor)_2.BF_3$ which have been reported (19) to be more stable than the 1:1 complexes.

The reaction of BF_3 with acetone was first reported in 1878 (27). Subsequently a number of 1:1 complexes of BF_3 and ketones have been prepared (16). Few studies of these have been carried out until recently, apparently because of their tendency to decompose on standing at room temperature (28). This thesis deals with NMR studies of ketone.BF_3 complexes; other spectroscopic methods have been applied previously. Ultraviolet spectrophotometry has been used to determine relative stabilities of the BF_3 complexes of a series of aromatic ketones (29). It was shown that the base strengths of the ketones increased in the order acetophenone $<$ p-methylacetophenone $<$ p-methoxyacetophenone. Thus the donor strength of the carbonyl oxygen is increased by the presence of an electron-releasing substituent on the aromatic ring. Susz and co-workers have carried out infrared spectroscopic studies of complexes of ketones with a series of Lewis acids including BF_3 (30). The carbonyl stretching frequency was found to decrease substantially (50-150 cm^{-1}) on complex formation. This was attributed to weakening of the carbon-oxygen bond as a result of electron pair donation from oxygen. The magnitude of the lowering of the carbonyl stretching frequency was found to vary with the strength of the Lewis acid involved in the complex, as estimated from the activity of the acids in Friedel-Crafts catalysis.

Infrared spectroscopic studies similar to those of Susz and co-workers have also been applied to complexes of carbonyl compounds other than simple ketones and have yielded information on the structure of the complexes. Studies by Lappert (31,32) and by Cook (33) involved measurement of the lowering of the carbonyl stretching frequency in ethyl acetate and xanthone, respectively, on complex formation. In these Lewis bases the carbonyl oxygen is one of two possible donor sites. Since the magnitudes of lowering of the frequency were similar to those observed by Susz in the case of simple ketones, it was concluded that the carbonyl oxygen is the preferred donor site. This conclusion appears to disagree with earlier studies which showed that ethers are better donors than ketones (19). However, the different order of relative donor strengths of the two types of oxygen when both are present in the same molecule can be attributed to a contribution from a resonance structure of the types II and III, which enhances the donor strength of the carbonyl oxygen.



II



III

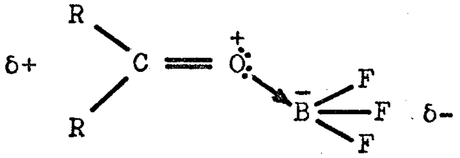
Cook (33) prepared complexes of xanthone with a wide range of Lewis acids including the boron trihalides. He obtained a good correlation between the magnitude of the decrease in the carbonyl stretching frequency and the Lewis acid strength as determined by other means. Thus complexes of the boron trihalides yielded shifts in the order $BF_3 < BCl_3 < BBr_3 < BI_3$. The shift obtained for the BI_3 complex was greater than that obtained for the complex of any other of a wide range of Lewis acids, and indicates that BI_3 is an extremely strong acid. This spectroscopic method appears to yield orders of relative Lewis acid strengths which are at least semi-quantitative.

The above outline of applications of spectroscopic techniques to the study of complexes of carbonyl donors illustrates some of the possibilities for the use of physical methods in obtaining structural data on donor-acceptor complexes. The application of NMR, probably the most versatile spectroscopic technique, to the study of BF_3 complexes is discussed in the following section.

(C) HIGH-RESOLUTION NMR STUDIES OF BORON TRIHALIDE COMPLEXES

(i) General

The formation of a donor-acceptor bond between two electrically neutral molecules decreases the density of electronic charge at the donor site and increases the density at the acceptor site as a result of the sharing of an electron pair which was previously localized on the donor:



Thus simple donor-acceptor complexes are highly dipolar in nature. NMR is especially useful as a technique for studying the formation of donor-acceptor complexes because it yields information about the electron density and structure around the magnetic nuclei. Other effects being equal, increased electron density about a magnetic nucleus causes increased screening of the nucleus and a shift to higher applied field in its resonance position. Conversely, decreased electron density causes a shift to lower field. Thus the changes in electron density on complex formation should result in "complexation shifts" to higher field in the acceptor, and to lower field in the donor resonances. The changes in charge density should be greatest at the site of the donor-acceptor bond but should still be significant at other sites in the molecule due to inductive effects and, in some cases, mesomeric effects. It has been found, and the present work further illustrates, that significant complexation shifts occur for donor nuclei which are several bonds removed from the donor site. In cases in which the inductive effect alone can operate, the complexation shift is found to attenuate rapidly as the distance from the site of the donor-acceptor bond is increased.

A complexation shift to high field in the ^{19}F resonance of BF_3 was first evident in an early study of fluorine chemical shifts by Gutowsky and Hoffmann in 1950 (34). The (diethyl ether).BF_3 complex was found to absorb 21 p.p.m. to higher field than pure BF_3. This large shift indicates that a considerable fraction of the gain in electronic charge on BF_3 is delocalized from the boron to the fluorines. From more recent studies it appears that BF_3 complexes with oxygen donors absorb in a fairly narrow region of the ^{19}F spectrum which is considerably shifted from the position of BF_3 itself. Thus the position of the fluorine resonance can provide evidence for complex formation (35).

Early applications of NMR to the determination of structures and stabilities of boron trihalide complexes have been summarized by Coyle and Stone ((17), pp. 93-95, 112-114). Several different types of information are obtainable in favourable cases.

(ii) Complexation Shifts as a Measure of Donor-Acceptor Interaction

Since donor-acceptor bond formation involves transfer of electronic charge, it should be possible to correlate the magnitudes of NMR complexation shifts with the strength of the donor-acceptor bonds. Good correlations of bond strengths with complexation shifts have been obtained in several studies of proton resonances of donor molecules. The proton resonances of acetonitrile (36) and trimethylamine (37) have been reported by Onyszchuk and co-workers to shift to low field on complexation with the boron trihalides; the relative magnitudes of the shifts for the different trihalides correlate well with estimates of relative bond strengths by other methods, and increase in the order $BF_3 < BCl_3 < BBr_3$. Kuhn and McIntyre (38) have investigated shifts to low field in the proton resonances of dimethylformamide (DMF) on complexation with a variety of Lewis acids and have found a similar correlation. Gore and Danyluk (39) have reported that BCl_3 complexes of ethers have greater ^1H complexation shifts than the corresponding BF_3 complexes. Thus ^1H NMR can be used to estimate relative strengths of acceptor molecules by chemical shift changes on complexation. Early studies involving changes in internal chemical shifts within ethyl groups in donor and acceptor molecules, summarized by Coyle and Stone ((17), pp. 113-114), showed that these shifts could be correlated with bond strengths in series of analogous compounds. However, the use of internal shifts appears to be less generally useful than the use of shifts with respect to an inert reference species such as TMS.

^{19}F complexation shifts of a fluorine-substituted donor molecule have been found to be a highly sensitive measure of acid strengths. Taft and Carten (40) studied ^{19}F complexation shifts of p-fluorobenzonitrile with several Lewis acids. The shifts were found to closely parallel the heats of dissociation of the corresponding pyridine complexes. The use of fluorine rather than proton resonance has the advantage that fluorine chemical shifts are in general much larger than proton shifts for similar changes in environment, so that very small differences in Lewis acid strengths might be determined by this method.

Boron-11 resonance studies (41, 42, 43) have shown that complexation shifts to high field occur in boron-containing Lewis acids. Mooney and co-workers (42, 43) claim that these can be correlated with the relative strengths of both acids and bases. The relative magnitudes of shifts to high field of a single acid such as BF_3 on complexation with different donors yield an estimate of relative strengths of the donors. However, it has been pointed out by Jones (35) that such estimates do not correlate well with heat of formation values in the literature. The relative magnitudes of ^{11}B shifts to high field of different Lewis acids on complexation with the same base yield an estimate of relative strengths of the acids (43). However, estimates of acid strengths made in this manner fail to take into account that π-bonded structures such as Ib (p. 13) are less probable in tetrahedral boron compounds. The reduction or elimination of contributions from such structures should affect the electron distribution about boron to different degrees in the different boron trihalides, so that ^{11}B complexation shifts should provide at best a rough estimate of acid strengths. In addition it has been observed (43) that for the ethyl di- and trichloroacetates the ^{11}B complexation shift is greater for the presumably weaker BF_3 complex than for the corresponding BCl_3 and BBr_3 complexes. This effect is the reverse of that expected, and indicates that ^{11}B shifts are not in general reliable as a method of estimating acid strengths.

A boron-11 NMR study (44) has provided evidence for the postulated π bonding contribution in the boron trihalides. A more recent ^{11}B study of the tetrahaloborate anions (45) shows a trend of chemical shifts similar to that observed in the trihalides. This suggests that some π bonding survives even in tetrahedral boron compounds. The nature of this proposed π bonding is not clear as there is no empty orbital in the boron valence shell; possibly an orbital of a higher shell is involved. If significant π bonding persists in tetrahedral boron compounds, its importance would likely depend on the nature of the donor. This might explain why ^{19}F complexation shifts of BF_3, discussed below, do not in general show a correlation with donor-acceptor bond strengths. However, the available data is not sufficient to draw definite conclusions.

Craig and Richards (46) found that in a series of complexes of simple ethers with BF_3, the magnitude of the ^{19}F complexation shift of BF_3 increased with increasing stability of the complex, as determined from equilibrium measurements. However, when ^{19}F complexation shifts of complexes of different classes of donors such as ethers, alcohols, and water are compared, no correlation of the shifts with the relative strengths of the donor-acceptor bonds is evident. Also the ^{19}F shifts are rather strongly dependent on temperature and concentration (47) and on solvent (this work). The apparently random variations of chemical shifts of the complexes with donor species and with minor factors such as temperature emphasize the fact that transfer of electronic charge from donor to acceptor is not the only factor in determining ^{19}F complexation shifts of BF_3 complexes.

(iii) Rapid Equilibria In Solution

In several studies of room temperature spectra of mixtures of an organic base and a boron trihalide it was found that mixtures in which $[\text{base}] > [BX_3]$ did not yield separate resonances for the free and the complexed base, but yielded instead a single set of resonances having chemical shifts intermediate between those of the free base and of the 1:1 complex (39, 40, 46-49). This indicates a rapid exchange of BX_3 among base molecules. In some cases (40, 47-49) this rapid exchange reaction was slowed down at low temperatures so that separate peaks due to the free and the complexed base were observed.

In some cases (40,46) the averaged chemical shifts were found to vary linearly with the acid-base ratio, $[BX_3]/[\text{base}]$, as acid was added until 1:1 proportions of acid and base were present. Addition of further acid then had no effect on the chemical shifts of the base. This behaviour is to be expected if all of the available acid complexes with base, up to 1:1 proportions, and if no complexes containing more than one mole of acid per mole of base exist. Thus the variations in chemical shifts confirm the 1:1 stoichiometry of the complexes and show that there is negligible dissociation in solution. Craig and Richards (46) carried out such a study on complexes of BF_3 and ethers. Using the observed linear relationships between chemical shifts and the acid-base ratio they were able to determine equilibrium constants for distribution of BF_3 between two ethers present in the same solution. These agreed well with equilibrium constants determined from changes in the chemical shift of the single averaged ^{19}F peak, and yielded the order of donor strengths $(CH_3)_2O > CH_3OC_2H_5 > (C_2H_5)_2O$. Thus equilibrium constants can sometimes be determined by NMR even when separate peaks arising from the different species are not visible.

In some cases non-linear plots of chemical shifts of the base vs. acid-base ratio have been reported (39,40,47). Taft and Carten (40) obtained non-linear plots in a "double-label" investigation of complex formation between p-fluorobenzonitrile and p-fluorophenylboron dichloride. The ^{19}F resonances of both the acid and the base yielded curves which were interpreted in terms of a partial dissociation of the complex in solution. From the chemical shift plot of either the acid or the base they were able to obtain the same formation constant for the complex in solution. Such a procedure must be applied with caution, however; it appears that formation constants of ether.BF_3 complexes in methylene chloride solution, calculated from curved plots of proton chemical shift vs. acid-base ratio obtained by Gore and Danyluk (39), are invalid.

Gore and Danyluk (39) concluded from proton NMR studies that ether.BF_3 complexes are dissociated to some extent in methylene chloride solution, and that the order of base strengths of the ethers is $(C_2H_5)_2O > (\underline{i}\text{-}C_3H_7)_2O > (CH_3)_2O$. These results were surprising since Craig and Richards (46) had reported negligible dissociation of mixtures of ethers and BF_3 and a different order of donor strengths (p.23). Results of Rutenberg, Palko and Drury (50) support the conclusion of Craig and Richards that dimethyl ether is a better donor than diethyl ether. The use of methylene chloride as a solvent by Gore and Danyluk would not be expected to reverse the order of base strengths. Some studies carried out in connection with the present work also appear to be inconsistent with Gore and Danyluk's conclusions. Proton spectra of methylene chloride solutions of diethyl ether and BF_3, at -50° with $[\text{ether}] > [BF_3]$, yielded separate resonances for free ether and the 1:1 complex, having the relative areas expected if there is negligible dissociation of the 1:1 complex. The conclusions of Gore and Danyluk do not follow from their plots, which do not show significant dissociation of the complexes. Their reported formation constants are too large to be measured by NMR, especially since considerable scatter is evident in their data; therefore their order of base strengths, which was determined from differences in formation constants, is not valid. Their conclusions thus appear to be the result of performing excessively detailed calculations from insufficiently accurate experimental data. Additional inaccuracy is likely to have arisen from their use of the methylene chloride peak as a reference in chemical shift measurement. It has been shown (51) that methylene chloride can take part in hydrogen bonding with oxygen donors, and that this can affect the position of its proton resonance signal.

Relative amounts of species in solution are determined more directly by the relative areas of separate resonance peaks due to the different species. Ogg and Diehl (48) used this direct method to estimate equilibrium constants for BF_3 distribution among different alcohols as donors, in solutions in which $[\text{total alcohol}] > [BF_3]$. Although the room temperature ^{19}F spectrum yielded only a single peak, spectra at low temperatures yielded separate peaks due to BF_3 complexes with the different alcohols present. The relative areas of these peaks yielded a direct measure of the relative proportions of the different complexes.

Knowledge of the relative proportions of the complexes, together with knowledge of the sample composition, allows calculation of equilibrium constants for BF_3 distribution among the different alcohol donors. Their results indicate that at -80° the base strengths are in the order $H_2O \gg CH_3OH > C_2H_5OH > n\text{-}C_3H_7OH$.

Diehl (47) studied proton spectra of mixtures of BF_3 and methanol of various acid-base ratios. The hydroxyl proton chemical shift was found to be highly dependent on the acid-base ratio; a curved plot of chemical shift vs. acid-base ratio was obtained with a broad minimum, corresponding to absorption at quite low field, for values of the acid-base ratio of about 0.6. This shift was interpreted as arising from the 2:1 complex, $(CH_3OH)_2.BF_3$. For a 1:1 acid-base ratio the hydroxyl shift was intermediate between the values for free methanol and for the broad minimum. The presence of only a single hydroxyl peak, even at temperatures which yielded separate ^{19}F resonances in solutions containing more than one species of alcohol, was attributed to a second rapid exchange process, more rapid than the BF_3 exchange, which interchanged hydroxyl protons among all possible environments.

(iv) Kinetic Studies Of BF_3 Exchange

The fact that BF_3 exchanges rapidly among donor sites in many of its complexes in solution has been demonstrated by the presence of averaged resonance signals, as described above. Quantitative measurements of lifetimes of the species over the temperature range in which signal shapes are dependent on lifetime have been carried out by several groups of workers. Diehl (47) determined lifetimes of BF_3 on the different donors, and the activation energy for BF_3 exchange, from ^{19}F

spectra of solutions of methanol and ethanol with BF_3, in which separate low temperature peaks due to the two BF_3 complexes merged at higher temperatures. An even more rapid proton exchange process was postulated to occur as well. Paasivirta and Brownstein (49) studied solutions of methanol and BF_3 in sulphur dioxide, which proved to be a convenient solvent for the study of mixtures in which $[\text{methanol}] < [BF_3]$. In such mixtures it was possible to identify two distinct exchange processes, BF_3 exchange and hydroxylic proton exchange, and to determine rates and activation energies for both processes. The rates of the two processes could be independently varied by appropriate variation of the reagent concentrations. Passivirta and Brownstein also obtained some interesting results from solutions in which $[\text{methanol}] > [BF_3]$, but misinterpreted them. A revised interpretation is given in Chapter V of this thesis.

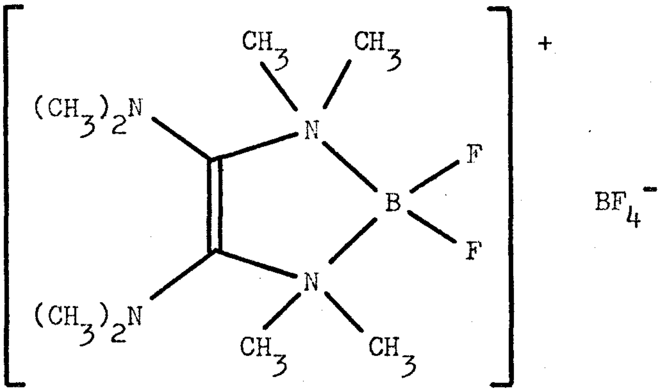
Brownstein and co-workers (52) carried out variable temperature ^{19}F NMR studies of a few ether and amine complexes of BF_3 in the presence of excess BF_3 in toluene solution. From the changes in line shapes with temperature due to the collapse of peaks due to free and complexed BF_3, lifetimes and activation parameters were calculated for the exchange process. Since the activation energies obtained are much less than the dissociation energies of the complexes it appears that exchange is caused by a bimolecular displacement mechanism rather than by dissociation of the complex. The rates of exchange were slower for complexes of nitrogen donors than for complexes of oxygen donors, in keeping with the ability of nitrogen to form stronger donor-acceptor bonds than oxygen. A displacement mechanism has also been proposed for

BF_3 exchange between methanol.BF_3 and excess BF_3 in sulphur dioxide solvent (49).

Rutenberg, Palko and Drury (50,53) determined rates of BF_3 exchange between two different ethers in mixtures of the ethers such that $[\text{ether}] > [BF_3]$. From the collapse of the ^{19}F peaks due to BF_3 complexes of the two ethers, activation energies were determined for the exchange process. It was found that the apparent activation energy for the process increased as the relative proportion of BF_3 to ether increased, up to 1:1 proportions. This was interpreted in terms of more than one mechanism for the exchange process. The mechanism of lower activation energy was postulated to involve displacement of base from the complex by a molecule of free base in a concerted (S_N2) mechanism, in which the activation energy is less than the heat of formation of the complex. The process of higher activation energy, which should predominate when there is little or no free base present, was postulated to involve a preliminary dissociation of the complex. In accordance with this postulate, the activation energy when 1:1 proportions of ether and BF_3 are present appears to be about equal to the heat of formation of the complex. In a few samples for which $[\text{ether}] < [BF_3]$ the exchange was much more rapid, indicating a mechanism of much lower activation energy, as was found in Brownstein's study (52). It is evident from these results that several different paths for exchange exist, and that different paths predominate under different conditions.

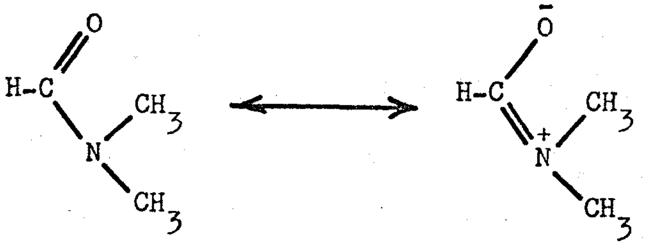
(v) Structure Determination

In favourable cases the complete molecular structure can be proved beyond reasonable doubt by high-resolution NMR. Thus in an early study Shoolery (54) was able to prove by ^1H, ^{31}P and ^{11}B resonance that the complex dimethylphosphine borane has the simple monomeric structure $(CH_3)_2HP{:}\longrightarrow BH_3$. Parry and co-workers (55) have recently used similar methods to show that phosphine borane has an analogous structure. Wiberg and Buchler (56) have used ^1H, ^{19}F and ^{11}B resonance to deduce the ionic structure IV for the addict of one mole of tetrakis-(dimethylamino)-ethylene with two moles of BF_3.



IV

Lappert and co-workers (57) presented NMR and infrared evidence to show that in the complex of dimethylformamide (DMF) with BCl_3 the oxygen atom, rather than the nitrogen atom, is the donor site. In DMF itself the methyl groups are nonequivalent due to hindered internal rotation about the central C-N bond. The hindered rotation is a consequence of a considerable degree of double bond character in this bond, arising from a contribution of the resonance structure Vb:

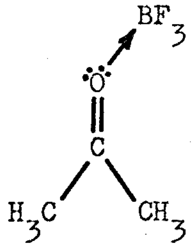


Va

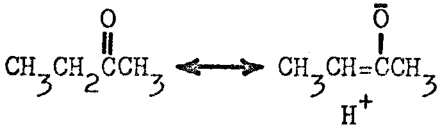
Vb

Lappert and co-workers obtained separate resonance signals for the cis and trans methyl groups in the 1:1 BCl_3 complex as well as in free DMF. This provides strong evidence against donation by nitrogen, which would destroy the contribution from structure Vb and allow rapid rotation about the resulting single C-N bond. Such rapid rotation would average the environments of the methyl groups and yield a single proton resonance for both methyl groups. Donation by oxygen, on the other hand, would favour structure Vb to a greater extent than it is favoured in free DMF because the donor properties of oxygen should be enhanced by this structure. The appearance in the complex, but not in free DMF, of a significant spin-spin coupling between the methyl protons and the aldehydic proton was interpreted by Lappert and co-workers as supporting a greater contribution of the structure Vb in the complex. Complexes of a series of other Lewis acids with DMF have all yielded spectra showing the presence of nonequivalent methyl groups, indicating that in all the cases studied donation is from the carbonyl oxygen (38). The increased contribution of structure Vb in the complexes over that in free DMF has been confirmed by a variable temperature NMR study of the rates of internal rotation of the methyl groups in the BF_3 complex. The activation energy for internal rotation was found to be considerably greater in the complex than in free DMF (58).

The first reported NMR investigation of a ketone complex with BF_3 was an attempt by Lappert (32) to observe separate methyl resonances of the acetone.BF_3 complex due to methyl groups cis and trans to BF_3, as in VI. He was unable to observe separate signals even at -60°, and postulated a rapid exchange of BF_3 to account for this. An investigation



VI

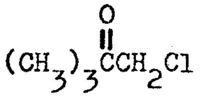


$$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 \longleftrightarrow CH_3CH{=}\overset{\overset{\bar{O}}{|}}{C}CH_3 \quad H^+$$

VIIa VIIb

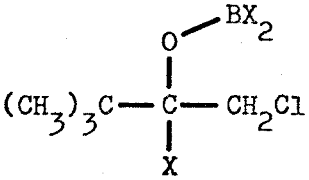
by Gates and Mooney (59) of the small coupling between α-protons across the carbonyl group in methyl ethyl ketone showed that, on complexing the ketone with BF_3, the coupling constant, $J_{H_\alpha,H_\alpha'}$, increases by a factor of three. This increase was attributed to a larger contribution from olefinic structures such as VIIb in the complex. Mooney and co-workers (43) have studied ^{11}B shifts of the boron trihalides on complexation with benzophenone.

Kaplan and Weisleder have recently reported the proton spectra of adducts of α-chloropinacolone (VIII) with the boron trihalides (60).



$$(CH_3)_3\overset{\overset{O}{\|}}{C}CH_2Cl$$

VIII



IX

The 1:1 BF_3 adduct yielded a simple proton spectrum in which the ketone resonances were shifted to low field. The adducts with BCl_3 and BBr_3, however, yielded an AB coupling pattern for the methylene resonance, i.e., a pattern showing that the two methylene protons are magnetically nonequivalent and strongly coupled. Magnetic nonequivalence of two protons which are chemically equivalent requires the presence of an asymmetric centre in the molecule ((2), p.379), which can only be explained readily if the adducts have the structure IX. Collapse of the AB pattern at higher temperatures was interpreted in terms of reversible addition of boron trihalide across the double bond. The adduct with BF_3 appears to be a normal donor-acceptor complex with the carbonyl oxygen acting as the donor.

(vi) Symmetry of Charge about Boron

The presence or absence of spin-spin multiplet structure due to coupling with boron, in the spectra of other nuclei in boron trihalide complexes, provides a potential source of information about the symmetry of electronic charge about boron. Boron-11, the major isotope, has a spin of 3/2 and a nuclear quadrupole moment, so that signals of nearby nuclei will be split into a 1:1:1:1 quartet if the boron environment is symmetrical. If the boron environment is sufficiently unsymmetrical the quartet should be collapsed due to rapid quadrupole relaxation of boron. The absence of splitting due to coupling with boron in the NMR spectra of all electrically neutral complexes of BF_3 with oxygen donors studied to date suggests the occurrence of such rapid quadrupole relaxation (35,52)[*]. The presence of such splittings has been observed in some electrically neutral complexes of nitrogen donors (37,52). It seems reasonable that the symmetry about boron could be lower in the complexes of oxygen donors because the donor-acceptor bond is much weaker than the three B-F bonds. However, several authors (e.g., Craig and Richards (46), Verkade et al. (61)) have suggested that collapse of the expected splittings might be

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[*] Splittings due to B-F coupling are present in the spectra of ionic complexes such as BF_4^- and BF_3OH^-. These are discussed in Chapters IV and X.

the result of rapid breaking and re-forming of donor-acceptor bonds. A choice between the two alternative possibilities is not readily made without extensive studies over a range of temperatures.

Miller and Onyszchuk (37) reported splittings due to coupling with boron in the proton spectra of the BCl_3 and BBr_3 complexes of trimethylamine, but no such splittings in the BF_3 complex. Their proposal of restricted rotation about the B-N bond in some of the complexes does not appear to account satisfactorily for this. Either rapid exchange of BF_3 or quadrupole relaxation of boron in the case of the BF_3 complex would appear more likely. Either explanation supports the postulate of weaker donor-acceptor bonding in the BF_3 complex than in the BCl_3 or BBr_3 complexes.

CHAPTER II

EXPERIMENTAL

(i) Materials

Boron trifluoride (Matheson) was bubbled through concentrated sulphuric acid containing boric anhydride and collected at liquid nitrogen temperature. It was then distilled from a trap at -78° to a trap at liquid nitrogen temperature, the initial and final cuts being rejected.

Reagent grade acetone (Mallinckrodt), methyl ethyl ketone, methyl isopropyl ketone, and pinacolone (Matheson Coleman and Bell), and practical grade mesityl oxide (Matheson Coleman and Bell) were dried over calcium chloride and magnesium sulphate, and fractionated; the fractions of boiling ranges 55.9-56.2°, 78.8-79.1°, 92.0-92.5°, 104.5-105.5°, and 128.5-128.6°, respectively, were used. In each case the amount required for the NMR samples was allowed to stand overnight over Linde 4A Molecular Sieves immediately prior to use.

Methylene chloride (Fisher Spectranalysed), acetone-d_6 (Stohler Isotope Chemicals), reagent grade methanol (Shawinigan), practical grade tetramethylsilane (Matheson Coleman and Bell) and reagent grade diphenyl ether (Fisher) were allowed to stand over Linde 4A Molecular Sieves before use.

$^{10}BF_3.CaF_2$ complex (Oak Ridge National Laboratory, estimated ^{10}B isotopic purity 97%) was heated gradually to 275° under high vacuum.

The $^{10}BF_3$ which evolved smoothly was collected at liquid nitrogen temperature and high vacuum distilled twice prior to use, each time rejecting small initial and final cuts.

Practical grade phorone (J.T. Baker), a brown liquid, was purified by vacuum sublimation onto a cold finger cooled by Dry Ice to give pale yellow needles which could be stored unchanged at 10°. Warming of the crystals to room temperature (29°) gave a pale yellow liquid.

Trichlorofluoromethane (Matheson) was allowed to stand at 0° over phosphorus pentoxide before use.

Anhydrous sulphur dioxide (Matheson) was condensed at -78° into a trap containing phosphorus pentoxide, warmed to -40° and allowed to stand for three hours.

Fluorosulphuric acid (Allied Chemical) was distilled twice in a stream of dry air in rigorously dried apparatus.

Sodium tetrafluoroborate (Harshaw), and the silver, ammonium and tetramethylammonium tetrafluoroborates (Alfa Inorganics) were used without further purification. The reagent grade solvents for the tetrafluoroborates, acetone (Mallinckrodt), acetonitrile (Fisher), dimethylformamide (Fisher), and dimethylsulfoxide (J.T. Baker), were also used without further purification, as were pivalonitrile (K & K Laboratories) and practical grade diglyme (Eastman Organic Chemicals).

(ii) Preparation of Samples

All NMR samples except the tetrafluoroborate solutions of Chapter X were prepared by standard high vacuum techniques (62,63). Reagents and solvent were degassed and stored on the vacuum line, the gaseous materials in storage bulbs. The BF_3 complexes were not prepared pure; instead, known amounts of acid and base were condensed from a calibrated volume directly into 5 mm. o.d. pyrex sample tubes into which suitable amounts of solvent had previously been distilled. Small amounts of tetramethylsilane and trichlorofluoromethane were added in the same fashion. In the case of less volatile reagents such as pinacolone and water an error in calculation of the amounts added was introduced by the non-ideality of the vapours. Care was taken to minimize such errors by the use of low pressures. Measured additions of diphenyl ether could not be carried out on the vacuum line because of low volatility. Instead, a known weight of diphenyl ether was added to the sample tube before attachment to the vacuum line; other materials were added on the vacuum line in the normal manner.

The samples were sealed off under vacuum with the contents still at liquid nitrogen temperature, then packed in Dry Ice and allowed to stand for more than an hour with occasional shaking. In many samples in which methylene chloride or acetone was the solvent this resulted in clear, colourless solutions at -78°; if solid remained it could be dissolved by some further warming, still keeping the solution below 0°. It was possible to obtain complete solution in these solvents, always keeping the sample temperature well below 0°, so that heat-sensitive samples such as those containing BF_3 in acetone solvent could be prepared under conditions allowing negligible decomposition. In other cases complete solution was effected by allowing the sealed samples to warm to room temperature. All samples containing BF_3 were stored at -78°; no appreciable discoloration occurred at this temperature even after standing for several months.

Approximate volumes of the solutions were determined by measuring the height of liquid in the sample tube and comparing this height with that of a known volume of liquid which had been added to the sample tube prior to the preparation of the sample. Since the number of moles of solute had been determined from condensation of a known pressure of vapour from a known volume, it was possible to calculate solution concentrations in moles per litre.

Tetrafluoroborate solutions were prepared directly in precision NMR tubes. Addition of the tetrafluoroborate salt was carried out in the dry box. The tubes were weighed after each addition of salt or solvent, and the molar proportions of the mixtures were calculated. The mixtures were degassed by passing a slow stream of nitrogen through the liquid for 10 minutes; this procedure also served to mix the sample and effect complete solution. Passage of nitrogen caused a negligible weight loss in solutions in water or dimethylsulphoxide, but a significant loss in solutions of acetone or acetonitrile.

The sample of pure $^{10}BF_3$ was made up in a 5 mm. o.d. quartz NMR tube, which was sealed off under vacuum. The sample was stored at liquid nitrogen temperature until use, and kept at temperatures below -25° at all times.

(iii) NMR Spectra

Spectra were obtained on a Varian Associates HR-60 NMR spectrometer operating at 60 Mc.p.s. for protons, 56.4 Mc.p.s. for fluorine, and 10.3 Mc.p.s. for boron-11. The spectra were calibrated by the usual audio sideband method, using a Muirhead-Wigan D-890-A decade oscillator. Sideband frequencies were checked occasionally with a

Hewlett-Packard 521C frequency counter. Accurate calibration of large ^{19}F chemical shifts with respect to trichlorofluoromethane was carried out by using the sidebands arising from the Varian V-3521 integrator, the frequency of which was found to be constant at 2034.9±0.3 c.p.s. over 18 months. Since most of the observed chemical shifts were in the region 8000-8400 c.p.s. from trichlorofluoromethane, the second sidebands of the standard and of the BF_3 complex generally occurred quite close together in the spectrum. Calibration of the separation of these centre sidebands, which are 180° out of phase with the normal signals, was accomplished by the usual method of applying audio sidebands, and gave highly reproducible chemical shift values for a given sample at a given temperature.

A Varian V-4340 variable temperature NMR probe was used to adjust the spinning sample tube to the required temperature. Low temperatures were obtained by passing cold air from a liquid air boiler into the Dewar jacketed assembly; high temperatures were obtained by passing heated air. The sample temperature was monitored by a copper-constantan thermocouple placed inside the jacket and attached to a Leeds and Northrup temperature potentiometer. Corrections for the difference between the monitored temperature and the true sample temperature were determined by placing a second thermocouple directly in a sample tube containing a suitable solvent.

(iv) Calculations

An IBM 7040 computer was used for the calculation of spectral shapes. Computer programmes for calculating line shapes resulting from various rates of chemical exchange of magnetic nuclei among six nonequivalent sites, and for the line shapes of a spin-1/2 nucleus coupled to a spin-3 nucleus undergoing various rates of quadrupole relaxation, are given in the Appendix. Matching of experimental and calculated spectra was done either visually to give a crude approximation of the rate of exchange (Chapter III), or by matching of measured spectral parameters of the observed spectra with those of a suitable range of calculated spectra to give a closer approximation of the rate of either chemical exchange (Chapter VII) or quadrupole relaxation (Chapter XI). The computer was also used to calculate exchange rates and activation energies directly from observed spectral parameters in a case in which a sufficiently simple coalescence pattern was obtained (Chapter VI).

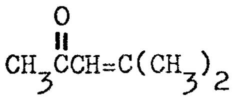
CHAPTER III

DILUTE SOLUTIONS OF BORON TRIFLUORIDE IN ACETONE

INTRODUCTION

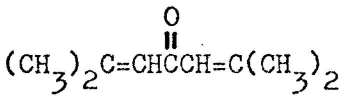
As has been discussed in Chapter I, the oxygen atom of the carbonyl group can behave as an electron pair donor, and in molecules which have more than one potential donor site can be the preferred site. Infrared studies, which have shown that the magnitude of the decrease of the carbonyl stretching frequency provides a qualitative measure of the strength of the donor-acceptor bond, indicate that complexes of simple ketones with BF_3 should have bond strengths similar to those of the BF_3 complexes of other carbonyl donors such as esters. However, in spite of the ready formation of complexes of simple ketones with BF_3 and the infrared evidence for a strong donor-acceptor bond, these complexes are much more prone to decomposition than other BF_3 complexes with carbonyl donors. Decomposition of BF_3 complexes of aliphatic methyl ketones was reported to become appreciable above 0^{o} (28), although earlier workers reported that the acetone.BF_3 complex was stable to 50^{o} (21). Decomposition might be initiated by traces of water or hydrofluoric acid; this could explain the different results obtained by different groups of workers. Most studies, including the present work, indicate that decomposition occurs at a considerable rate at room temperature. The reaction proceeds to yield a dark polymeric organic material and "hydration products of BF_3" (28).

The high reactivity of the complexed ketones apparently results from their ability to undergo aldol-type condensation reactions catalysed by the Lewis acid. Under the influence of aqueous protonic acids, dimerization and dehydration of acetone yields mesityl oxide (X). Lewis acids such as $ZnCl_2$ allow condensation of an additional



$CH_3\overset{\overset{O}{\|}}{C}CH=C(CH_3)_2$

X



$(CH_3)_2C=CH\overset{\overset{O}{\|}}{C}CH=C(CH_3)_2$

XI

molecule of acetone, followed by dehydration to yield phorone (XI). A strong Lewis acid such as BF_3 can evidently cause further condensation reactions. X and XI are susceptible to further aldol-type condensation because of the conjugated system linking the carbonyl group to the methyl groups; thus many different complex structures of higher molecular weights might be built up. These would contain extended conjugated systems, which can explain the intense dark colour of the reaction product.

The early stages of the decomposition reaction of acetone.BF_3 in excess acetone were studied in detail by ^{19}F NMR in the present work.

RESULTS AND DISCUSSION

(i) Room Temperature ^{19}F Spectra

Solutions of boron trifluoride in acetone, approximately one molar and initially colourless, progressively darkened through yellow and straw colour to dark brown on standing for two hours at 27°. On further standing, the liquid became black and completely opaque.

A series of room temperature ^{19}F spectra, obtained on a fresh 1.2 M solution of BF_3 in acetone prepared at low temperatures, is shown in Figure 2. Figure 2a, obtained as soon as possible after warming the sample to room temperature, already has another peak in addition to that expected for the acetone.BF_3 complex. Further spectra obtained at suitable time intervals show the gradual disappearance of the original peak and its replacement within two hours by a new peak 1.41 p.p.m. to higher field. The new peak became sharper as the original peak disappeared.

The appearance of the new peak is not directly related to the darkening of the solution since after 14 minutes, when the solution still had only a pale yellow colour, almost half of the fluorine was incorporated in the new species. Darkening of the solution continued when changes no longer occurred in the ^{19}F spectrum. The new peak did not become significantly sharper than shown in Figure 2d, even after the sample was allowed to stand at room temperature for several days. After a few weeks at room temperature new small ^{19}F peaks appeared and increased in size on further standing. Thus further slow decomposition reactions apparently occur; these were not investigated further.

(ii) Low Temperature ^{19}F Spectra of Fresh Solutions

The fact that the room temperature ^{19}F peaks were broad and not completely separated (Figure 2) suggested that a rapid reversible chemical exchange process, resulting in partial coalescence of the peaks, was occurring in addition to the slower decomposition reaction. If this were the case, sharper peaks should be obtained at lower

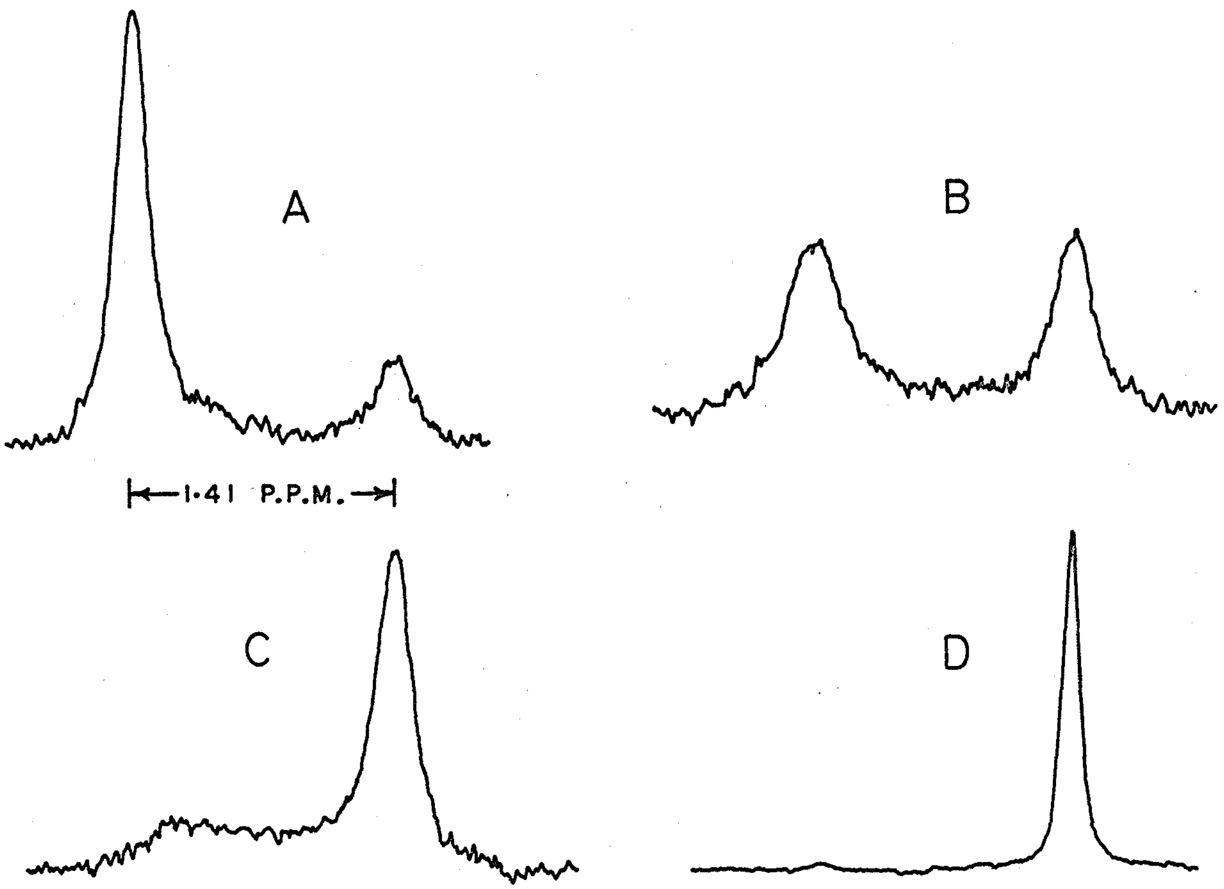


Fig. 2 Room temperature ^{19}F spectra of a 1.2 M solution of BF_3 in acetone. Reaction times at room temperature:

A. 4 minutes; colourless solution
B. 14 minutes; pale yellow solution
C. 34 minutes; orange solution
D. 108 minutes; dark brown solution

temperatures. The use of lower temperatures has the additional advantage, in the present study, that the decomposition reaction becomes very slow below about 0°C. Sealed samples stored at -78° showed no signs of decomposition after a month.

Solutions of BF_3 in acetone, containing essentially no decomposition products, could be prepared and sealed off on the high vacuum system without warming the samples above -40°. Such a sample, stored at -78° until use, yielded the -80° ^{19}F NMR spectrum shown in Figure 3a. The main peak, which is attributed to the 1:1 complex acetone.BF_3, is split into two peaks of relative areas 1:4 and of relative chemical shift 0.066 p.p.m. (3.70 ± 0.1 c.p.s. at 56.4 Mc. p.s). This splitting is of suitable magnitude and direction to be the result of an isotope shift, caused by a small difference in chemical shift between fluorine atoms attached to boron-10 and those attached to boron-11. The relative areas of the peaks are in accord with the natural abundance of the boron isotopes (^{10}B, 18.83%, and ^{11}B, 81.17%). In all previous examples of fluorine isotope shifts (64) the fluorine attached to the heavier nucleus has been found to absorb at higher field, as in the present case. Similar, rather smaller fluorine-on-boron isotope shifts (0.050 p.p.m.) have been observed in liquid boron trifluoride (65) and in solutions of the tetrafluoroborate anion (66-68). The isotope shift is the only splitting observed in the spectrum of the acetone.BF_3 complex; there is no evidence of coupling of ^{19}F to ^1H or ^{11}B.

A second small peak with multiplet structure is present in Figure 3a. This arises from $H_2O.BF_3$, as described in Chapter IV; a trace of water was apparently present in the solvent acetone, in spite

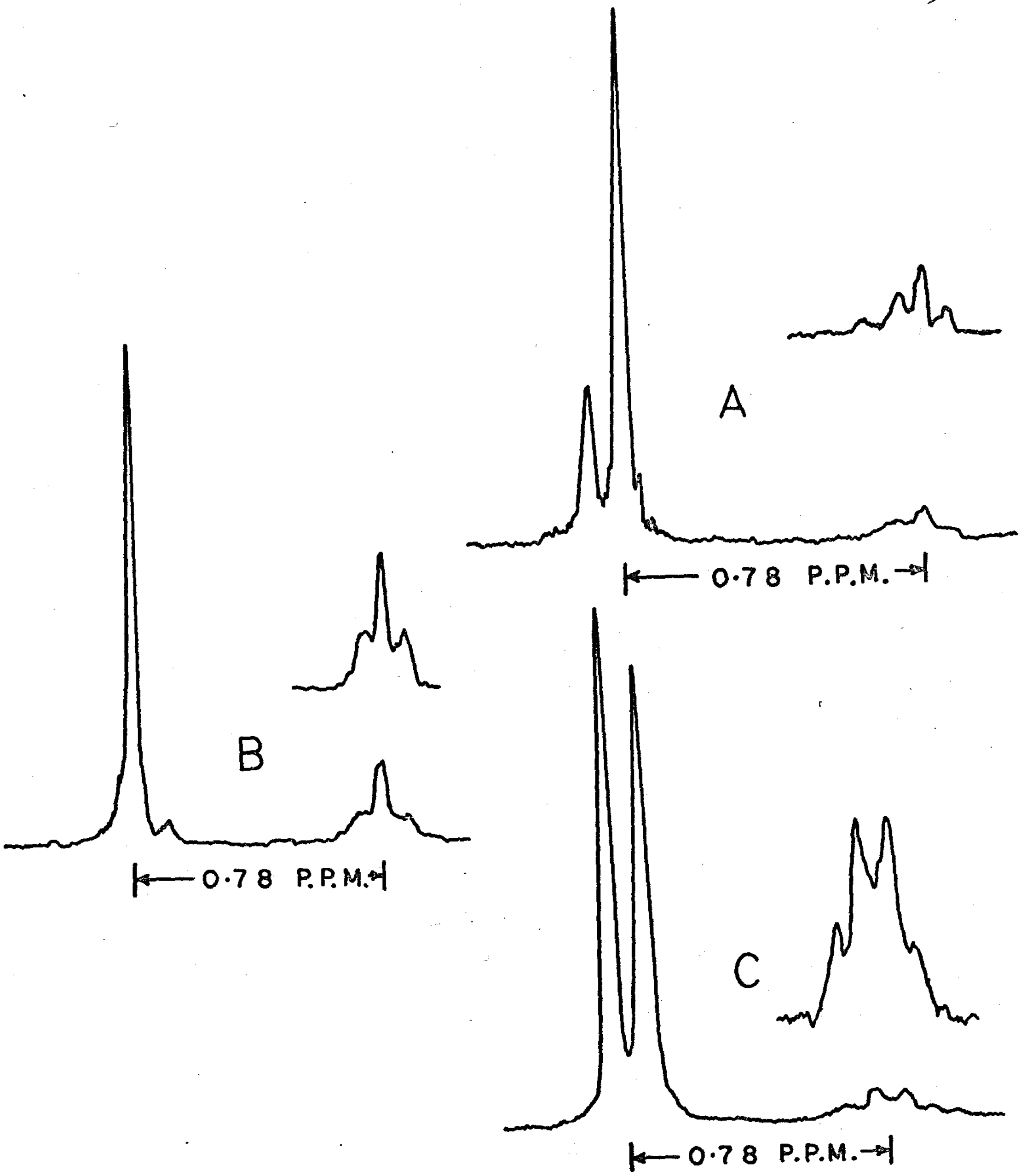


Fig. 3 Low temperature (-80°) ^{19}F spectra of freshly prepared solutions of BF_3 in acetone.

A. natural abundance BF_3

B. $^{10}BF_3$

C. $^{10}BF_3$: $^{11}BF_3$ = 53:47

of the drying procedures used. Since water is a much stronger Lewis base than acetone (Chapter IV), the water which was present was able to complex with an equimolar amount of BF_3. Since the BF_3 is also rather dilute, a significant fraction of the BF_3 thus became complexed with water.

Proof that the splitting of the acetone.BF_3 peak (Figure 3a) is indeed due to an isotope shift was provided by low temperature ^{19}F spectra of isotopically substituted samples. A solution of $^{10}BF_3$ in acetone yielded the -80° spectrum shown in Figure 3b. A single sharp main peak was obtained, with a second, very small peak about 0.066 p.p.m. to higher field, corresponding to the few percent of boron-11 present as isotopic impurity. A solution of almost equimolar $^{10}BF_3$ and $^{11}BF_3$ in acetone yielded the -80° spectrum shown in Figure 3c. The acetone.BF_3 absorption consists of a doublet of almost equal intensities. Electronic integration yielded 53±2% of $^{10}BF_3$, in agreement with the 50±2% calculated in preparing the sample. The changes in the relative sizes of the peaks separated by 0.066 p.p.m. with the changes in the isotopic ratio prove the presence of an isotope shift, and also illustrate that ^{19}F NMR spectra could be used in certain favourable cases to determine approximate isotopic abundances of other elements.

(iii) Low Temperature ^{19}F Spectra of Partially Decomposed Solutions

A 1.5 M solution of BF_3 in acetone was allowed to react for one hour at room temperature (22°), then cooled to -80°. The ^{19}F spectrum was then obtained at -80° and at several higher temperatures (Figures 4 and 5). Below 0° the temperature dependence of the spectra was reversible. Above 0° there was a tendency for the decomposition reaction

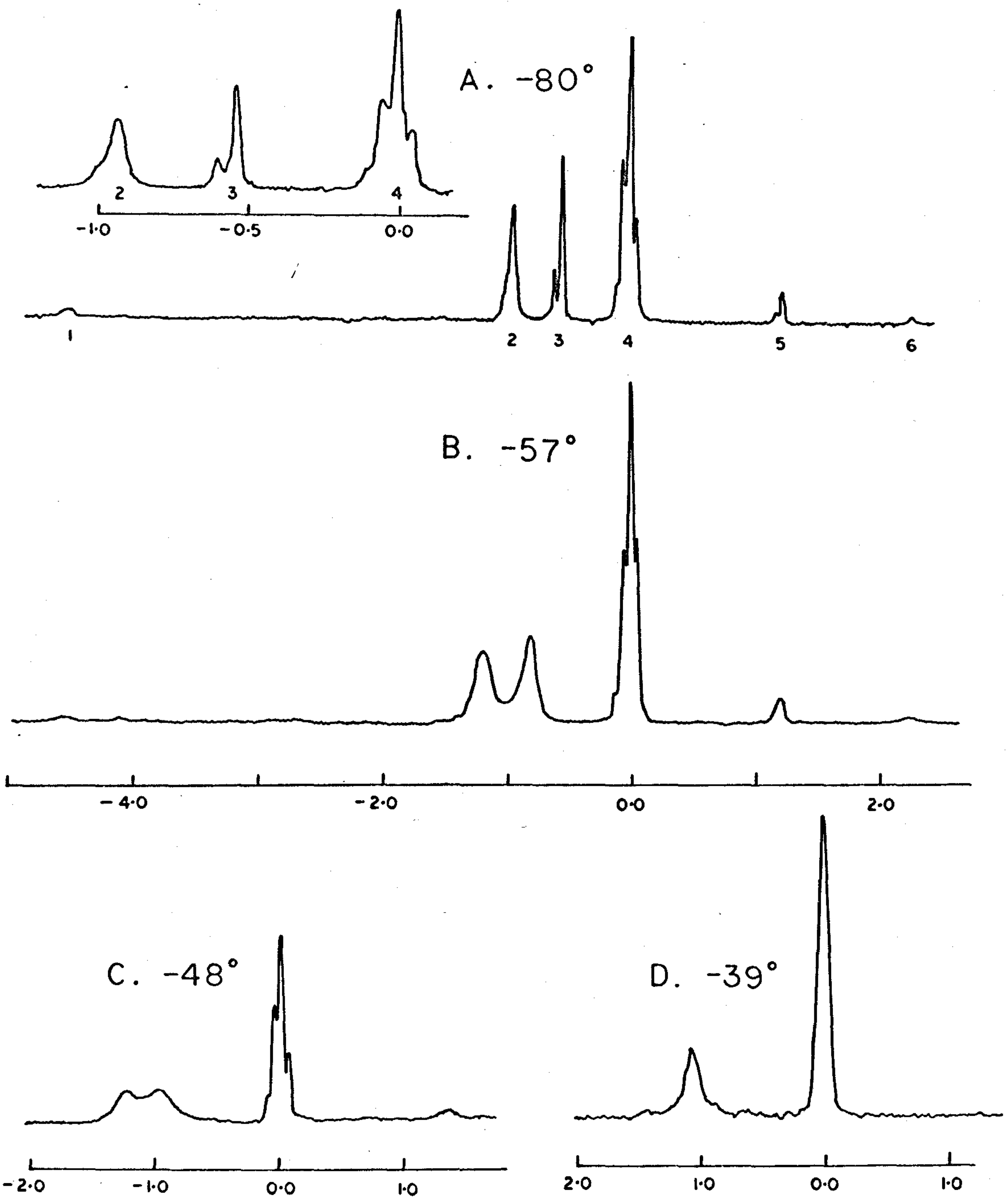


Fig. 4

Low temperature ^{19}F spectra of a 1.5 M solution of BF$_3$ in acetone, after one hour of reaction at room temperature. Calibration is in p.p.m. from peak 4.

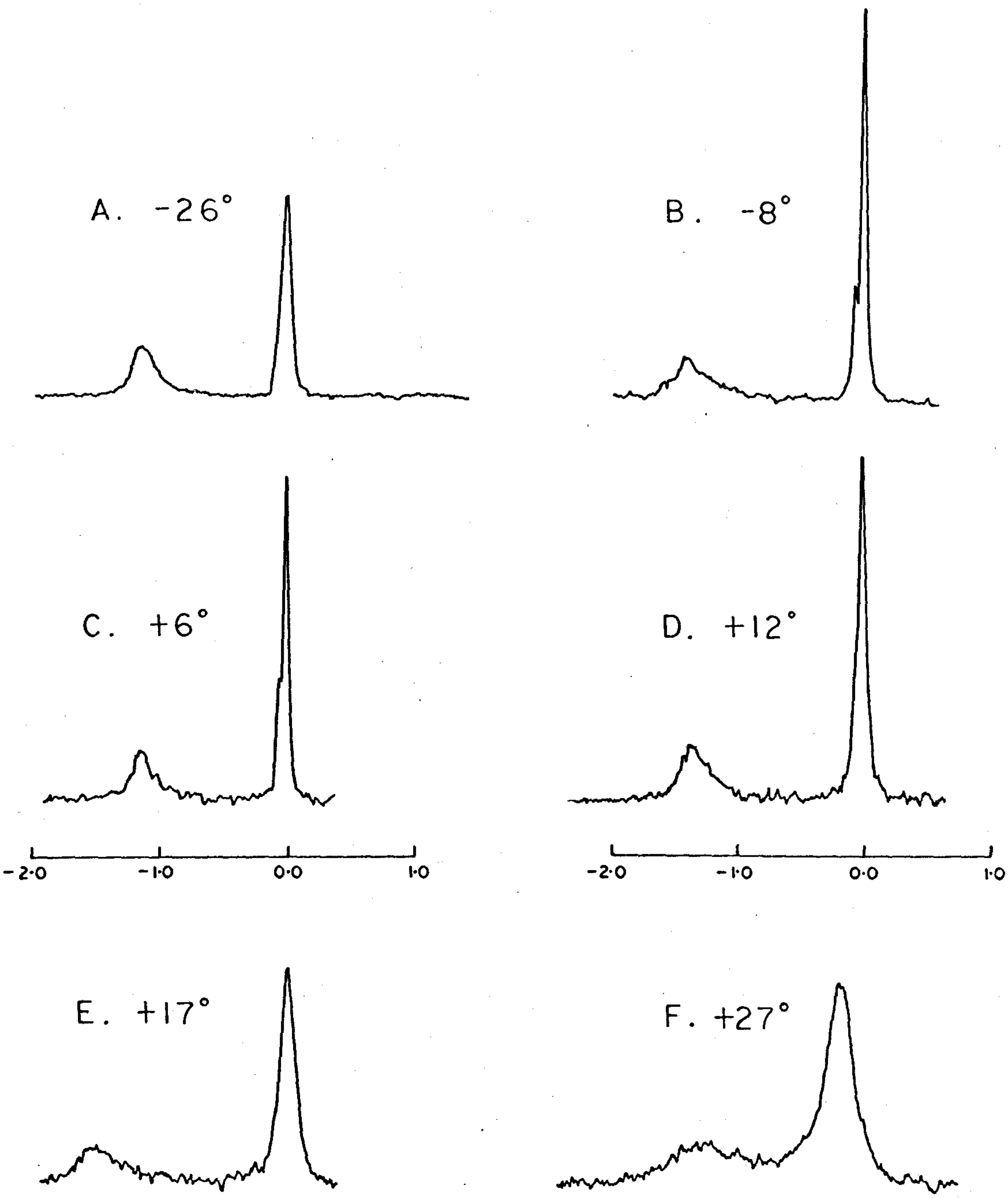


Fig. 5

^{19}F spectra between -26° and +27° of a 1.5 M solution of BF_3 in acetone, after one hour of reaction at room temperature. Calibration is in p.p.m. from peak 4.

to proceed, so that some changes in relative peak areas were observed after a period at a higher temperature. The collapse of the separate low temperature peaks as the temperature is raised must result from a rapid reversible exchange of fluorine atoms among the various species.

For convenience in the following discussion, the low temperature ^{19}F peaks are numbered from low to high field as in Figure 4a. They are calibrated in parts per million (p.p.m.) from peak 4, which from its fine structure is known to arise from $H_2O.BF_3$ (Chapter IV). Chemical shifts at -80° with respect to internal $H_2O.BF_3$ are given in Table II for all of the samples investigated. The shifts were almost constant in all of the samples; the presence of the standard pattern facilitated assignment of some of the peaks. It is of interest that in the deuterated samples the shifts with respect to $D_2O.BF_3$ were 0.19 ± 0.05 p.p.m. to lower field than the shifts with respect to $H_2O.BF_3$ in the non-deuterated samples. This is probably due chiefly to a high-field shift of $D_2O.BF_3$ with respect to $H_2O.BF_3$, indicating that D tends to be a better electron donor than H and allows a slightly greater buildup of electron density on the BF_3.*

Chemical shifts of the peaks with respect to internal trichlorofluoromethane can be measured accurately; that of the $H_2O.BF_3$ peak at -80° in the 1.5 M solution is $+146.58\pm0.1$ p.p.m. However, the use of chemical shifts in distinguishing between different complexes of BF_3 is severely limited by strong dependence of the shifts on temperature and concentration (47). The chemical shifts with respect to trichlorofluoromethane of all the resonances shown in Figure 4a were strongly temperature

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*Changes in ^{19}F chemical shifts of the other peaks as well are likely to occur on deuteration; these are likely to be smaller since the sites of isotopic substitution are further removed from the donor site.

TABLE II

-80° ^{19}F CHEMICAL SHIFTS OF PARTIALLY DECOMPOSED SOLUTIONS OF BF_3 IN ACETONE

$[BF_3]$ (moles/liter at -80°)	Isotopic Substitution	Chemical Shifts (p.p.m. from $H_2O.BF_3$*)						
		1	1A	2	3	4	5	6
1.5	-	-4.50	-	-0.93	-0.51	0	1.29	2.58
1.1	-	-4.59	-4.08	-0.95	-0.54	0	1.33	2.42
1.2	^{10}B	-4.56	-4.00	-0.89	-0.50	0	1.28	2.44
1.6	50% ^{10}B, 50% ^{11}B	-4.55	-4.05	-0.93	-0.50	0	1.28	2.46
0.9**	-	-4.59	-4.13	-0.91	-0.50	0	1.24	2.44
1.1	deuterated	-4.70	-4.32	-1.14	-0.72	0	1.07	-
1.0	deuterated	-4.69	-4.27	-1.13	-0.73	0	1.14	-
average shifts of non-deuterated samples		-4.56	-4.06	-0.92	-0.51	0	1.28	2.47
average shifts of deuterated samples		-4.70	-4.30	-1.14	-0.72	0	1.10	-
change of chemical shift on deuteration		-0.14	-0.24	-0.22	-0.21	-	-0.14	-

[*] 146.58 p.p.m. to high field of trichlorofluoromethane.

[**] also contains mesityl oxide, 0.5M.

dependent; changes in relative shifts within the group on changing the temperature were found to be much less, although still considerable over large differences in temperature.

All of the peaks in Figure 4a have chemical shifts in a quite narrow fraction of the total fluorine spectrum, corresponding to the usual range for fluorine on tetrahedral boron (52). Proof that all of the peaks arise from fluorine on boron is obtained from spectra of partially decomposed solutions of isotopically substituted BF_3. Figure 6 shows the low temperature spectra of partially decomposed solutions of $^{10}BF_3$, and of almost equimolar $^{10}BF_3$ and $^{11}BF_3$, in acetone. The pattern of chemically shifted peaks in both spectra is quite similar to that of Figure 4a, except that a new small peak, labelled 1A, is visible at quite low field. The $^{10}BF_3$ solution yielded sharp singlets for all peaks except peak 4 (a triplet). The solution of almost equimolar $^{10}BF_3$ and $^{11}BF_3$ yielded a spectrum with all peaks split into doublets except peak 4 (a quartet). In the latter spectrum the almost equal size of the F-on-^{10}B and F-on-^{11}B peaks allowed the isotope splitting to be detected even on peaks 1, 2, and 6 which were considerably broadened so that splitting could not be observed when natural abundance BF_3 was used (i.e., see peak 2 in Figure 4a, inset). The presence of the isotope splitting on all of the peaks proves that they all arise from fluorine on boron.

There are two reasons for believing that the spectra are due to BF_3 complexes rather than to such species as RBF_2 or $ROBF_2$. First, no other peaks have been observed in the ^{19}F spectrum which could arise from the fluorine which would have been split off, for example as

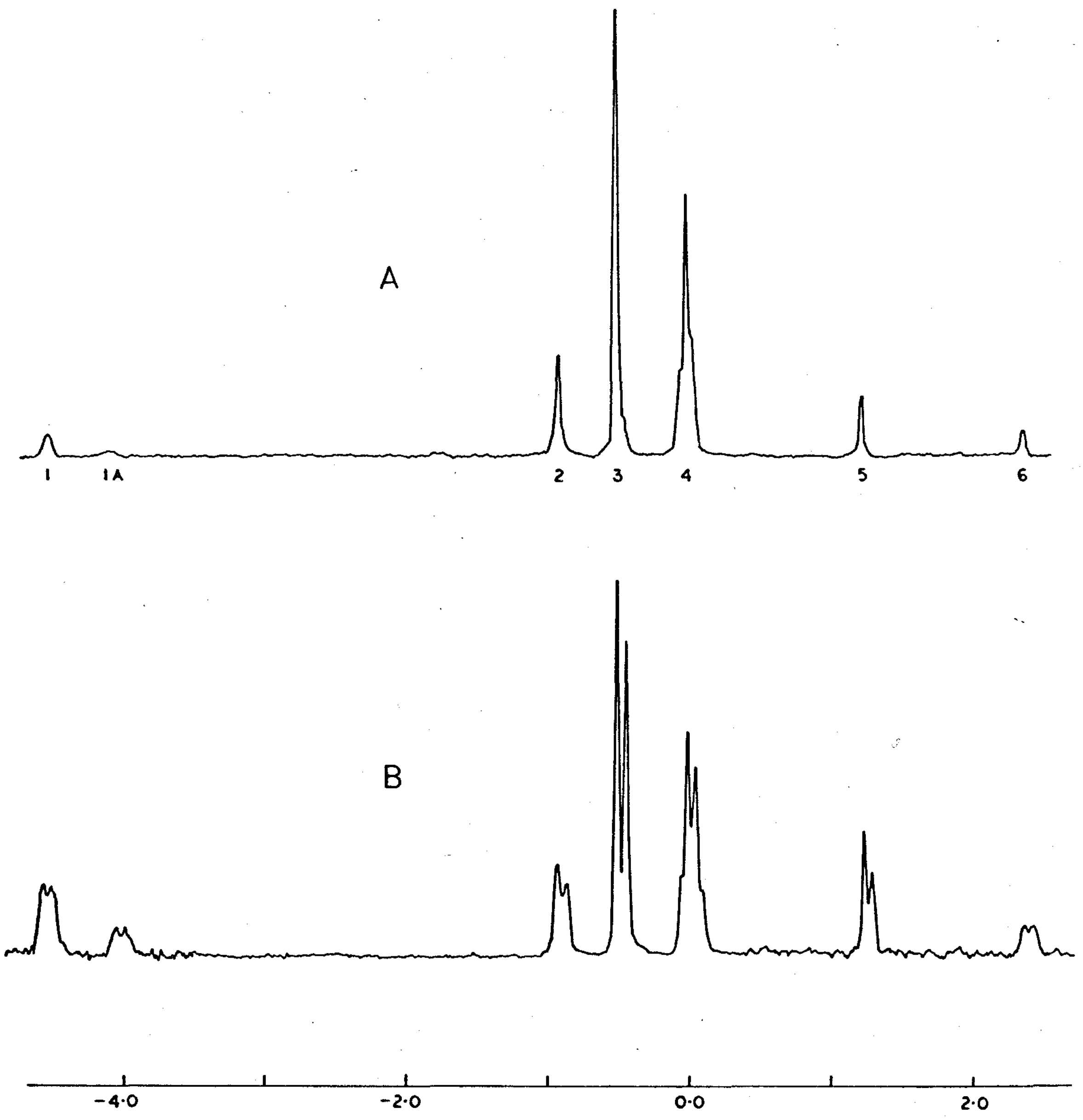

Fig. 6

-80° spectra of partially decomposed solutions of BF_3 in acetone, calibrated in p.p.m. from peak 4.

A. $^{10}BF_3$;

B. $^{10}BF_3$: $^{11}BF_3$ = 53:47

Peaks 1, 1A, 5, and 6 were obtained at a high power level.

fluoride ion or alkyl fluoride. Second, Figure 6b can be considered to be made up of two complete superimposed spectra like that of Figure 6a, offset by 0.066 p.p.m. The isotope shifts are remarkably similar on all peaks and are considerably different from the value of 0.050 p.p.m. found for the BF_4^- ion (66-68). The considerable change of 0.016 p.p.m. with a change of donor from fluorine to oxygen suggests a dependence of the isotope shift on the donor atom. The similarity of all the isotope shifts in the partially decomposed solution of BF_3 in acetone suggests that all the peaks arise from complexes of BF_3 with oxygen donors.

(iv) Identification of ^{19}F Peaks

In order to determine which of the peaks of Figure 4a was due to the initial species, acetone.BF_3, and which were due to intermediates and to the final product, low temperature NMR was used to monitor the decomposition reaction. Figure 7 illustrates the changes in appearance of the -80° spectrum of 1.1 M solution of BF_3 in acetone as the reaction at room temperature was allowed to proceed. Peak 3, initially very large and diminishing throughout the reaction, is due to the species initially present, acetone.BF_3. Peak 4, known from its fine structure to arise from $H_2O.BF_3$ (Chapter IV), gains in relative intensity throughout the reaction; hence $H_2O.BF_3$ is the final fluorine-containing reaction product. The changes in relative intensities of the other peaks are not as striking, and conclusions can not be drawn directly from the spectra.

The relative amounts of the various fluorine-containing species which give rise to the observed peaks can be determined more accurately

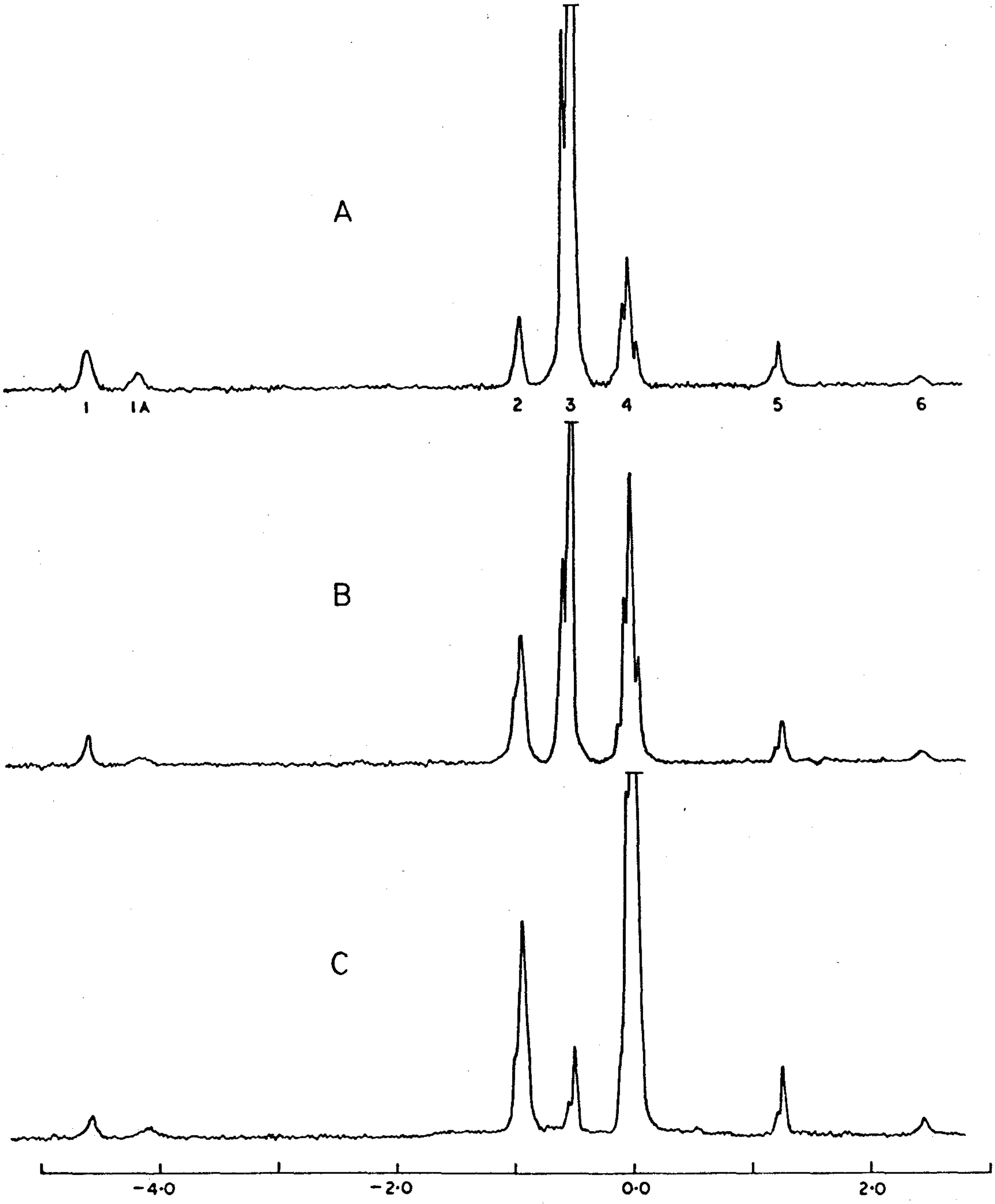

Fig. 7

-80° ^{19}F spectra of a 1.1 M solution of BF_3 in acetone after reaction at room temperature for
(a) 7 minutes;
(b) 22 minutes;
(c) 102 minutes.

Calibration is in p.p.m. from peak 4.

by electronic integration of the peak areas. The use of NMR spectrum integrals to monitor complex reactions has recently become important (13). In the present case this had to be done at low temperatures because of the rapid reversible chemical exchange process which caused coalescence of peaks above -50°. Thus the samples were warmed to room temperature (+22°) and held at this temperature for known periods of time, then quenched to -80° and spectrum integrals obtained. The errors involved in this method due to time lag in obtaining temperature equilibrium were believed to be small, since the small (5 mm.) diameter of a standard NMR sample tube allows rapid equilibration. Successive warming and quenching, each time obtaining spectrum integrals, was continued allowing suitable time intervals at +22°, until a single ^{19}F peak, due to the final fluorine-containing reaction product, was predominant.

Figure 8 is a plot of the changes in relative areas of the -80° ^{19}F peaks against reaction time at 22°. The numbering scheme is the same as in previous Figures; peak 6 never became larger than 1% of the total peak area, so that meaningful integral values could not be obtained. Figure 8 confirms the conclusions, drawn from Figure 7, that peak 3 is due to the initial species and peak 4 to the final species. The relative areas of peaks 1, 2, and 5 are seen to vary in such a way that they can with confidence be assigned to intermediate fluorine-containing reaction products, presumably complexes of BF_3 with the higher ketones formed in the acetone condensation reaction. Their later disappearance is not likely to be due to the disappearance of the organic donor involved. Instead, the additional water produced

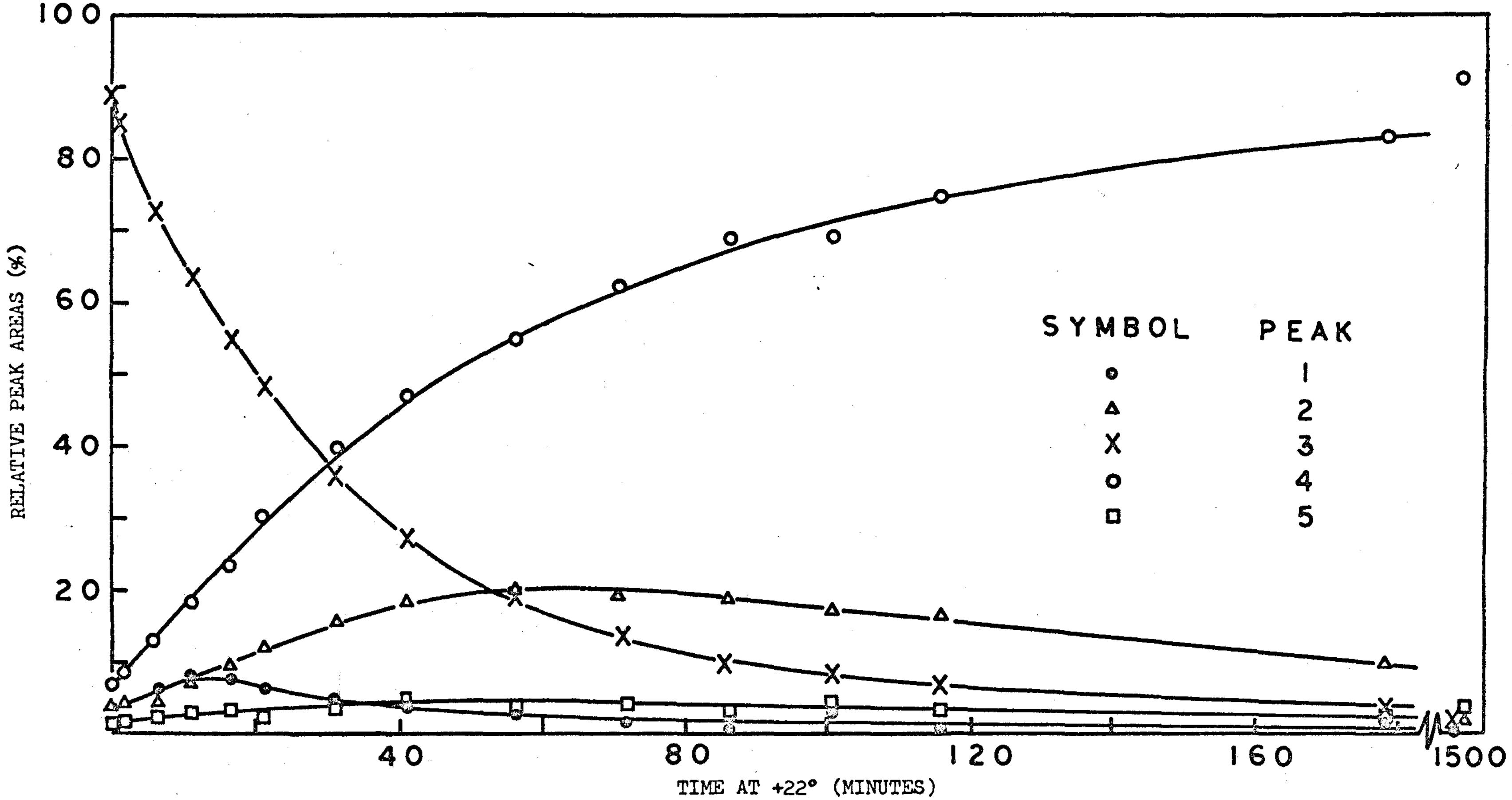

Fig. 8 Plot of the changes in relative areas of the -80° ^{19}F peaks (Figure 7) with reaction time at +22°

in the continuing condensation-dehydration reaction apparently competes successfully with the organic donors for the limited amount of BF_3 available, so that eventually the $H_2O.BF_3$ peak is the only major peak.

Proton spectra provide evidence of the ability of water to displace acetone from its complex (Chapter IV). In solutions which have undergone considerable decomposition the solvent acetone peak still accounts for most of the proton absorption, with only small peaks present due to other organic materials and to water. The very different appearance of the ^{19}F spectrum, with the $H_2O.BF_3$ peak predominant, shows that water can almost entirely displace the organic species from their BF_3 complexes. It also appears, from relative ^1H and ^{19}F peak areas, that the organic species other than acetone can displace acetone from its complex. If the other organic species are conjugated unsaturated ketones such as mesityl oxide (X), their greater base strength is easily explained. On formation of the complex, the unfavourable buildup of positive charge on the carbonyl group can be minimized by donation of electronic charge from the conjugated system. Electron donation from substituent methyl groups by the inductive effect or by hyperconjugation is effective not only for methyl groups directly attached to the carbonyl carbon as in acetone but also for those in vinylogous positions, such as the two methyl groups attached to the β-carbon atom in mesityl oxide.

It appears that peaks 1A and 6 do not arise from the BF_3-catalysed condensation-dehydration reaction. They are present in some but not all of the samples studied, and when present have different peak areas in otherwise similar samples. The areas of these peaks do not appear to vary greatly as the reaction proceeds. Peaks 1A and 6 apparently arise from trace Lewis base impurities in the solvent, which are able to displace acetone from its BF_3 complex so that they become noticeable in the ^{19}F spectrum although their concentrations are probably very low.* Very different preparative procedures would likely lead to different trace impurities; thus acetone-d_6 apparently contains none of the impurity which gives rise to peak 6. The behaviour of peaks 1A and 6 as the sample temperature is raised provides evidence for preferred complexation of the donors giving rise to these species (pp. 70-72).

Peaks 1, 2 and 5 apparently arise from BF_3 complexes of donors formed in the acetone condensation reaction. The most likely donors are unsaturated ketones such as mesityl oxide (X) and phorone (XI). The identification of peaks arising from complexes of X and XI was attempted by preparing samples each of which contained one of these ketones, as well as BF_3, in acetone.

A solution of mesityl oxide and BF_3, in the ratio 1:2, in acetone solvent yielded a -80° ^{19}F spectrum containing two large peaks of relative chemical shift 0.44 p.p.m. and a few very small peaks. Figure 9a shows the spectrum at a high power level so that the small peaks are visible. A comparison of the relative chemical shifts of all the peaks present yielded a pattern very similar to that observed in partially decomposed samples of BF_3 in acetone (Table II), and indicated that the two large peaks corresponded to peaks 2 and 3. This

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* This is analogous to the explanation for the presence of an $H_2O.BF_3$ peak in freshly prepared solutions of BF_3 in dried acetone (p.44; Figure 3).

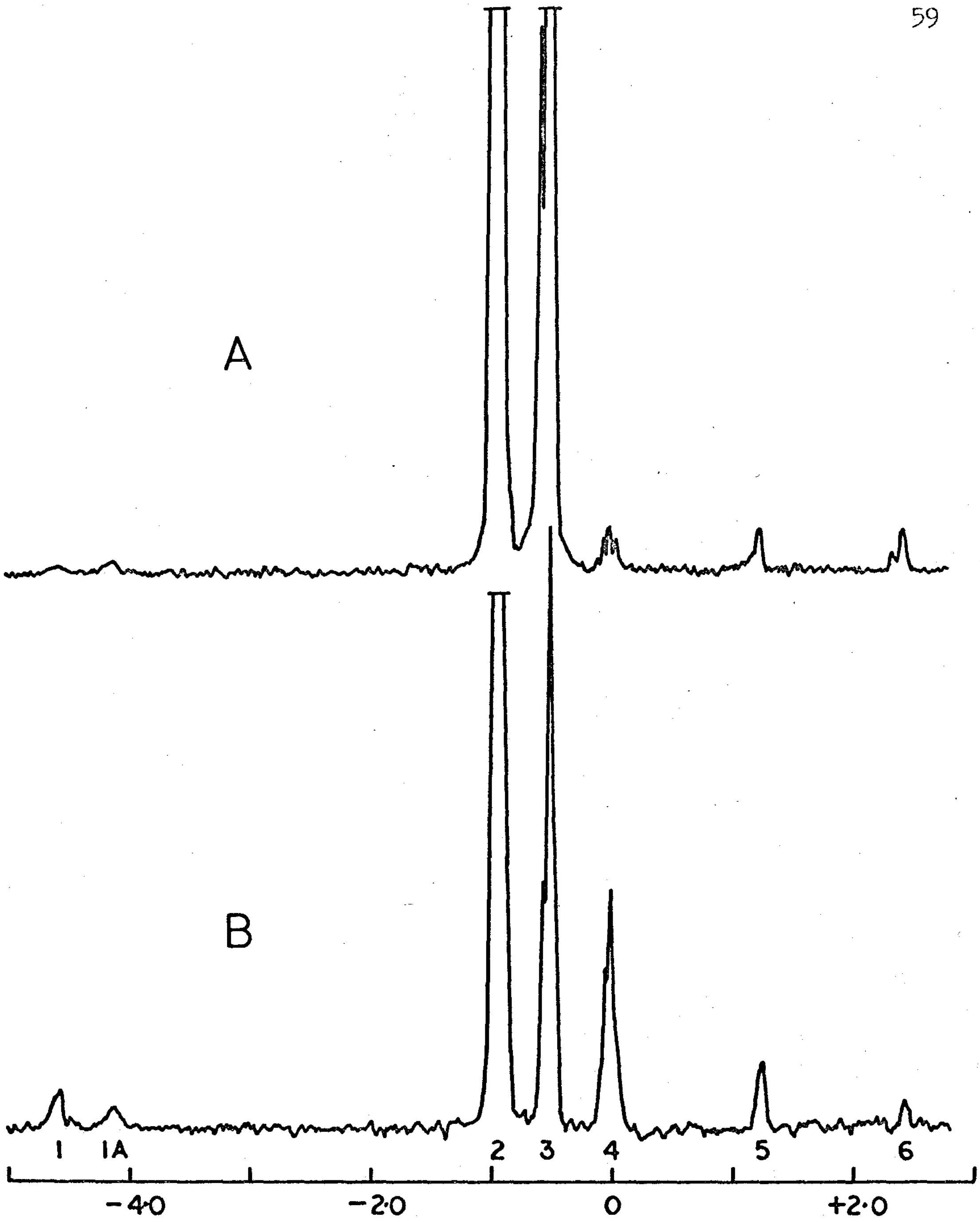

Fig. 9 -80° ^{19}F spectra of a solution of mesityl oxide (0.6 M) and BF_3 (0.9 M) in acetone, calibrated in p.p.m. from the small peak labelled 4.

A. Freshly prepared solution; high power level.

B. After 25 minutes of reaction at +22°; normal power level.

assignment of peaks was confirmed by the presence of skewed quartet fine structure on the small peak corresponding to peak 4. Since peak 3 arises from acetone.BF_3, the other large peak, peak 2, must arise from (mesityl oxide).BF_3. To obtain further evidence supporting this assignment of peaks, room temperature decomposition of the sample was allowed to proceed for 25 minutes. In the resulting -80° spectrum (Figure 9b), the expected diminution of peak 3 and growth of peak 4 was observed.* This usual pattern of changes in peak areas is further proof that the peaks have been assigned correctly. Electronic integration showed that most of the decrease in the initial large peaks was at the expense of the acetone.BF_3 peak. This is a further indication that acetone forms a weaker complex than mesityl oxide; as water is formed and competes successfully for BF_3, it removes BF_3 preferentially from the acetone complex. It is interesting that the stronger complex, (mesityl oxide).BF_3, yields a ^{19}F resonance to low field of the resonance of acetone.BF_3.

The low temperature ^{19}F spectrum of a partially decomposed solution of BF_3 in acetone-d_6 is shown in Figure 10a. A small amount of purified phorone was added in a dry atmosphere; the resulting -80° spectrum is shown in Figure 10b. A new large peak, 1.74 p.p.m. to low field of $H_2O.BF_3$ in a region of the spectrum which had previously been clear, is assigned to the phorone.BF_3 complex. A few new impurity peaks are also present. Since none of the usual set of ^{19}F peaks corresponds to the phorone.BF_3 peak, it appears that phorone is not produced in significant amounts in the condensation reaction. The

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* This spectrum, unlike that of Figure 9a, was obtained at a normal power level since the small peaks had gained sufficient intensity to be visible under normal conditions.

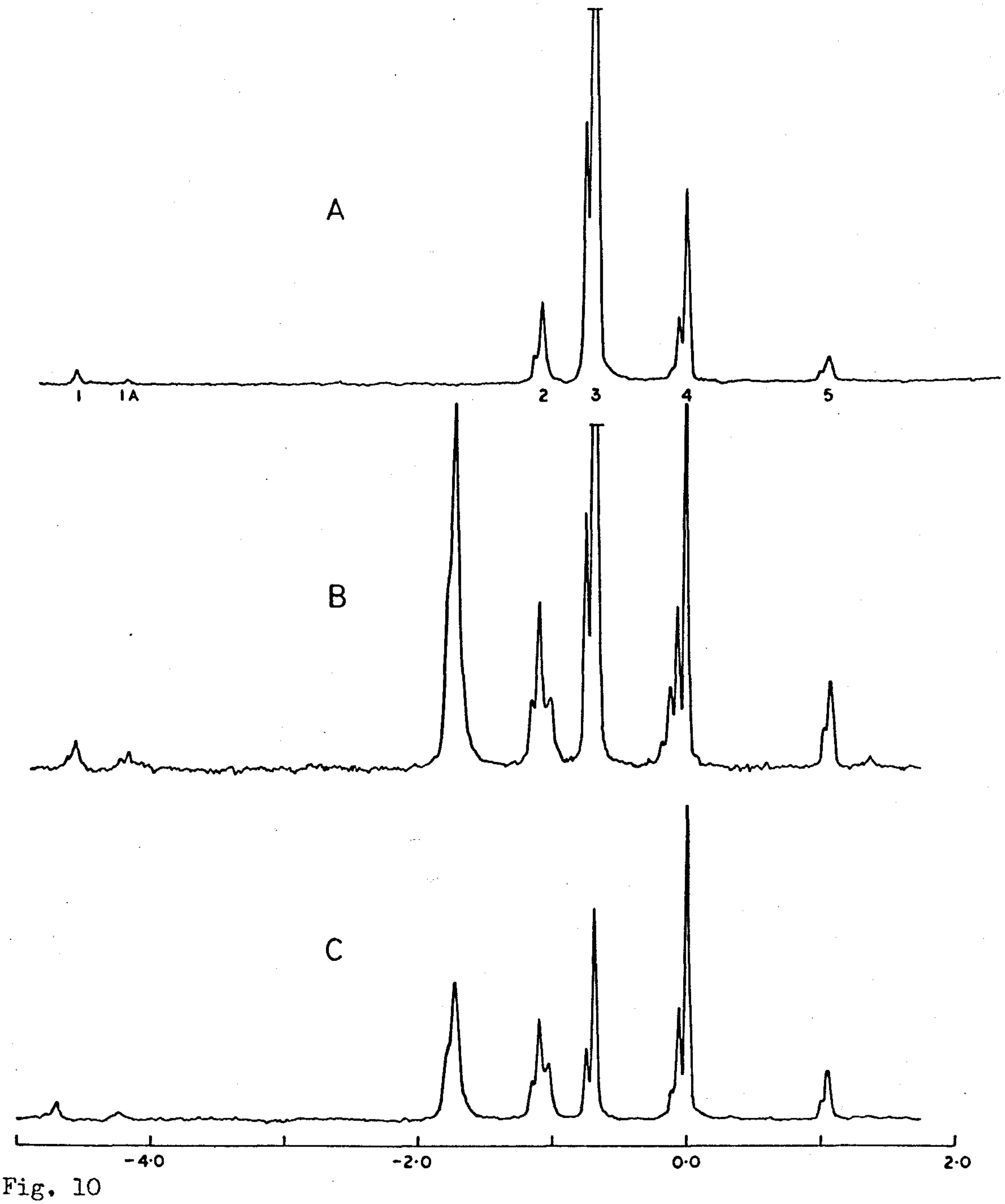

Fig. 10

-80° ^{19}F spectra of a solution of BF_3 in acetone-d_6, after 12 minutes of reaction at +22°.

A. before addition of phorone

B. immediately after addition of phorone

C. after a further 21 minutes of reaction at +22°

The spectra are calibrated in p.p.m. from peak 4.

large size of the phorone.BF_3 peak which results from the addition of only a small amount of phorone shows that phorone, like mesityl oxide, can displace acetone from its complex. The possibility remains that phorone might be produced in the condensation reaction but be more reactive than the other ketones in further condensation, so that its concentration would never become large enough to give an observable ^{19}F peak. To investigate this possibility, the solution was allowed to react at +22° for 21 minutes; the resultant -80° spectrum is shown in Figure 10c. Comparison of the relative peak areas of Figures 10b and 10c shows the expected increase in intensity of peak 4, with a marked decrease in the intensities of the phorone.BF_3 and the acetone.BF_3 peaks; the (mesityl oxide).BF_3 peak is not seriously affected. Thus phorone reacts much more rapidly than mesityl oxide; the results do not exclude the possibility of formation and rapid further reaction of phorone.

Peaks 1 and 5 were not identified. The demonstration that peak 2 arises from (mesityl oxide).BF_3 shows that at least one of the intermediate fluorine-containing products consists of a condensed α,β-unsaturated ketone; it is likely that peaks 1 and 5 arise from complexes of similar, higher molecular weight ketones. The absence of phorone suggests favoured formation or greater stability of linearly conjugated rather than cross-conjugated systems.

Other possible structures for the donors giving rise to peaks 1 and 5 could not be excluded. Acid-catalysed rearrangement of mesityl oxide is known to yield an equilibrium mixture containing 9% of the non-conjugated isomer 4-methyl-4-pentene-2-one (69), a species which could account for one of the unknown peaks. Small peaks could also arise from the enol forms of the ketones. Since alcohols tend to be better Lewis bases than ketones (19), the enol would likely form a stronger donor-acceptor bond with BF_3; this might partially compensate for the lesser stability of the free enol. Donors in which condensation has occurred but not dehydration would not be expected to be present in significant amounts because of their expected short lifetime, but they have not been rigourously excluded.

One or two of the small peaks which appeared on phorone addition (Figure 10b) could arise through acid-catalysed rearrangement of phorone to yield non-conjugated isomers (70).

(v) Changes in the Rate of the Condensation Reaction

Figure 8 shows that peak 4, arising from $H_2O.BF_3$, continued to increase in size as the condensation reaction proceeded until it was the only important peak. Its skewed quartet structure remained present through the first few hours of reaction but later collapsed; after 24 hours the peak had only a simple isotope shift of 0.066 p.p.m. It has been shown (Chapter IV) that the fine structure is present only when there is no appreciable amount of uncomplexed water in solution. The collapse of the fine structure probably occurred when sufficient water had been produced that $[H_2O] > [BF_3]$. It is of special interest that the fine structure survives over the time of reaction included in the curves of Figure 8. Since essentially all of the water becomes complexed as it forms, the rate of increase of the $H_2O.BF_3$ peak provides a measure of the rate of the dehydration reaction, which itself should closely parallel the rate of the ketone condensation reaction. In view of this it is of interest that the rate of increase of peak 4 falls off as the peak becomes larger; this indicates a falling off of the rate of the condensation reaction, and hence of the catalytic effect of the BF_3.

Decreasing effectiveness of BF_3 as a catalyst is to be expected if an essential condition for the condensation of a mole of ketone is the existence of a donor-acceptor bond between BF_3 and a ketone carbonyl group. As the reaction proceeds, the water which is formed complexes preferentially with the BF_3, so that the amount of ketone.BF_3 decreases; hence the rate of further reaction decreases. The catalytic effect of BF_3 thus appears to be due to its ability to form a complex with the carbonyl group. Most Brønsted acids, including $H_2O.BF_3$ (Chapter IV), are not strong enough to protonate acetone, a very weak Brønsted base, so that the "proton complex" of acetone, which might react in a fashion similar to the BF_3 complex, is not formed. However, very strong Brønsted acids such as anhydrous sulphuric acid are able to protonate acetone (71). The protonated acetone so formed is apparently quite reactive towards excess free acetone; addition of a small amount of oleum to anhydrous acetone causes decomposition at room temperature similar to that caused by BF_3, yielding organic products of similar colour and odour. This confirms that the observed decomposition is dependent on electron pair donation by acetone to a strong Lewis acid such as the proton, or BF_3, in the presence of excess acetone.

(vi) Kinetics of BF_3 Exchange

Some conclusions about the BF_3 exchange process can be drawn from the changes in appearance of the spectra above -50° (Figures 4 and 5). Peak 4 survives as a separate entity to a much higher temperature than the other peaks. This indicates that $H_2O.BF_3$, which gives rise to peak 4, has the longest lifetime of all the complexes present, and probably has the strongest donor-acceptor bond.

The extent to which $H_2O.BF_3$ is less labile than the other complexes is of interest. It was desired to determine this by calculation of rates of BF_3 exchange. It was presumed that activation energies for the different exchange processes would parallel the strengths of the donor-acceptor bonds involved. In a complex system undergoing chemical exchange the simplest NMR method for obtaining the average lifetime of a nucleus in one environment is to observe the broadening of the resonance line due to that environment under conditions of slow exchange, i.e., where there is negligible overlap of that peak with other peaks in the spectrum. This method can yield average lifetimes τ for each of n species which give rise to n peaks in the spectrum, each τ being determined independently of the shapes of the other peaks. However, this method is normally applicable only in a narrow temperature range. In the present case, calculations are possible for peak 4 only in a very different temperature range than that for the rest of the peaks. Because of this a direct comparison of lifetimes is of very little value. Even among the peaks which broaden and coalesce in a similar temperature range, some are too small to allow meaningful determinations of line broadening due to exchange.

Use of the slow exchange method to calculate lifetimes of BF_3 attached to mesityl oxide, acetone, and water (peaks 2,3, and 4) did not yield consistent results. Calculations from broadening of the peaks due to (mesityl oxide).BF_3 and acetone.BF_3, which apparently exchange BF_3 mainly with each other and which therefore should yield similar activation energies, yielded instead activation energies differing by a factor of three. At least part of the discrepancy arises from an additional broadening of the (mesityl oxide).BF_3 peak, which is apparently the result of a small proton-fluorine coupling since the peak is sharper in deuterated samples. This illustrates that the slow exchange method is very dependent on the requirement for sharp lines in the absence of exchange.

Whatever the cause of the errors, the slow exchange method did not provide useful information. In such a complex system rate determinations from the intermediate stages of chemical shift collapse must make use of the full line shape expression, equation (11)(p.72). Theoretical spectra can be calculated for various values of the bond lifetimes and compared with the observed spectra. Comparison leads to better trial values of the lifetimes, so that calculated spectra can eventually be obtained which closely resemble the experimental spectra.

In principle it should be possible, by the trial and error method of matching spectra, to duplicate any spectrum of partial collapse due to chemical exchange. It would appear that successful matching would confirm the values of the bond lifetimes used in the calculations and hence would yield a great deal of kinetic data for the process. In practice, however, only limited information can be obtained when more than two or three different sites are involved. The bond lifetime of each species present is an independent variable which must be adjusted for optimum agreement of observed and calculated spectra. In the present case of six site exchange the changes in shape of the spectrum are not sufficiently distinctive to allow all six bond lifetimes to be determined.

Additional difficulties arise. The relative probabilities of exchange can be affected by the exchange mechanism. This is not known, although a reasonable guess can be made on the basis of related studies (p.73). A difficulty which also occurs in the simpler case of two site chemical exchange is that relative chemical shifts may not remain constant over the temperature range of coalescence. In the present case several chemical shifts are involved, any of which could vary with temperature.

In spite of these difficulties it was desired to duplicate the experimental spectra as closely as possible. Successful duplication would confirm that the inconsistencies in earlier calculation at the slow exchange limit were due to extraneous effects which caused anomalous peak widths. It should be noted that successful duplication of the calculated spectra does not prove the exchange mechanism assumed in the calculations.

Computer matching was first attempted on the spectra of Figures 4 and 5. To obtain a manageable problem it was necessary to make assumptions which would decrease the number of independently variable bond lifetimes. The assumption of equal donor-acceptor bond lifetimes for all the species present did not lead to calculated spectra in agreement with those observed; peak 4 did not remain separate while the other peaks coalesced. A qualitative fit of observed and calculated spectra was obtained, however, by assuming equal donor-acceptor bond lifetimes for all of the species but $H_2O.BF_3$. When this species was assumed to have a bond lifetime 1000 times as long as that of the others, good agreement was obtained for the entire range of observed signal shapes (Figure 11). In the calculated spectra no allowance was made for the isotope shift or additional fine structure; the overall spectral shape is not seriously affected by these small splittings. Low temperature chemical shift values were used in all the calculated spectra; the fact that no allowance was made for temperature dependence of the relative chemical shifts accounts for the considerable discrepancy in peak separations, at higher temperatures, between observed and calculated spectra in the Figure. This discrepancy is not believed to have too great an effect on the signal shape.

The qualitative agreement of observed and calculated line shapes indicates that there is no gross error in the assumptions made. However, the artificiality of the assumptions should be kept in mind. A constant ratio of bond lifetimes over a temperature range, as is assumed, would not in fact occur; only the order of magnitude of the ratio is believed to be significant. It is very unlikely that the bond lifetimes of several different species would be equal; it is probably safe to assume only that they are equal to within an order of magnitude.*

The considerably greater base strength of mesityl oxide with respect to acetone (p. 57) suggests that acetone.BF_3 should be consid-

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* With the exception of peak 6; see next page.

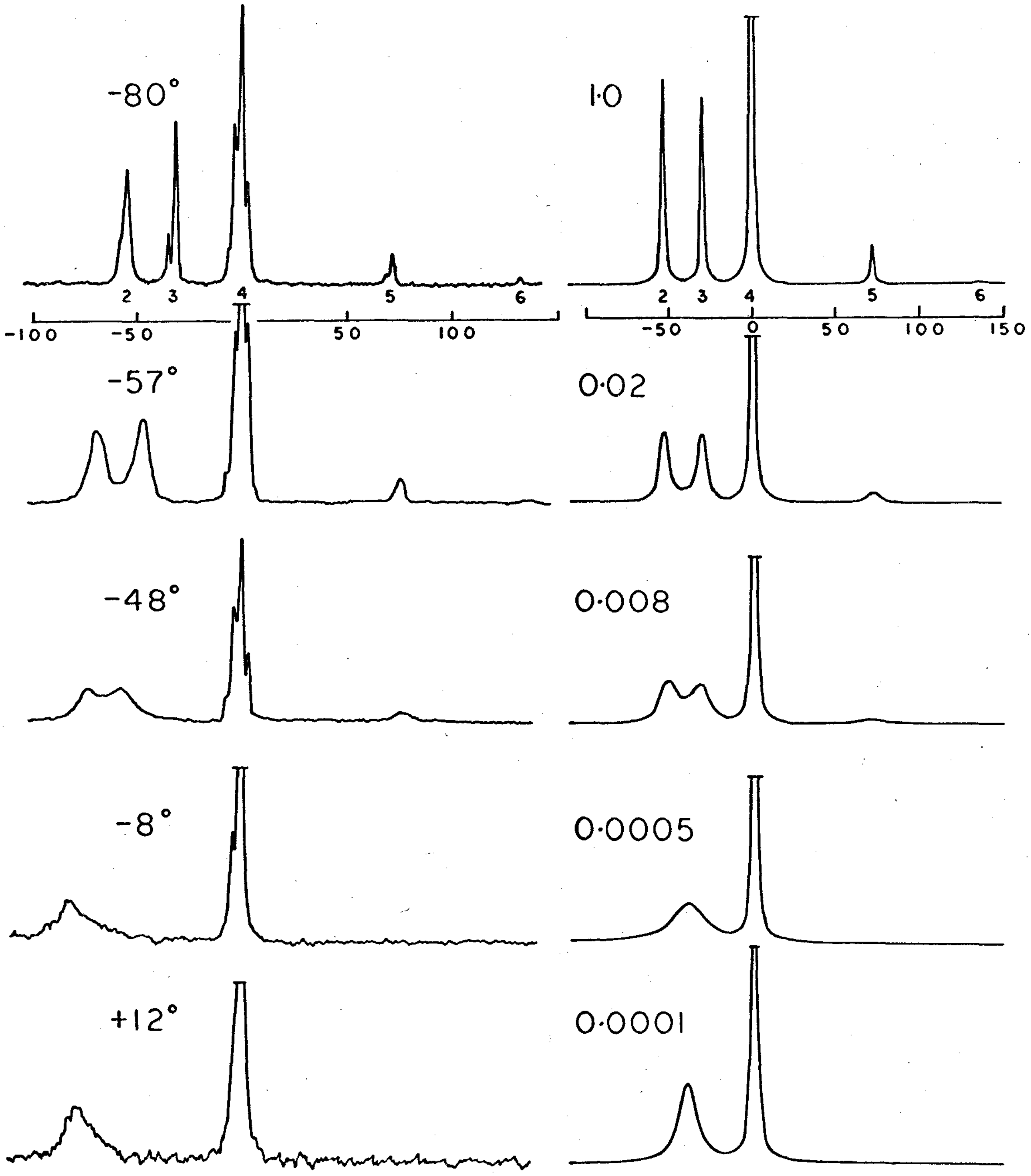

Fig. 11

Computer fit of some ^{19}F spectra of a partially decomposed 1.5 M solution of BF_3 in acetone, for the ratio $L_4/L = 1000$. The BF_3 bond lifetimes L (in seconds) are indicated for the calculated spectra. The spectra are calibrated in c.p.s. from peak 4.

erably more labile than (mesityl oxide).BF_3. If this were the case, BF_3 would exchange among molecules of the acetone.BF_3 complex more rapidly than between acetone.BF_3 and (mesityl oxide).BF_3; however, this more rapid exchange would not have any effect on the ^{19}F spectrum because it would not involve any change in the environment of the fluorine atoms. Thus the assumption of equal bond lifetimes for a number of species would still allow matching of spectra even if a single one of these species had a much shorter lifetime with respect to self-exchange.

Spectra of a second sample (Figure 12) differed from spectra of the first in that peak 6 was much larger (3.1% of the total peak area, compared with considerably less than 1% in the first sample). In this sample, peak 6 was found to remain separate to a higher temperature than was predicted from calculations based on the assumption of equal donor-acceptor bond lifetimes for all species but $H_2O.BF_3$. This effect was not observable in the previous sample, presumably because of the very small size of the peak. In order to obtain agreement of calculated and observed spectra when peak 6 was a considerable size, it was necessary to assume the donor-acceptor bond lifetime of this species to be intermediate between those of $H_2O.BF_3$ and of the ketone.BF_3 species. The fairly good fit shown in Figure 12 was obtained for the ratio of bond lifetimes

$$\text{ketone.BF}_3 : \text{peak 6 species} : H_2O.BF_3 = 1:20:1000.$$

The intermediate bond lifetime of the species giving rise to peak 6 indicates an intermediate bond strength. This lends weight to the postulate (p.58) that peak 6 arises from a Lewis base impurity which

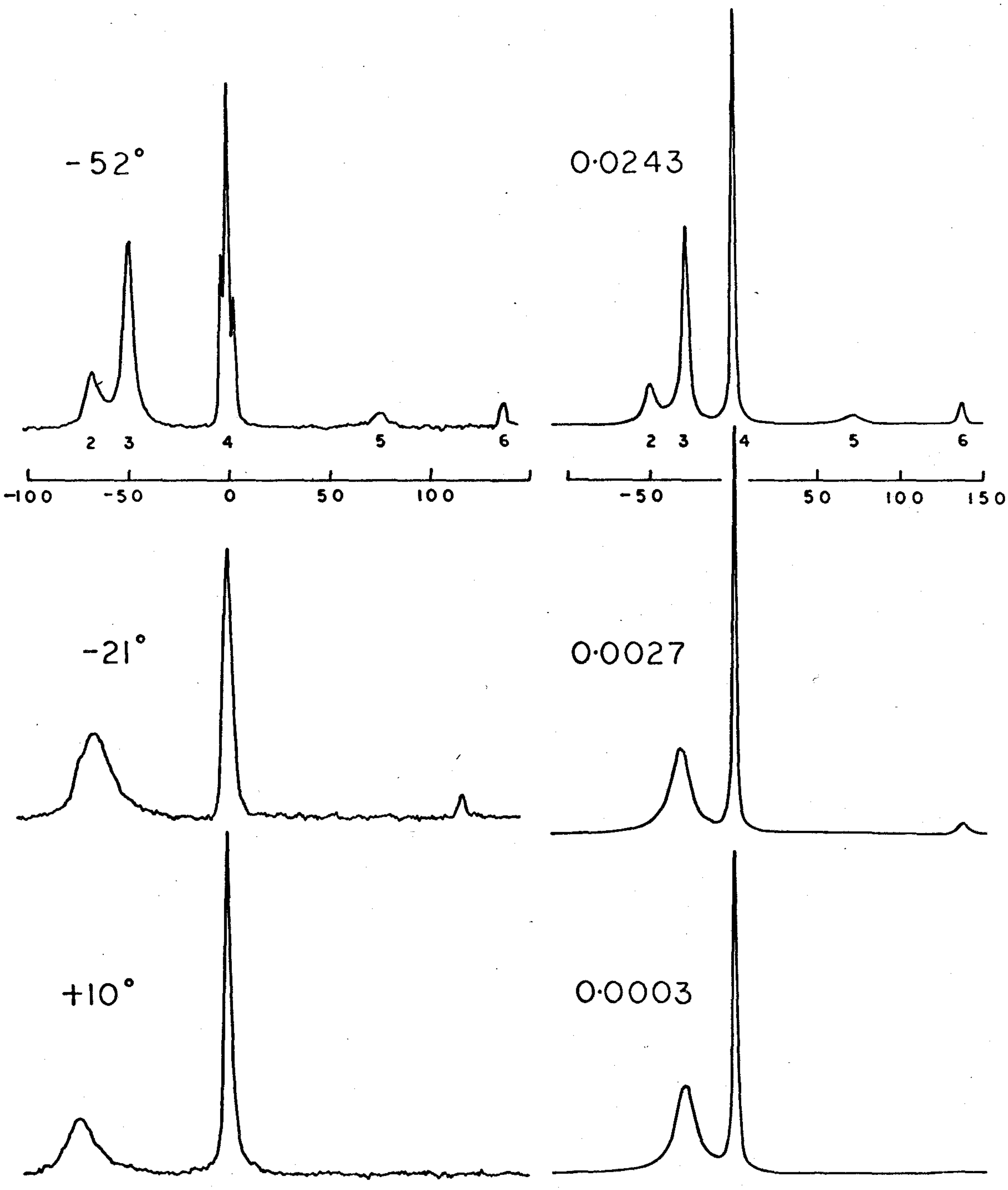

Fig. 12

Computer fit of some ^{19}F spectra of a partially decomposed 1.2M solution of $^{10}BF_3$ in acetone, for the ratio $L:L_4:L_6$ = 1:1000:20.
The lifetimes L (in seconds) are indicated for the calculated spectra. The spectra are calibrated in c.p.s. from peak 4.

has sufficient base strength to displace the ketonic species from their complexes.

The low temperature spectrum of a third sample had a well-defined peak 1A, 1.5% of the total peak area. This peak, like peak 6, persisted to a higher temperature than was predicted by assuming for it a lifetime equal to that of the ketone.BF_3 species. This suggests that it originates in a similar manner to peak 6, as was proposed earlier.

The approximations involved in calculating theoretical spectra for six site exchange are such that further information can probably not be obtained. The calculations have, however, illustrated that a general exchange of BF_3 among donor sites is occurring and shown that the order of lability of the donor-acceptor complexes is ketone.BF_3 $>$ (trace impurity).BF_3 $>$ $H_2O.BF_3$.

THEORY

The general line shape expression for a spin-1/2 nucleus undergoing chemical exchange among n different environments of chemical shifts ω_n (radians/sec.) and relative proportions p_n, can be given ((1), Chapter 10) by

$$I\,(\omega) \propto \mathrm{Re}\left\{\mathbf{W}\cdot\mathbf{A}^{-1}\cdot\mathbf{1}\right\}, \tag{11}$$

where Re $\{\ \}$ denotes "the real part of",

$\mathbf{W}$ is the vector $\left[p_1 \ldots\ldots\ldots p_n\right]$,

$\mathbf{1}$ is the vector $\begin{bmatrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{bmatrix}$, and $\mathbf{A}^{-1}$ is the inverse of the complex matrix $\mathbf{A}$, defined by

$$A_{m,m} = i\,(\omega_m - \omega) - \frac{1}{\mathcal{T}_m} , \qquad (12)$$

$$A_{m,n} = P_{m,n} , \quad m \neq n , \qquad (13)$$

where $P_{m,n}$ is the probability of a nucleus on site m making the transition to site n, and $\frac{1}{\mathcal{T}_m}$ is the inverse lifetime of each state m, given by

$$\frac{1}{\mathcal{T}_m} = \sum_{\substack{n \\ n \neq m}} P_{m,n} .$$

The diagonal matrix elements $A_{m,m}$ as written above assume infinitely sharp lines in the absence of exchange. Allowance can be made for the observed natural line widths at half height of about 1 c.p.s. (2π radians/sec.) by including an appropriate term:

$$A_{m,m} = i\,(\omega_m - \omega) - \frac{1}{\mathcal{T}_m} - 2\pi . \qquad (14)$$

The choice of P_{mn} terms requires an assumption about the mechanism of BF_3 rearrangement. There are two especially likely mechanisms:

a) exchange between two moles of complex:

$$D.BF_3 + D'.BF_3^* \longrightarrow D.BF_3^* + D'.BF_3 \qquad (15)$$

b) displacement by free base:

$$D.BF_3 + D' \longrightarrow D'.BF_3 + D \qquad (16)$$

Both of these have been reported to occur in ether.BF_3 complexes (50,53). Their relative importance depends on the relative proportions of free and complexed base; the presence of excess base favours equation (16). The present calculation assumes the first mechanism (equation (15)). Excess base is present, but almost entirely as the very weak base acetone which apparently cannot compete for BF_3 with the other donors. Since it appears to be the weakest base it is unlikely to be able to displace other bases from their complexes. If, as seems likely, other free base molecules are present only in negligible amounts, the dominant exchange mechanism should be that of equation (15).

This mechanism involving BF_3 exchange between two molecules of complex provides that, for a given sample at a given temperature, there will be an average donor-acceptor bond lifetime L_m for each species m of complex.* Exchange of BF_3 can then take place between all the possible pairs of complexes. Since all the species appear to be similar in the nature of the bonding, the relative likelihood of BF_3 exchange among different pairs should be dependent mainly on the strength of the donor-acceptor bonds, rather than on other effects which would contribute to the pre-exponential term in the rate expression. Thus it is reasonable to assume that the rate of exchange varies inversely as the bond strengths of the complexes involved.

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*The distinction between the bond lifetime, i.e. the average lifetime of the donor-acceptor bond of a species, and the environmental lifetime, i.e., the lifetime in a given environment of the nucleus being observed, should be kept in mind. Only the latter can be observed directly in the NMR experiment. However, the bond lifetime is required for the A matrix; the full line shape expression (11) makes use of the vector W to allow for exchange among different molecules of the same species so that the calculated line shapes involve environmental lifetimes. To illustrate the distinction between bond and environmental lifetimes, if only acetone.BF_3 were present in excess acetone, exchange of BF_3 among different acetone molecules would still take place, i.e., the bond lifetime would still be short. However, since only one environment would exist for all the BF_3, the environmental lifetime of fluorine would be infinite, and the exchange would have no effect on the ^{19}F spectrum.

$P_{m,n}$, the probability of transfer of a BF_3 on any site m to any other site n, can be given by

$$P_{m,n} = \frac{p_n}{L_q} , \qquad (17)$$

where $m \neq n$, and L_q is the greater of L_m and L_n. $H_2O.BF_3$ is known to have a stronger bond than the other complexes, and should exchange BF_3 more slowly. As an approximation it was assumed that the average bond lifetimes of all the other species were the same and equal to L. The bond lifetime of $H_2O.BF_3$ (peak 4 in the spectrum), designated L_4, was assigned a different value, so that

$$L_4 = f\,L$$

Thus the $P_{m,n}$'s can be summarized:

$$P_{m,n} = \frac{p_n}{L} \qquad m \neq n \neq 4 ,$$

$$P_{4,n} = \frac{p_n}{L_4} \qquad n \neq 4 ,$$

$$P_{m,4} = \frac{p_4}{L_4} \qquad m \neq 4 .$$

This gives the A matrix for six site exchange as follows:

$$A = \begin{bmatrix} i(\omega_1-\omega)-\frac{1}{\mathcal{T}_1}-2\pi & \frac{p_2}{L} & \frac{p_3}{L} & \frac{p_4}{L_4} & \frac{p_5}{L} & \frac{p_6}{L} \\ \frac{p_1}{L} & i(\omega_2-\omega)-\frac{1}{\mathcal{T}_2}-2\pi & \frac{p_3}{L} & \frac{p_4}{L_4} & \frac{p_5}{L} & \frac{p_6}{L} \\ \frac{p_1}{L} & \frac{p_2}{L} & i(\omega_3-\omega)-\frac{1}{\mathcal{T}_3}-2\pi & \frac{p_4}{L_4} & \frac{p_5}{L} & \frac{p_6}{L} \\ \frac{p_1}{L_4} & \frac{p_2}{L_4} & \frac{p_3}{L_4} & i(\omega_4-\omega)-\frac{1}{\mathcal{T}_4}-2\pi & \frac{p_5}{L_4} & \frac{p_6}{L_4} \\ \frac{p_1}{L} & \frac{p_2}{L} & \frac{p_3}{L} & \frac{p_4}{L_4} & i(\omega_5-\omega)-\frac{1}{\mathcal{T}_5}-2\pi & \frac{p_6}{L} \\ \frac{p_1}{L} & \frac{p_2}{L} & \frac{p_3}{L} & \frac{p_4}{L_4} & \frac{p_5}{L} & i(\omega_6-\omega)-\frac{1}{\mathcal{T}_6}-2\pi \end{bmatrix} \qquad (18)$$

Numerical solutions of the line shape equation (11) can now be obtained for input data consisting of the chemical shifts and the corresponding relative peak areas, together with estimated values of L and f. The programme used is shown in the Appendix, Figure 37. Empirical variation of L and f yielded trial spectra in the form of an approximate computer plot which could be compared directly with experimental spectra. By successive approximations of L and f it was possible to obtain fairly good agreement with the observed spectra over the entire temperature range (Figure 11).

The line shape expression and computer programme were easily modified to include a third different donor-acceptor bond lifetime for peak 6; successive approximations again led to good agreement of calculated and observed spectra (Figure 12).

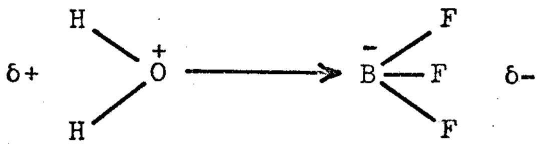
CHAPTER IV

THE ADDUCT $H_2O.BF_3$

INTRODUCTION

The existence of the donor-acceptor complexes $H_2O.BF_3$ and $(H_2O)_2.BF_3$ has been well established (72). The degree of ionic dissociation in the molten complexes has been estimated as 10% and 17% respectively (19, 73). Solid state NMR studies at 90°K have shown that the crystalline complexes are not ionic; closely related studies involving rapid cooling of the liquid to 90°K and "freezing in" of the liquid structure have confirmed that ionic dissociation occurs to a considerable extent in the molten complexes (74). A single crystal x-ray diffraction study has confirmed a hydrogen bonded structure for the 2:1 complex (75).

It is generally believed that the monohydrate is a simple donor-acceptor complex with the structure $H_2O \longrightarrow BF_3$. This behaves as a strong acid due to withdrawal of electron density from the O-H bonds:



Thus in aqueous solution $H_2O.BF_3$ is extensively converted to the ionic form of the dihydrate, $H_3O^+.BF_3OH^-$. The solutions also undergo extensive disproportionation to yield HBF_4 and $HBF_2(OH)_2$, and hydrolysis to yield $HBF(OH)_3$ and $B(OH)_3$ (76). Diehl has reported the ^{19}F spectra of such solutions (47). He observed separate broad resonances which he attributed to HBF_4, HBF_3OH, $HBF_2(OH)_2$, and $HBF(OH)_3$ in concentrated solutions at -30°; no fine structure was visible. Coalescence of the peaks was observed at higher temperatures, indicating that the disproportionation reaction is rapid, apparently because of the high acidity of the medium. A similar rapid disproportionation does not occur in a concentrated solution of KBF_3OH in water at room temperature as fine structure due to B-F coupling was observed ((77), p. 79).

Water is a sufficiently strong Lewis base to displace many organic donor molecules from their donor-acceptor complexes. For example, methanol is completely displaced from the complex $(CH_3OH)_2.BF_3$ on standing with a stoichiometric amount of water (78). In an early ^{19}F NMR study (48), Ogg and Diehl noted that water has a considerably greater BF_3 affinity than a wide range of alcohols. Since adducts of alcohols with BF_3 are reported to be more stable than adducts of carbonyl compounds (19), it is to be expected that acetone would also be displaced from its BF_3 complex by water.

^{19}F spectra of solutions of the acetone.BF_3 complex in acetone and methylene chloride solvents are described elsewhere in this thesis. These spectra contained a small unexpected peak which was shown to arise from the simple molecular $H_2O.BF_3$ complex. The detailed proof of structure of this complex by NMR is reported in the present chapter.

RESULTS AND DISCUSSION

Low temperature (-80°) proton and fluorine NMR spectra of a solution of water and BF_3, in a mole ratio of 1:2 (0.44 M and 0.86 M) in acetone solvent are shown in Figure 13. The proton spectrum (Figure 13a) has two small peaks, to low field of the solvent acetone peak, which can be attributed to species complexed with BF_3. The small peak at 2.81δ may be assigned to acetone complexed to BF_3; the 0.64 p.p.m. shift of the acetone peak to low field on complex formation is in reasonable agreement with the value of 0.59 p.p.m. found for solutions of acetone and BF_3 in methylene chloride (Chapter VI). The small low field peak at 12.42δ has a 1:3:3:1 quartet fine structure with a spacing of 2.93±0.1 c.p.s. The fluorine spectrum (Figure 13b) consists of two major peaks of chemical shifts 146.05 and 146.59 p.p.m. to high field of $CFCl_3$, each further split by fine structure. The low field peak is assigned to the 1:1 complex of BF_3 with acetone, since this is the major peak in samples of BF_3 in acetone containing only a trace of water.

This peak is split by a ^{10}B-^{11}B isotope shift of 0.066 p.p.m. (p. 44). The high field ^{19}F peak has a skewed quartet structure with unequal splittings. The splittings are similar in size to those of the ^{1}H low field quartet, and to the isotope shift on the low field ^{19}F peak (3.72±0.1 c.p.s. at 56.4 Mc./sec.). The splitting pattern can be accounted for by an isotope shift of 0.066 p.p.m., as for the low field peak, and also a splitting of each of the F-on-^{10}B and F-on-^{11}B peaks into a 1:2:1 triplet with spacings of 2.93 c.p.s. Figure 13c shows the theoretical spectrum based on these assumptions,

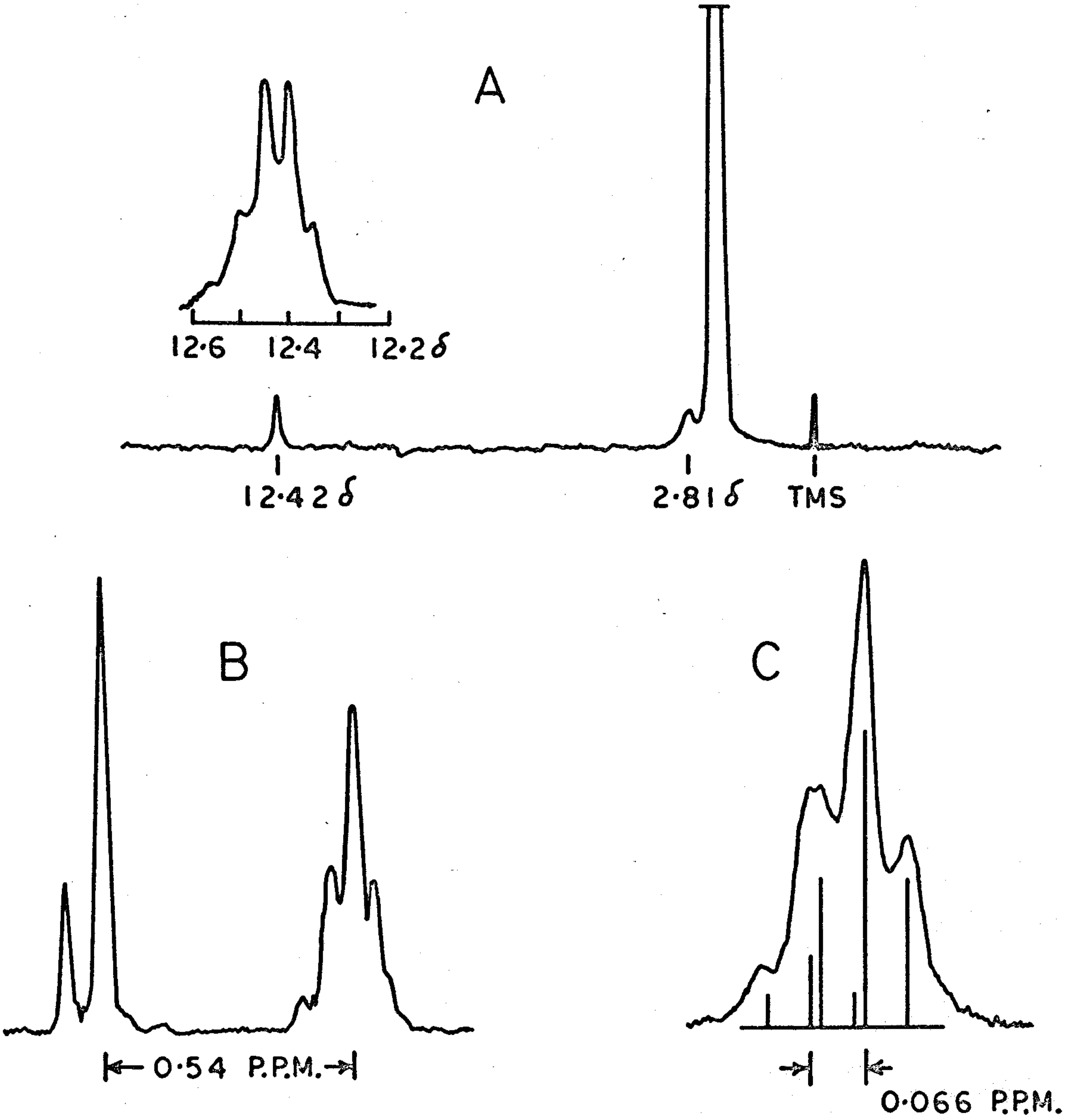


Fig. 13

Spectra of an acetone solution of water and BF_3, in the mole ratio 1:2 at -80°

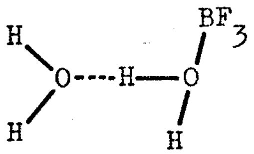
A. ^1H spectrum (60 Mc.p.s.)

B. ^{19}F spectrum (56.4 Mc.p.s.)

C. The high field multiplet of the ^{19}F spectrum, with the theoretical spectrum superimposed.

together with the observed spectrum. Agreement is good.

The presence of a 1:2:1 triplet in the ^{19}F spectrum and a 1:3:3:1 quartet with the same splitting in the ^{1}H spectrum is convincing evidence for spin coupling between three equivalent fluorines and two equivalent protons. This proves the existence in solution of the simple molecular complex $H_2O.BF_3$. The high acidity of this complex, which is the BF_3 analogue of the proton complex of water, H_3O^+, is shown by its very low field proton resonance, which occurs in the same region of the proton spectrum as H_3O^+ and other strong acids (79,80). Other plausible structures for a complex of water with BF_3 in acetone, such as $H_3O^+.BF_3OH^-$ and $(CH_3)_2C{=}OH^+.BF_3OH^-$, would not yield the observed coupling pattern and can thus be excluded. The 2:1 molecular complex XII can be excluded by the ^{1}H spectrum which does not have any peak which can be attributed to the second molecule of water. A 2:1 complex can also be excluded by considering the relative areas of the ^{19}F peaks. In preparing the sample, sufficient water was added to complex with 50% of the BF_3 if a 1:1 complex is formed, or 25% of the BF_3 if a 2:1 complex is formed. Thus 50% of the total F-on-B peak area should be found in the $H_2O.BF_3$ skewed quartet if a 1:1 complex is formed, or 25% if a 2:1 complex is formed, assuming that BF_3 complexes quantitatively with water rather than with acetone as is indicated



XII

by the ^{1}H spectrum. By electronic integration, 56% of the total peak area in the ^{19}F spectrum was found to be in the $H_2O.BF_3$ peak; this indicates a 1:1 complex.

The conclusion that all the water is present as the 1:1 complex $H_2O.BF_3$, in a sample made up in acetone solution so that $[H_2O] < [BF_3]$, depends on the correctness of the assumption concerning the origin of the observed peak splittings. The assumption was confirmed by low temperature studies of the ^{19}F spectra of some isotopically substituted samples.*

Figure 14a shows the -80° ^{19}F spectrum obtained when $^{10}BF_3$ is used. The high field multiplet becomes a symmetrical 1:2:1 triplet. The acetone.BF_3 absorption consists of a single main peak, with a very small peak just visible on the high field side, arising from about 3% of $^{11}BF_3$ present as isotopic impurity. The use of BF_3 containing approximately 50% of ^{10}B and 50% of ^{11}B yielded the low temperature spectrum shown in Figure 14b. The high field multiplet is a 1:3:3:1 quartet resulting from the overlap of two 1:2:1 triplets of almost equal intensity, due to $H_2O.{}^{10}BF_3$ and $H_2O.{}^{11}BF_3$. The acetone.BF_3 peak is a doublet, the peaks having almost equal intensities. Figures 14a and 14b confirm the postulated contribution of the isotope shift to the skewed quartet structure of the high field peak of the ^{19}F spectrum of Figure 13.

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* These were prepared as samples of BF_3 in acetone; the $H_2O.BF_3$ peak arose during partial decomposition as described in Chapter III. Other peaks present as a result of the decomposition reactions did not interfere with the $H_2O.BF_3$ peak and can be neglected in this discussion.

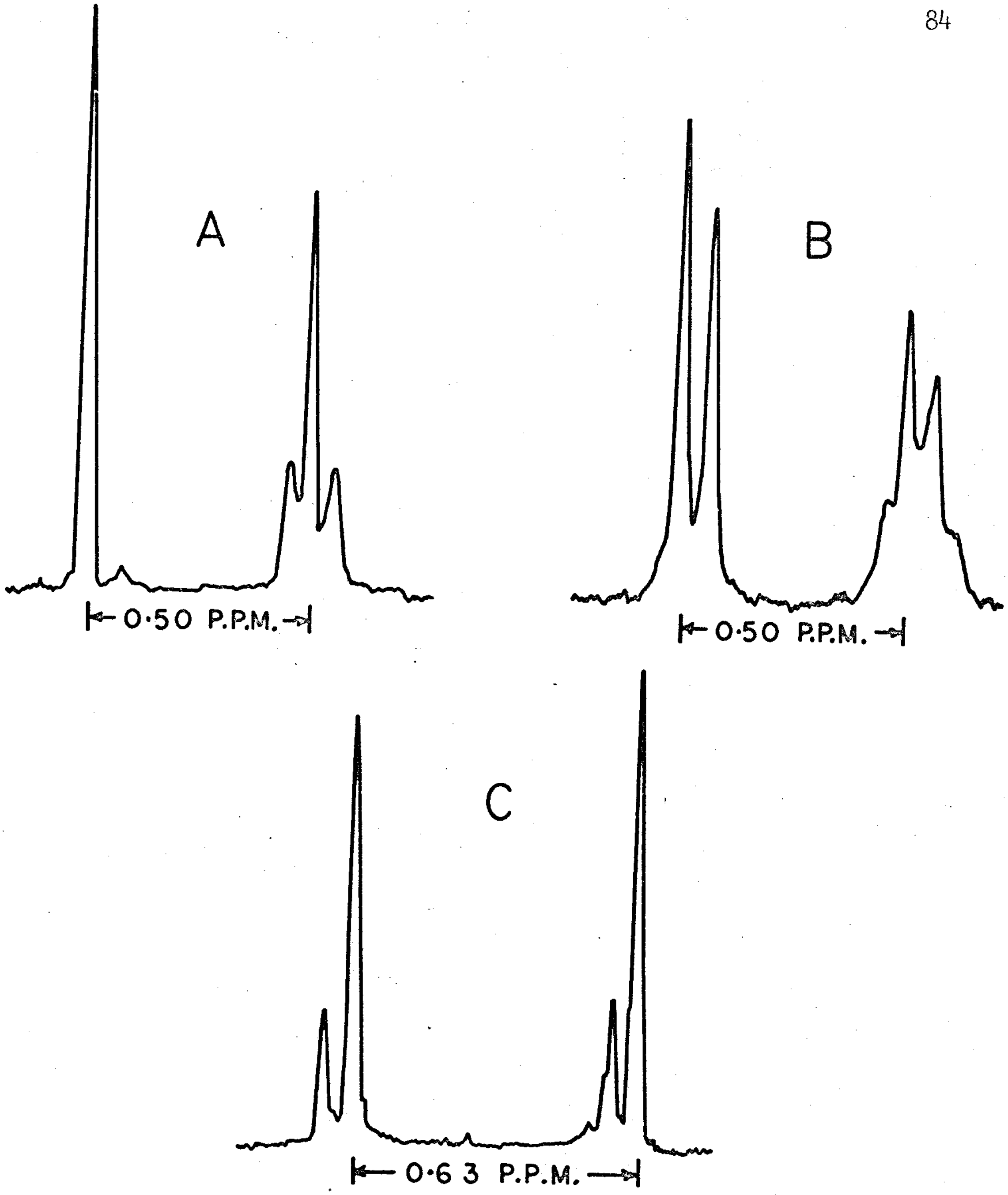

Fig. 14

^{19}F spectra of solutions of water and BF_3 in acetone at -80°, such that $[H_2O] < [BF_3]$.

A. $^{10}BF_3$; B. $^{10}BF_3:{}^{11}BF_3 = 53:47$;

C. natural abundance BF_3 and D_2O in acetone-d_6

Proof that the ^{19}F 1:2:1 triplet (or overlapping triplets) arises from coupling with protons was obtained from a solution of natural abundance BF_3 in acetone-d_6 containing D_2O. In the -80° ^{19}F spectrum (Figure 14c), both the acetone-$d_6.BF_3$ and $D_2O.BF_3$ peaks were split into two peaks of relative intensities 1:4 by an isotope shift of 0.066 p.p.m.; no additional splitting was present on either peak. Thus deuterium substitution destroys the 1:2:1 triplet structure, proving that the triplet in the ^{19}F spectrum of $H_2O.BF_3$ arises from coupling with protons.* It is of interest that the relative shift of the two peaks has increased by about 0.1 p.p.m.; this may be due to greater donor ability of D_2O with respect to that of H_2O.

The evidence obtained from the isotopic substitution experiments is sufficient to remove any doubts that the species observed is the simple 1:1 complex, $H_2O.BF_3$, with $J_{H-F}=2.93\pm0.1$ c.p.s.

The triplet-quartet fine structure of the $H_2O.BF_3$ resonance is sensitive to the relative proportions of water and BF_3, and could not be observed under any conditions when $[H_2O] > [BF_3]$. A single broad ^1H peak, which may be attributed to all the hydroxylic protons, shifted from 12.42δ to higher field as the proportion of excess water was increased from zero. This is attributed to a fast reaction which

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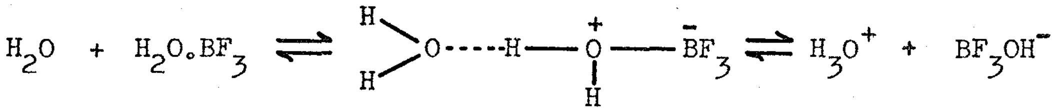
* Coupling with two equivalent deuterium atoms (I=1) should yield a 1:2:3:2:1 quintet, but since J_{D-F} is only 0.15 times the corresponding J_{H-F} and J_{H-F} itself is small in this case, only a broadening of the ^{19}F lines would be expected. In this case the peaks were somewhat broadened for other reasons and therefore no effect at all due to D-F coupling could be detected.

exchanges all the hydroxylic protons when "free" water is present, i.e., water in which the oxygen is not directly bonded to BF_3; this includes one of the water molecules in $(H_2O)_2.BF_3$. The proton exchange reaction can be represented as follows:


(19)

Both ionic and covalent forms of the 2:1 complex are known to be present in the molten complex (19,73). In samples in which $[H_2O] > [BF_3]$ the ^{19}F peak due to $H_2O.BF_3$ still has an isotope shift. This is expected since the postulated rapid exchange reactions of equation (19) involve protons only; fluorine atoms remain bonded to either ^{10}B or ^{11}B for a time that is long on the NMR time scale at -80°.

Even in samples in which $[H_2O] < [BF_3]$, the J_{H-F} fine structure collapses above -30°. This could arise either from proton exchange or from BF_3 exchange between different donor sites, or from a combination of the two. BF_3 exchange between acetone.BF_3 and $H_2O.BF_3$ is known to occur since at room temperature the ^{19}F peaks are broad and are beginning to coalesce. However, the possibility of proton exchange as well cannot be excluded. A study by Paasivirta and Brownstein (49) of $CH_3OH.BF_3$ with excess BF_3 in sulfur dioxide solvent showed that there are two separate exchange processes, between free and complexed BF_3 and between hydroxylic protons, and that the rates of exchange may be independently varied by appropriate variation of reagent concentrations. They were able to unambiguously identify proton exchange through the collapse of splitting due to coupling between the methyl and hydroxyl protons of methanol. Both Paasivirta and Brownstein's study of $CH_3OH.BF_3$ and the present study of $H_2O.BF_3$ indicate that proton exchange is very rapid in the presence of excess base, and can become slow on the NMR time scale only when all of the hydroxylic species is complexed with BF_3 in a 1:1 ratio.

For $H_2O.BF_3$ no coalescence of NMR peaks can be observed which, like the collapse of methyl-hydroxyl proton splitting in $CH_3OH.BF_3$, can be caused only by proton exchange. Although it seems likely that proton exchange and BF_3 exchange proceed independently in $H_2O.BF_3$ as was observed by Paasivirta and Brownstein in $CH_3OH.BF_3$, a detailed study was not considered to be worthwhile in the absence of separate, non-interfering ways of detecting the two types of exchange.

Although proton-fluorine coupling gives rise to the triplet-quartet fine structure in $H_2O.BF_3$, Paasivirta and Brownstein (49) did not report any similar fine structure for $CH_3OH.BF_3$. We confirmed the absence of this fine structure by observing the ^{19}F spectrum of an acetone solution of water and methanol with an excess of BF_3 over the amount required to complex with both. The peak due to $H_2O.BF_3$ had the skewed quartet structure shown in Figure 13b while the $CH_3OH.BF_3$ peak showed only an isotope shift of 0.068 p.p.m.

It is clear from the evidence presented that acetone is much inferior to water as an electron pair donor to BF_3. Thus when $[H_2O] < [BF_3]$, no ^1H peak due to free water is visible at the expected position of 5.1 δ (Figure 13a). Also it was found that when $[H_2O] > [BF_3]$ only an extremely small peak arising from the acetone.BF_3

complex could be observed in the ^{19}F spectrum in spite of the presence of a large excess of acetone. Thus the position of equilibrium in the reaction

$$H_2O + \text{acetone.}BF_3 \rightleftharpoons \text{acetone} + H_2O.BF_3 \qquad (20)$$

is far to the right.

It is interesting that the alternative reaction

$$\text{acetone} + 2(H_2O.BF_3) \longrightarrow \text{acetone.}BF_3 + (H_2O)_2.BF_3 \qquad (21)$$

does not occur to a significant extent. The absence of the products of equation (21) shows that the $H_2O.BF_3$ donor-acceptor bond is much stronger than the acetone.BF_3 bond, a conclusion which is strongly supported by data on relative rates of exchange of BF_3 (Chapter III). Since the additional factor favouring (21), namely the formation of $(H_2O)_2.BF_3$ from $H_2O.BF_3$, has no apparent effect, it appears that the bonding energy of the second water molecule in $(H_2O)_2.BF_3$ is small. This is expected if only a hydrogen bond is involved. The reported (72) greater stability of the 2:1 complex with respect to BF_3 evolution can be ascribed to the equilibrium

$$H_2O.BF_3 \rightleftharpoons H_2O + BF_3 \qquad (22)$$

rather than to special stability resulting from 2:1 proportions. The existence of a stable crystalline 2:1 complex can be ascribed to crystal packing favouring the inclusion of a hydrogen bonded water molecule. Proton NMR spectra (74), and an X-ray diffraction study (75), of the crystalline 2:1 complex are in accord with a hydrogen bonded structure.

It is noteworthy that coupling with boron is not observed in $H_2O.BF_3$, in either the ^1H or the ^{19}F spectrum. Since proton-fluorine coupling is observed the donor-acceptor bond is definitely strong enough to transmit spin-spin interactions. The absence of splitting due to coupling with boron is attributed to quadrupole relaxation of boron arising from asymmetry of charge about boron and a considerable electric field gradient at the boron nucleus. The effect of the electric field gradient on quadrupole relaxation of ^{11}B and hence on the ^{19}F spectrum is clearly shown in the series BF_4^-, BF_3OH^- and $H_2O.BF_3$. The BF_4^- ion, which has tetrahedral symmetry, should have a zero field gradient at the boron nucleus; thus its ^{19}F resonance is split into a 1:1:1:1 quartet by coupling with the long-lived ^{11}B spin states (Chapter X). The BF_3OH^- ion is isoelectronic with BF_4^- and thus would be expected to have a fairly symmetrical charge distribution about boron. The symmetry should be considerably greater than for most complexes of oxygen donors with BF_3, and the boron spin states should be fairly long-lived. Fine structure consisting of a 1:1:1:1 quartet broadened by quadrupole relaxation has in fact been observed in the ^{19}F spectrum of the BF_3OH^- ion; the ^{11}B 1:3:3:1 quartet also showed broadening due to quadrupole relaxation (66,77). Thus the decrease of symmetry caused by replacing F^- by the quite similar OH^- is sufficient to cause some quadrupole relaxation of the boron nuclei. It is not surprising that protonation of the fairly symmetrical species BF_3OH^-, to give the highly unsymmetrical dipolar species $H_2\overset{+}{O}\rightarrow\overset{-}{B}F_3$, should greatly increase the electric field gradient at the boron nucleus. This results in much more effective quadrupole relaxation of boron and complete collapse of the ^{19}F fine structure due to ^{11}B-^{19}F coupling. A similar dependence of the appearance of splitting due to

B-F coupling on the electric field gradient about boron has been reported for BF_3 complexes of nitrogen donors (52).

The absence of fine structure in the ^1H spectrum due to ^{11}B-^1H coupling is further evidence for quadrupole relaxation. It is possible that J_{B-F} would fortuitously be zero as in Chapter X, but unlikely that J_{B-F} and J_{B-H} would both be zero.

The inertness of acetone with respect to proton transfer allows boron trifluoride monohydrate to exist in the molecular form in solution. In the more basic solvent water, $H_2O.BF_3$ loses a proton, while the strongly acidic solvent fluorosulphuric acid destroys the complex through displacement of BF_3 by a proton (81):

$$H_2O.BF_3 \; + \; HSO_3F \longrightarrow H_3O^+SO_3F^- \; + \; BF_3 \qquad (22)$$

The inertness of acetone with respect to proton transfer, together with a low freezing point and a moderate dielectric constant which allows it to solvate dipolar species, makes it a good NMR solvent for $H_2O.BF_3$. Its usefulness as an NMR solvent depends also on its considerable Lewis basicity with respect to BF_3. It can displace only a negligible amount of water from the $H_2O.BF_3$ complex, but is a strong enough base to behave as a scavenger of any excess BF_3. This prevents the existence of free BF_3 which would probably exchange with the 1:1 complex and cause collapse of the fine structure due to J_{H-F}. The scavenging effect is especially useful because of the difficulty in obtaining precise 1:1 proportions of water and BF_3 in solution, as a result of the acetone decomposition reaction which yields water. This BF_3-catalysed decomposition, which occurs at a considerable rate above $0^{\circ}C$, is the most serious disadvantage of acetone as a solvent for BF_3 complexes.*

The great difference in BF_3 affinities between water and acetone may seem surprising, but actually is analogous to the known large difference in proton affinities of these compounds. A logarithmic scale, similar to the pK_b scale for measuring proton affinities, would be useful for the same reason in measuring BF_3 affinities.

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* The rate of decomposition appears to be increased by the presence of methanol. Solutions of methanol with excess BF_3 in acetone, stored at -78° for several days, had a large peak due to $H_2O.BF_3$ in ^{19}F spectrum whereas similar samples of BF_3 in acetone without methanol did not yield a large $H_2O.BF_3$ peak until they had been warmed to room temperature for a considerable time.

CHAPTER V

EXCHANGE REACTIONS IN THE SYSTEM BORON TRIFLUORIDE-METHANOL. A MODIFIED INTERPRETATION

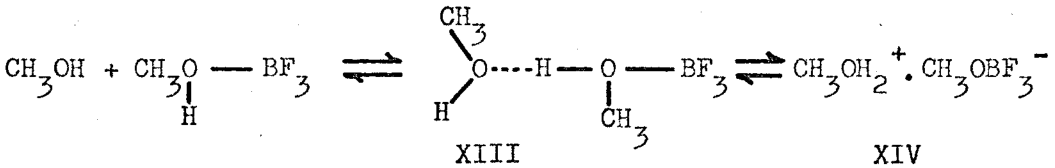
INTRODUCTION

Solutions of boron trifluoride in excess methanol have been reported to contain the three species methanol, (methanol)$_2$.BF$_3$ and methanol.BF$_3$ (16,20). The crystalline 2:1 and 1:1 complexes have been isolated at low temperatures, and electrical conductivity and related studies performed over a range of temperatures (82). The results indicate that the molten 2:1 complex is dissociated into ions to the extent of 7.3%, and the 1:1 complex to the extent of 2.2% (19,73). High-resolution NMR has been applied to the system by Diehl (47) and to solutions of the components in sulphur dioxide by Paasivirta and Brownstein (49). Both groups of workers found evidence for a variety of exchange reactions when $[\text{methanol}] > [\text{BF}_3]$. Diehl observed only a single hydroxyl proton resonance at all compositions and temperatures studied. He postulated that a very rapid proton exchange process occurs in solution, which is much more rapid than the BF$_3$ exchange process which can be followed by ^{19}F NMR when mixed alcohols are used. Paasivirta and Brownstein obtained similar results in sulphur dioxide solution, and also at low temperatures observed two separate peaks due to methyl groups which coalesced at higher temperatures. The chemical shifts and coalescence temperature of the two low temperature methyl peaks varied greatly with the relative proportions of methanol and BF_3 in solution.

Paasivirta and Brownstein interpreted their results in terms of rapid chemical exchange processes involving three species, free methanol and the 2:1 and 1:1 complexes, which were tacitly assumed to be discrete molecular species. This led to difficulties in explaining the presence of only two methyl peaks in the low temperature spectrum. It was erroneously concluded that one of the peaks is due to an averaging of free methanol with the 1:1 complex, and that the other is due to an averaging of free methanol with the 2:1 complex. This conclusion is invalid because it requires that the free methanol molecules be arbitrarily divided into two groups, one of which exchanges rapidly only with the 1:1 complex, the other only with the 2:1 complex. In fact if free methanol were to exchange rapidly with both complexes, methanol in either complex could be rapidly incorporated into the other complex by an intermediate step involving free methanol, and only a single methyl peak would be obtained. In the present work an alternative explanation is presented.

DISCUSSION

The difficulties experienced by Paasivirta and Brownstein in interpreting their experimental data are apparently the result of their lack of consideration of the probable structure of the 2:1 complex. It probably has both the hydrogen bonded structure XIII and the ionic structure XIV, which interconvert rapidly with each other, and with the free methanol and the 1:1 complex, by hydroxyl proton transfer



$$CH_3OH + CH_3\underset{H}{\underset{|}{O}} - BF_3 \rightleftharpoons \overset{CH_3}{\underset{H}{O}}\cdots H - \underset{CH_3}{\underset{|}{O}} - BF_3 \rightleftharpoons CH_3OH_2^{+} \cdot CH_3OBF_3^{-} \qquad (23)$$

XIII XIV

according to the reaction scheme (23). Similar structures for the $(H_2O)_2 \cdot BF_3$ complex have been discussed in Chapter IV. The rapid exchange of hydroxyl protons has previously been proposed by Diehl (47) to explain the presence of only a single hydroxyl proton resonance signal in methanol-BF_3 mixtures. The existence of both hydrogen bonded and ionic structures of the 2:1 complex is consistent with Greenwood and Martin's observation of partial ionization in the molten complex (73).

The reaction scheme (23) can account for all of the features of the proton spectra. Rapid interchange of all hydroxyl protons yields a single hydroxyl peak. However, the reactions shown do not interchange BF_3 molecules among donor sites; BF_3 exchange is a considerably slower process, which can be slowed sufficiently on the NMR time scale to yield separate peaks due to free and complexed methanol. Thus the observed two low temperature methyl peaks obtained by Paasivirta and Brownstein can be attributed to i) methyl groups attached to oxygen not involved in a donor-acceptor bond with BF_3, and ii) methyl groups which form part of the linkage CH_3-O-BF_3. By analogy with other examples of changes in donor chemical shift on complex formation, the peak arising from methyl groups involved in CH_3-O-BF_3 linkages should occur to low field of the peak due to "free" methyl groups. The collapse of the two peaks at higher temperatures can be attributed to exchange of BF_3 among different donor sites.

The chemical shifts of the two low temperature methyl peaks observed by Paasivirta and Brownstein are strongly dependent on sample composition (Figure 6 of (49)). Rapid proton exchange as in equation (23) accounts for this since each observed low temperature methyl peak is a weighted average of peaks arising from distinct chemical species. The high field "free" methyl peak is made up of contributions from CH_3OH and $CH_3OH_2^+$, as well as from the hydrogen bonded molecule of methanol in the 2:1 complex XIII. The methyl resonances in $CH_3OH_2^+$ and in the hydrogen bonded molecule of methanol in XIII would be expected to occur at lower field than that of free methanol; hence a low field shift is expected as the addition of BF_3 increases the concentrations of these species. Similarly the low field "complexed" methyl peak of $CH_3OH.BF_3$ should shift to higher field as addition of methanol increases the concentrations of both $CH_3OBF_3^-$ and the hydrogen bonded 2:1 complex; in both $CH_3OBF_3^-$ and in the complexed molecule of methanol in XIII there should be a fractional negative charge on the methyl group.

The strong dependence of the coalescence temperature of the "free" and "complexed" methyl peaks on the acid-base ratio (Figure 6 of (49)) indicates more than one mechanism for BF_3 exchange. A variety of exchange mechanisms have been postulated to occur in mixtures of ethers and BF_3 by Rutenberg and co-workers (50,53), who found that the rate of BF_3 exchange at a given temperature decreases, and the apparent activation energy for the exchange process increases, as the acid-base ratio is increased towards unity. In the case of methanol-BF_3 solutions in sulphur dioxide the opposite trend was observed;

Paasivirta and Brownstein's Figure 6 indicates that as the acid-base ratio is increased the rate of exchange at a given temperature increases. This opposite trend can be attributed to the equilibria of equation (23), which cannot occur in complexes of ethers. If the ratio $[BF_3]/[\text{methanol}]$ is small, much of the methanol.BF_3 should lose a proton or be strongly hydrogen bonded, as discussed above. Thus the BF_3 should be present largely in species in which there is increased electron density on the adjacent oxygen, which should strengthen the donor-acceptor bond. If the ratio approaches 1:1, most of the BF_3 should be present in the electrically neutral 1:1 complex which, with lower electron density on the oxygen, would have a weaker donor-acceptor bond. Thus BF_3 exchanges more readily among donor sites as the acid-base ratio increases towards unity.

In the following section the results of some experiments which were carried out to supplement those of Paasivirta and Brownstein are presented. These results, and the earlier results of Paasivirta and Brownstein, are interpreted according to the reaction scheme given above.

RESULTS AND INTERPRETATION

Proton spectra were obtained over a range of temperatures for three samples of methanol and BF_3 in sulphur dioxide, of acid-base ratios less than unity. The behaviour of the spectra on varying the temperature confirms the experimental results which Paasivirta and Brownstein reported for similar solutions. The results are given in Table III and Figure 15.

It is reasonable to assume that all the BF_3 present would complex with methanol in a 1:1 ratio. Species containing the linkage CH_3-O-BF_3, which according to the present interpretation give rise to the low field methyl peak, should thus have a concentration equal to that of the BF_3 in the sample. The concentration of CH_3-O species not directly linked to BF_3, $[\text{free } CH_3O]$, would then have a concentration equal to $[CH_3OH] - [BF_3]$. In Table III concentrations are calculated in this fashion, and the expected relative peak areas according to the present interpretation given, together with the observed relative areas. The relative areas given by Paasivirta and Brownstein in Table II of (49) are recalculated in terms of percent of total methyl area in the low field peak, rather than in terms of relative areas of the low and high field methyl peaks.

It is evident from Table III that the predicted relative areas of the methyl peaks agree quite well with the observed areas, with the exception of Paasivirta and Brownstein's sample d. The serious discrepancy in calculated and observed relative areas in this sample presumably arises from an error in preparing the sample or in measuring the spectra, since the new sample f, made up with very similar proportions of methanol and BF_3, yielded the expected relative peak areas. The discrepancies of a few percent between calculated and experimental relative areas in the other samples are apparently within the experimental error. The generally good agreement of calculated and experimental areas is strong evidence that the above interpretation of the results is valid.

Figure 15 shows the variation of chemical shifts of the separate low temperature "free" and "complexed" methyl peaks with acid-base ratio.

TABLE III

RELATIVE AREAS OF "FREE" AND "COMPLEXED" METHYL PEAKS IN METHANOL - BF_3 SOLUTIONS IN SULPHUR DIOXIDE

Sample	Source	Acid-Base Ratio	[Total CH_3OH]	[BF_3]	[Free CH_3O] ††	% of Methyl Area in the Low Field Peak Predicted	Observed	Discrepancy
a	†	0.578	0.83	0.48	0.35	57.8	59.5	+1.7
b	†	0.420	0.69	0.29	0.40	42.0	39.6	-2.4
c	†	0.157	0.70	0.11	0.59	15.7	12.8	-2.9
d	†	0.397	1.16	0.46	0.70	39.7	17.0	-22.7
e	*	0.095	4.30	0.41	3.89	9.5	5.2	-4.4
f	*	0.386	1.47	0.57	0.90	38.6	36.5	-2.1
g	*	0.788	1.03	0.81	0.22	78.8	(71)**	-

† (49); concentrations in molalities

* this work; concentrations in molarities

†† assumes that all BF_3 complexes with methanol

** two immiscible layers were present at -68°, the only temperature at which two separate methyl peaks were observed.

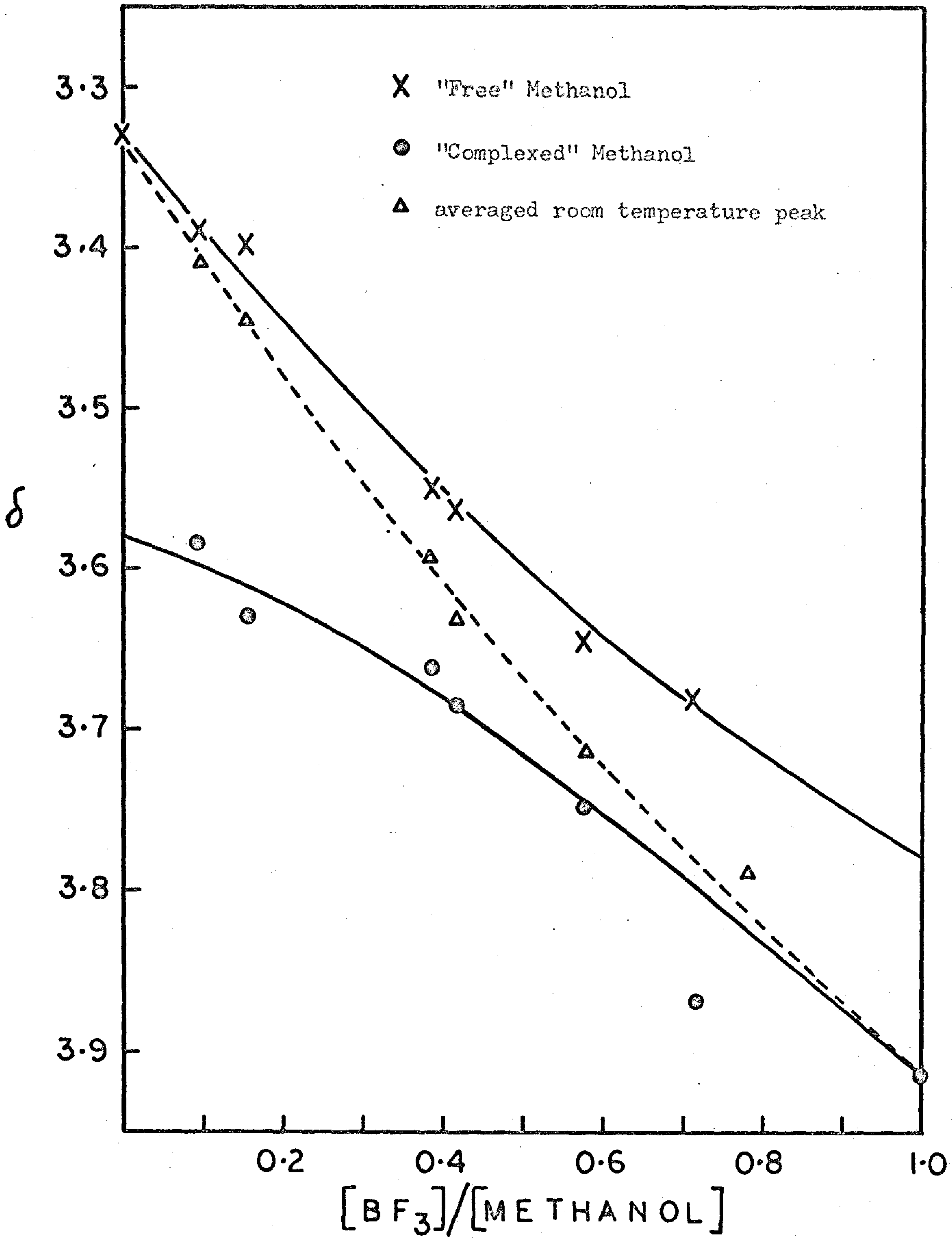


Fig. 15

Plot of methyl proton shifts vs. acid-base ratio for methanol-BF_3 solutions in sulphur dioxide.

Some of the points were obtained by measurement of Paasivirta and Brownstein's Figure 6. The trend of both peaks to lower field with increasing acid-base ratio is evident. It should be possible to obtain the methyl chemical shifts of the "free" and "complexed" methanol molecules in the 2:1 complexes by extrapolation of the curves. Thus the "free" methyl peak shifts to lower field as the contributions from $CH_3OH_2^+$, and from the hydrogen bonded molecule of methanol in XIII, increase with increasing acid-base ratio. It seems likely that as 1:1 proportions are approached the concentration of free methanol should rapidly approach zero while there are still significant amounts of the ionic and covalent forms of the 2:1 complex in solution. Thus the chemical shift of the "free" peak, extrapolated to the acid-base ratio of unity, should give the methyl chemical shift of "free" methanol in the 2:1 complex, an averaged shift of $CH_3OH_2^+$ and the hydrogen bonded molecule of methanol in XIII. Similarly, extrapolation of the "complexed" peak to zero acid-base ratio should give the methyl chemical shift of "complexed" methanol in the 2:1 complex, an averaged chemical shift of $CH_3OBF_3^-$ and the complexed molecule of methanol in XIII, if it is assumed that the concentration of molecular methanol.BF_3 becomes negligible at very low BF_3 concentrations. The extrapolations of Figure 15 give methyl chemical shifts for the 2:1 complex as follows: "free", $3.76 \pm 0.05\delta$, and "complexed", $3.58 \pm 0.05\delta$.

Both of the methyl chemical shifts for the 2:1 complex obtained by extrapolation of Figure 15 are between the values for free methanol (3.33δ) and for the 1:1 complex (3.91δ). It is of interest that in the 2:1 complex the molecule of methanol directly bonded to BF_3 has a methyl absorption at higher field than that of the molecule not directly bonded to BF_3. This can be explained if a considerable proportion of the 2:1 complex is in the ionic form XIV. Since H^+ is analogous to BF_3 in that both are strong Lewis acids, CH_3OH and $CH_3OBF_3^-$ can be considered to be analogous species. It is reasonable that both of these species should have methyl resonances to higher field than $CH_3OH_2^+$ or $CH_3OH{\cdot}BF_3$. The latter two species are analogous in that both have a positive charge on the oxygen atom, which should deshield the adjacent methyl group.

Olah and Namanworth (83) have recently reported the proton spectrum of $CH_3OH_2^+$ in a mixture of fluorosulphuric acid, antimony pentafluoride, and sulphur dioxide. The methyl resonance occurred at 4.35 p.p.m. to low field of the TMS peak of a separate sample of TMS in chloroform, or approximately at 4.85 p.p.m. to low field of external (capillary) TMS. Since the magnetic susceptibility of the solvent mixture has not been reported these values cannot be accurately converted to chemical shifts with respect to internal TMS. However, the methyl chemical shift is likely to be about 4.4δ, which is considerably to low field of the extrapolated chemical shift value for the "free" methyl group in the 2:1 complex, 3.76δ. This suggests that the hydrogen bonded structure XIII, in which the low field shift of the methanol resonance should be considerably smaller than in the ionic structure XIV, is present to a greater extent than the ionic structure.

It is of interest that the hydroxyl chemical shift, which by its striking dependence on acid-base ratio gave evidence for some type of 2:1 complex in mixtures of methanol and BF_3 (47), is quite temperature dependent in sulphur dioxide solutions. The samples studied showed a considerable shift, about 1 p.p.m., of the hydroxyl peak to lower field on lowering the temperature. This might be due to a greater extent of hydrogen bonding, or to a larger concentration of the ionic structure XIV, at lower temperatures. The ion $CH_3OH_2^+$ should have its OH_2^+ resonance at quite low field, as has been observed by Olah and Namanworth (83).

CHAPTER VI

BF_3 EXCHANGE IN KETONE.BF_3 COMPLEXES IN METHYLENE CHLORIDE SOLVENT

INTRODUCTION

Several NMR studies of BF_3 adducts of oxygen donors, described in Chapter I, have shown that BF_3 exchange among donor sites, and between complexed and free BF_3, is rapid on the NMR time scale at room temperature. However, the exchange processes can often be slowed sufficiently by lowering the temperature that separate signals can be observed. The BF_3 complexes of the ketones acetone, methyl ethyl ketone (MEK), methyl isopropyl ketone (MIK), and pinacolone (methyl t-butyl ketone) are now shown to behave in a similar fashion.

RESULTS AND DISCUSSION

(i) Room Temperature Proton Spectra

Room temperature proton spectra of methylene chloride solutions of simple ketones and BF_3, in various molar ratios, contain a single set of resonances corresponding to the spectrum of the ketone used. The chemical shifts of the ketone peaks with respect to internal tetramethylsilane (TMS) appear to vary linearly with the acid-base ratio, $[BF_3]/[\text{ketone}]$, as the relative proportion of BF_3 is increased until 1:1 proportions are obtained, as is shown in Figure 16 for the four ketones studied. Since separate resonances were not observed for free and complexed ketone in mixtures in which $[\text{ketone}] > [BF_3]$, in spite

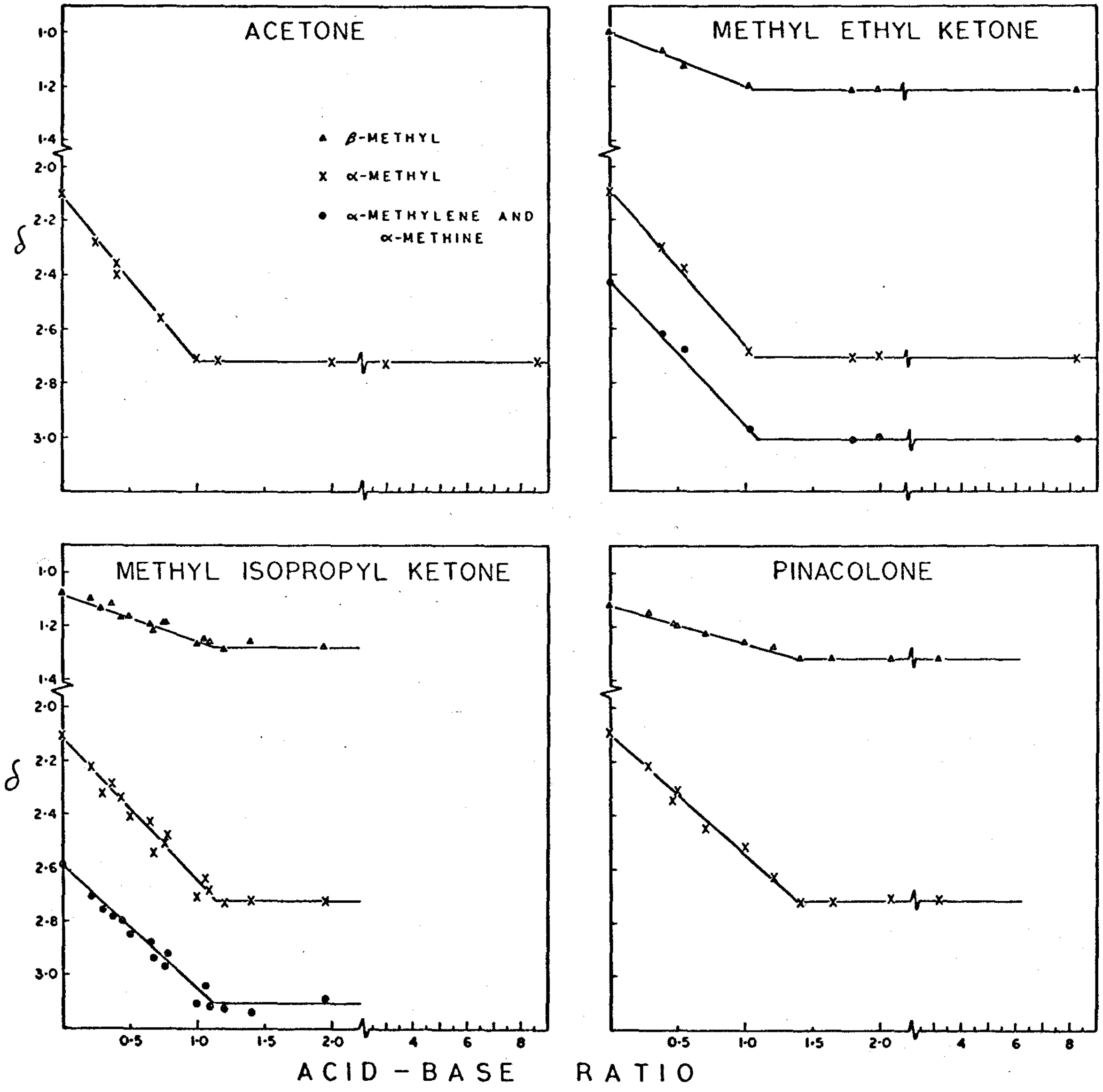


Fig. 16

Variation of ketone chemical shifts with the acid-base ratio, $[BF_3]/[\text{ketone}]$.

of the considerable chemical shift differences between free and complexed ketones indicated in Figure 16, it is evident that a rapid exchange of BF_3 occurs among different donor molecules. The absence of further changes in chemical shifts as further BF_3 is added beyond 1:1 proportions indicates that the additional BF_3 does not complex; in accord with previous studies it appears that only 1:1 complexes are formed between ketones and BF_3. The linearity of the plots, with a sharp break corresponding to 1:1 proportions, shows that there can be no more than a small degree of dissociation of the complex.*

The low field complexation shifts in the proton spectra decrease with increasing distance from the donor site, as is shown in Table IV; the shift is almost three times as large for α- as for β-protons. The similarity of the complexation shifts for equivalent groups of protons in the different ketones suggests that the charge distribution in the complex is not seriously affected as the number of β-methyl groups is increased. The coupling constant within the ethyl and isopropyl groups, $J_{\alpha\beta}$, is practically unaffected by complexation. This contrasts with the behaviour of the small coupling across the carbonyl carbon, $J_{H_\alpha, H_\alpha'}$, which in MEK increases by a factor of three on complex formation with BF_3 (59).

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* In the plots for both MIK and pinacolone a sharp break is obtained, but with an apparent deviation from 1:1 proportions. The deviation is believed to arise from non-ideal behaviour of the vapour of these ketones, leading to condensation into the NMR sample tubes of greater amounts than those recorded.

TABLE IV

PROTON SHIFTS TO LOW FIELD, AND CHANGES IN $J_{\alpha\beta}$, ON COMPLEXATION OF KETONES WITH BF_3

	Proton Shifts (p.p.m.)				$J_{\alpha\beta}$ (c.p.s.)	
	α-CH_3	α-CH_2	α-CH	β-CH_3	Free	Complexed
acetone	0.59	-	-	-	-	-
methyl ethyl ketone	0.60	0.61	-	0.21	7.0	6.6
methyl isopropyl ketone	0.61	-	0.54	0.21	7.0	7.1
pinacolone	0.61	-	-	0.21	-	-

The 0.59 p.p.m. complexation shift of acetone, which was found to be essentially independent of temperature, does not agree with the value of 0.32 p.p.m. at -70° previously reported by Lappert (32) for a solution in the same solvent. However, the very similar α-methyl complexation shift obtained for MEK agrees well with the value obtained by Gates and Mooney (59). The discrepancy in Lappert's value may arise from the presence in his solution of moisture which would displace some of the acetone from its complex, or from his use of cyclohexane as a standard. It was later shown (84) that cyclohexane does not give a single peak at -70°, but instead in split into a complex pattern approximating a doublet, due to slowing of the ring inversion process.

(ii) Low Temperature Proton Spectra

Only a single set of ketone resonances could be observed at -50° in any of the samples studied. At -90°, however, each sample which contained fewer moles of BF_3 than of ketone yielded a spectrum containing one set of peaks with chemical shifts corresponding to those of the free ketone and a second set of peaks with chemical shifts corresponding to those of the 1:1 complex (Figure 17). The relative areas of the two sets of peaks varied in the expected manner among different samples, the "free ketone" set decreasing in size as the relative concentration of BF_3 increased towards 1:1 proportions. Electronic integration of the peak areas in solutions having an acid-base ratio of 0.5 showed that the areas of corresponding "free" and "complexed" peaks were equal, within experimental error; this confirms that 1:1 complexes exist in solution and that they are dissociated to a negligible extent. The absence of a set of peaks due to free ketone in -90° spectra of samples in which $[\text{ketone}] \leqslant [BF_3]$ further confirms that dissociation is negligible.

At temperatures above -90°, samples in which $[\text{ketone}] > [BF_3]$ yielded spectra in which the separate peaks due to free and complexed ketone were partially collapsed due to moderately rapid chemical exchange. It was observed that, in samples containing similar concentrations of any of the four ketones studied, coalescence of corresponding pairs of "free" and "complexed" peaks occurred at similar temperatures. Since the collapse of closely similar complexation shifts is involved (Table IV), it seems that the rate of BF_3 exchange is not greatly affected by steric hindrance due to the presence of extra β-methyl groups. This is not surprising because of the considerable distance separating the carbonyl oxygen from the additional substituents. The similarity of the exchange rates for the four ketones also suggests that the charge distribution in the complex is not much affected by the number of β-methyl groups.

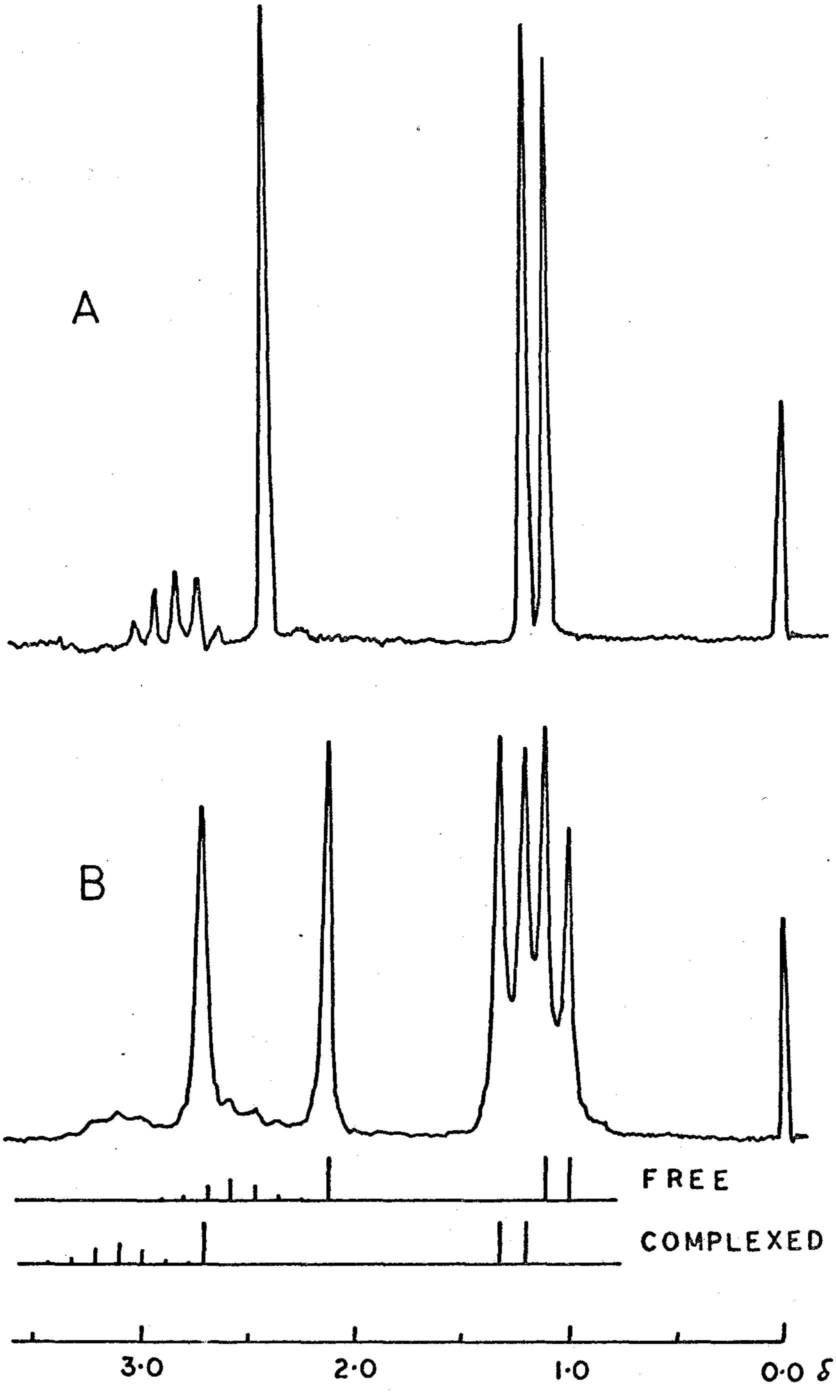

Fig. 17

Proton spectra of a methylene chloride solution of MIK and BF_3, in the molar ratio 2:1.
A. room temperature; B. - 90°

In order to obtain the activation energy for BF_3 exchange in a typical sample, a detailed kinetic study was carried out, over almost the entire range of signal shapes, on a sample of acetone and BF_3, of relative proportions 2:1 (0.30 M and 0.15 M) in methylene chloride. Acetone is suitable for such a study since the only resonances observed arise from the free and complexed α-methyl peaks, which have a large relative chemical shift and hence undergo coalescence over a fairly wide temperature range. The absence of interfering peaks such as the α-methylene and α-methine peaks of MEK and MIK in the region of the spectrum affected by α-methyl peak coalescence, and the absence of broadening of the α-methyl peaks due to α,α' coupling such as occurs in these two ketones (59,85) are further reasons for choosing acetone.

Rates of BF_3 exchange were determined over a wide range of temperatures and signal shapes by the following methods.

1) From the width at half-height of the coalesced single peaks, we have

$$\tau = \left[\frac{2\nu^2}{\frac{1}{2}\pi^2 \nu_{AB}^{\;4} + 4\pi^2 \nu_{AB}^{\;2} \nu^2 - 8\pi^2 \nu^4} \right]^{1/2} \qquad (24)$$

in which 2ν (c.p.s.) is the peak width at half-height, ν_{AB} (c.p.s.) is the peak separation at slow exchange (i.e., the chemical shift), and $2\tau = \tau_A = \tau_B$, where τ_A and τ_B are the mean lifetimes of a magnetic nucleus on sites A and B. This equation is derived from equation (10.29) of (2).

2) From the separation of the peak maxima below the coalescence temperature, we have

$$\mathcal{T} = \left[\frac{1}{2\pi^2 \nu_{AB}^{\ 2} \left[1 - \frac{\nu_{obs}}{\nu_{AB}} \right]^2} \right]^{1/2} \qquad (25)$$

in which ν_{obs} is the observed peak separation, and $2\mathcal{T}$ and ν_{AB} are defined as above. This equation is equivalent to equation (10.31) of (2).

3) Width at half-height of the high field "free ketone" peak in the slow exchange limit, which gives $\mathcal{T}_A = 2\mathcal{T}$, by equation (9) (p. 8).

A computer programme was used to calculate rates of reaction, $\frac{1}{2\mathcal{T}}$, and the activation energy for the process. The Arrhenius plot of the results (Figure 18) shows some scatter of points. The three methods of calculation yield considerably different slopes, and hence considerably different activation energies, for the exchange process. Least squares values of the Arrhenius activation energy (E_a) were calculated from the data obtained by each method, and also from the combined data. The values obtained, for the methods as numbered above, are 1) 9.3, 2) 17.4, 3) 8.3, and combined, 11.1 Kcal./mole.

A least squares calculation of the activation energy from the data obtained by methods 1) and 3) also gave an activation energy of 11.1 Kcal./mole. Since the values obtained for the two methods separately are much lower than this, a serious systematic error may be present; the calculated activation energy may be in error by ±3 Kcal./mole. The discrepancies illustrate the danger of attempting to obtain activation energies from a single method involving approximations,

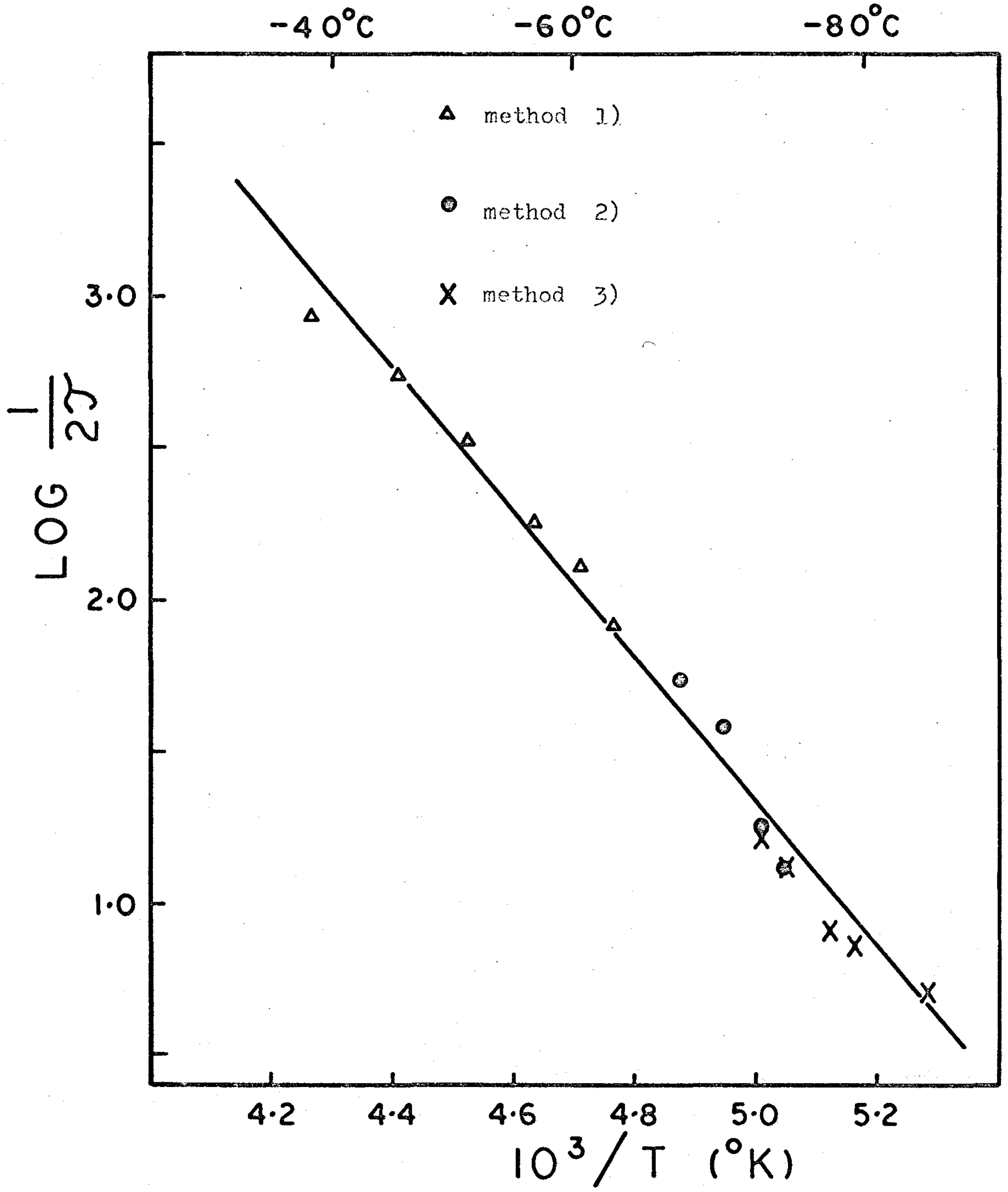

Fig. 18

Arrhenius plot for BF_3 exchange among donor sites in a solution of acetone and BF_3 in a 2:1 molar ratio in methylene chloride.

or over too narrow a range of spectral shapes. The discrepancies are not too surprising because of the small number of points determined by each method. However, some of the discrepancy might be attributed to the use of approximate rate expressions. Gutowsky and co-workers (12) have recently emphasized that such expressions often lead to serious systematic errors, and have recommended the use of complete line-shape numerical methods such as are used in Chapters III and VII of this thesis. Another source of error in the present case arises from an additional broadening of the low field "complexed" peak. This broadening was observed at -90° in spectra of the BF_3 complexes of all four of the ketones; it affects all the peaks arising from protons in α-positions (e.g., Figure 17b). In samples in which $[\text{ketone}] = [BF_3]$ the broadening was visible at temperatures up to -40°. In no case could the broadening be observed at room temperature. It is probable that the disappearance of this broadening is the result of rapid exchange of BF_3 among donor sites.

The broadening of the α-proton resonances in the 1:1 complexes might be due to a small coupling of the α-protons to boron or to fluorine, the effects of which would disappear as exchange of BF_3 becomes rapid. Alternatively the broadening could result from cis-trans isomerism about the double bond of the complexed carbonyl group, as in structure VI (p.31), which could be slow on the NMR time scale at low temperatures. The existence of the bent C-O-B bond required by this hypothesis and expected by analogy with the structure of olefins has not been proved. However, X-ray diffraction studies of adducts of mercuric chloride with the ketones cyclohexane-1,4-dione (86) and acetophenone (30) have shown that bent C-O-Hg bonds are present. Observation of such isomerism in acetone.BF_3 by proton NMR was attempted without success by Lappert (32). Since separate cis and trans methyl peaks could not be observed in the present study, carried out at higher resolution and at lower temperatures than Lappert's study, either the interconversion of methyl groups must be very rapid even at -90°, or the non-equivalent methyl groups must have very similar chemical shifts. The latter possibility could yield an apparent broadening of the α-methyl resonance of the complex if the chemical shift difference of the cis and trans methyl peaks is too small to be resolved.

(iii) Fluorine Spectra

Samples in which $[\text{ketone}] > [BF_3]$ gave a single major ^{19}F peak at about 148 p.p.m. to high field of trichlorofluoromethane.* The peak position varied by up to 1 p.p.m. in different samples, with no pattern evident in the variations. Below about -20° the peak was split by an isotope shift; the disappearance of this splitting at higher temperatures and the related disappearance of a small higher field peak observed in some samples is described in Chapter VII. The sharpness of the main peak at temperatures between -20° and -90° is further evidence that essentially all of the BF_3 is complexed, since in this temperature range free BF_3 should exchange with the 1:1 complex rapidly enough to cause broadening of the peak, as is discussed below.

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* All ^{19}F chemical shifts in this chapter are given with respect to trichlorofluoromethane.

The ^{19}F chemical shifts of the BF_3 complexes of the four ketones appear to be almost identical; although variations of up to 1 p.p.m. were observed in different samples, these did not appear to depend on the ketone used. Further evidence of very similar chemical shifts was provided by a solution of BF_3 with both acetone and pinacolone, such that $[\text{acetone}]:[\text{pinacolone}]:[BF_3] = 1:1.08:1.82$. This gave only a single ^{19}F resonance, with an isotope shift, at -80° despite the presence of sufficient BF_3 to complex with most of both ketones. Since the proton spectrum at the same temperature showed separate peaks due to the free and complexed ketones, indicating that BF_3 exchange is slow, the single peak is apparently due to similar chemical shifts of the two complexes rather than to exchange averaging. The near identify of the ^{19}F chemical shifts is a further indication that the number of β-methyl groups has very little effect on the distribution of charge in the donor-acceptor bond.

Solutions in which $[\text{ketone}] < [BF_3]$ gave a single ^{19}peak at room temperature. At -90° two peaks, still slightly broadened by exchange, could be detected at about 124 and 148 p.p.m. The high field peak can with confidence be assigned to the 1:1 complex since its chemical shift agrees closely with that of the single peak obtained in the presence of excess ketone. The low field peak must then be assigned to free BF_3; its chemical shift is in good agreement with that of solutions of BF_3 in methylene chloride when no base is present, i.e., 122.2 p.p.m. at -90° (this work) and 125.3 p.p.m., temperature not specified (87). In confirmation of this assignment of peaks, an increase in the relative proportion of BF_3 caused an increase in the relative size of the low field peak. The large ^{19}F

complexation shifts of BF_3 have been discussed in Chapter I; the ketone.BF_3 complexes absorb in the usual region for BF_3 complexes with oxygen donors.

Electronic integration of the low temperature ^{19}F peaks did not give relative peak areas consistent with the amounts of free BF_3 and of 1:1 complex calculated to be present in the sample tube; in all cases the relative area of the low field "free BF_3" peak was less than expected. This is explained by the presence of gaseous BF_3, possibly at several atmospheres pressure, in the space above the solution in the sample tube. It is possible to calculate the amount of BF_3 which is lost from solution in this way (87) but this was not done in the present study. The absence of complexes containing more than one mole of BF_3 per mole of ketone is indicated by the replacement of the single sharp -50° peak showing an isotope splitting, in samples in which $[\text{ketone}] \geqslant [BF_3]$, by a peak broadened by BF_3 exchange in samples in which $[\text{ketone}] < [BF_3]$.

A detailed kinetic study was carried out on a sample of pinacolone (0.9 M) and excess BF_3 in which the peaks arising from free BF_3 and from the 1:1 complex were approximately the same size.* The presence of peaks of equal areas allowed the use of the same rate expressions as were used for determining rates of BF_3 exchange between acetone.BF_3 and excess acetone. The numbering of the methods is the same as on p.109; in this case method 3) makes use of the width at

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* From -90° ^{19}F peak areas, the proportions in solution were: free BF_3, 49±2%; 1:1 complex, 51±2%.

half-height of the peak due to the 1:1 complex. The Arrhenius plot of the results (Figure 19) yields a good straight line. The three methods led to least squares E_a values of 1) 12.6, 2) 9.5, 3) 12.6, and combined, 12.1 Kcal./mole. These values are more self-consistent than those obtained in the ^1H rate study, as is reasonable since more points were obtained and also since the coalescence pattern does not appear to be affected significantly by extraneous broadening, and can be followed over a wider range of temperature. No fine structure due to B-F coupling was observed on either peak. The high field peak was broadened by the isotope shift of 3.7 c.p.s., but this effect is negligible compared to the very great broadening due to collapse of the two peaks of relative chemical shift greater than 1000 c.p.s. Method 2) results in the largest errors because of extremely broad resonances obtained in the intermediate region of coalescence. The signal shapes were difficult to observe; in a considerable temperature range the power level had to be increased considerably, with danger of saturation, merely to see the peaks above the base line, so that rate calculations were not attempted in this range. The method was used only in the region immediately below the coalescence temperature.

The best estimate of the activation energy is 12.1±1.0 Kcal./mole. Although a good Arrhenius plot was obtained, there remains the danger of systematic error throughout the calculations. The quantity of free BF_3 in the gas phase should increase to some extent as the temperature is raised, with a resultant change in the relative areas of the ^{19}F peaks in solution. At higher temperatures at which the peaks have

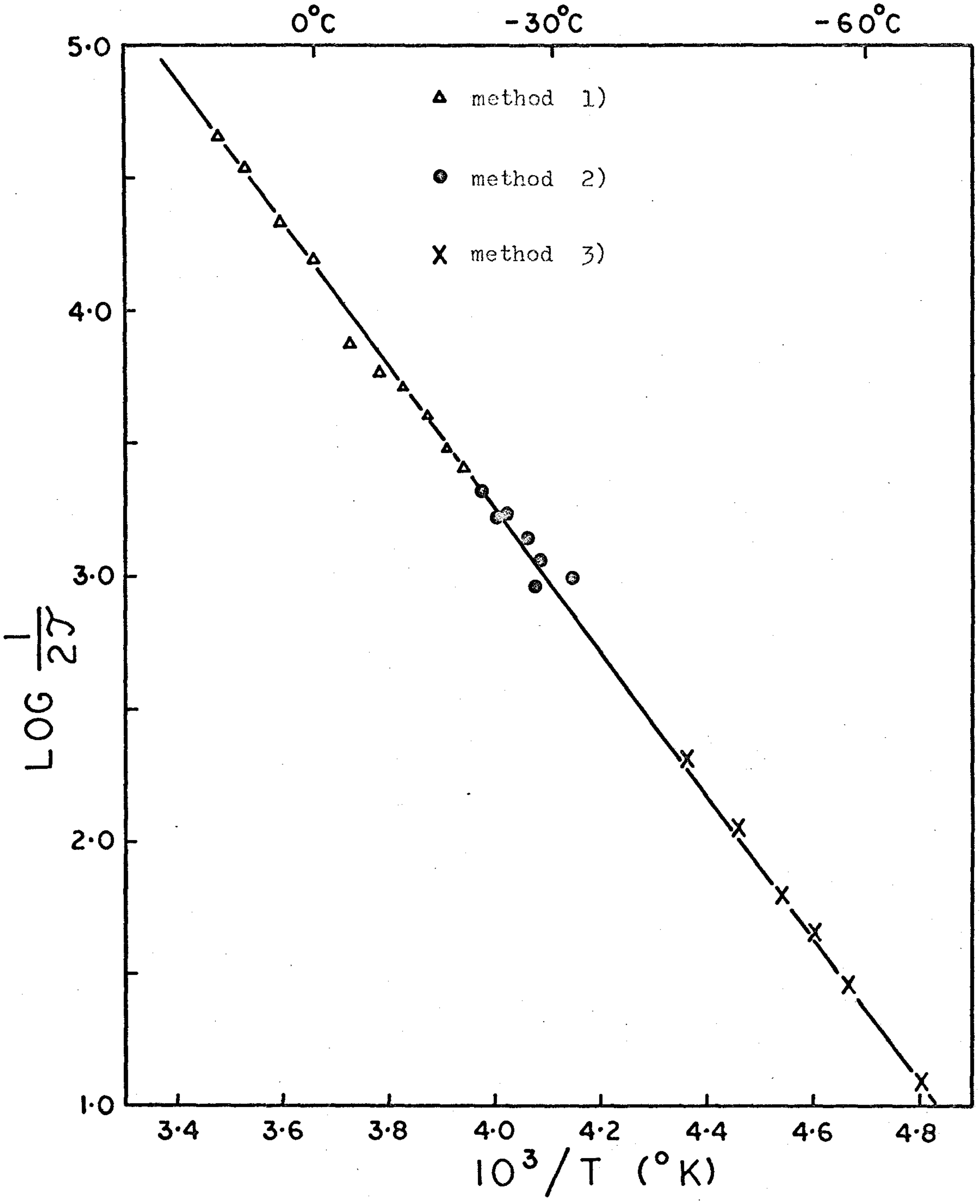

Fig. 19

Arrhenius plot for BF_3 exchange between 1:1 complex and free BF_3 in a solution of pinacolone and BF_3 in a 1:2 molar ratio in methylene chloride.

coalesced, such changes cannot be detected by NMR and can lead to erroneous values for rates of exchange. Changes in the relative chemical shift at higher temperatures could cause similar errors. The good linearity of the Arrhenius plot suggests, but does not prove, that these effects are not too serious.

Substitution of pinacolone for acetone in the ^{19}F rate study of exchange in the presence of excess BF_3 led to better solubility of the complex, so that a more concentrated solution could be used which allowed the very broad coalescence pattern to be observed over most of the range of line shapes.* The use of different ketones in the kinetic studies of rates of exchange in the presence of excess ketone and of excess BF_3 limits the value of a comparison of the results to some extent. However, this limitation does not appear serious since any differences in activation energies within the series of ketones appear to be less than the experimental error in determining the activation energies. It should be kept in mind that the apparent activation energy observed is likely to vary with relative proportions of acid and base since two or more mechanisms of different activation energies may contribute to the exchange process (50,53). It is of special interest, however, that the activation energies for exchange are quite similar in the cases studied when either acid or base is present in excess. This contrasts with the results of earlier studies

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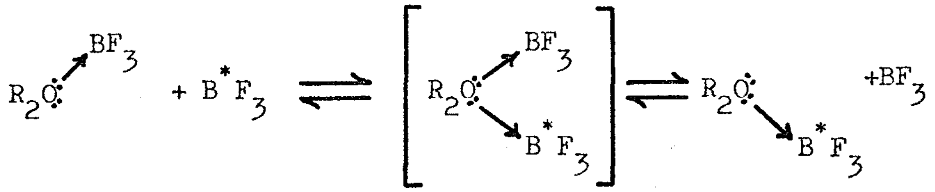
* In the sample used, some crystals formed on standing at -78° over several hours; however, the solution could be readily supercooled, so that good spectra could be obtained down to -90°.

by Rutenberg and Palko (53), discussed in Chapter I, which indicate that exchange in ether.BF_3 complexes becomes much faster, and the activation energy much less, in the presence of excess BF_3. A mechanism involving participation of the second of the oxygen donor's two lone pairs in the transition state might be involved in the exchange of excess BF_3 with the ether complexes:



(26)

XV

This mechanism would become important only in the presence of excess BF_3, and would allow exchange to occur more readily than either of the two competing mechanism postulated by Rutenberg and co-workers to occur in the presence of excess base (equations (15) and (16), p.73). If the above mechanism is valid for the observed more rapid exchange of BF_3 among ether molecules in the presence of excess BF_3, the absence of a similar more facile route for exchange in the presence of excess BF_3 in the ketone-BF_3-methylene chloride system indicates that the postulated transition state XV cannot form. Two alternative explanations of this appear reasonable. First, the second lone pair of the carbonyl oxygen may be completely unreactive towards a second molecule of BF_3; this would be in agreement with the reported (19) lower Lewis basicity of ketones with respect to ethers. Second, a weak complex may form between the "free" BF_3 and the methylene chloride solvent, as is suggested in Chapter IX. Rutenberg and Palko studied liquid mixtures of ethers and BF_3 without a solvent, so that the free BF_3 in their solutions can be considered to be free of any such secondary interactions, and thus may be more highly reactive than "free" BF_3 in methylene chloride. "Free" BF_3 in methylene chloride may be tied up sufficiently strongly by interaction with the solvent to prevent the formation of any significant amount of the very weakly bonded transition state XV. If either of these proposed explanations is correct, the exchange of excess BF_3 with the ketone complexes in methylene chloride solution should require a dissociation-recombination mechanism, which should have an activation energy equal to the heat of formation of the complex. A study of the behaviour of solutions of ether and BF_3 in methylene chloride would be of interest. If the presence of excess BF_3 does not increase the rate of BF_3 exchange in this solvent, it could be concluded that a specific methylene chloride solvent effect operates.

(iv) Boron-11 Spectra

It was not possible to observe separate ^{11}B peaks due to free and complexed BF_3 even at -90° in samples in which $[\text{ketone}] < [BF_3]$. Each sample studied gave a single rather broad peak; the peak width increased as the temperature was lowered, as is shown in Figure 20. This effect was observed for the pure liquid (diethyl ether).BF_3 complex as well as for solutions of ketone and BF_3. Rapid quadrupole relaxation of the boron spin states, a process which becomes more efficient as the temperature is lowered, probably contributes to the broadening, which might mask splittings due to a boron-fluorine coupling constant of up to 10 c.p.s. An exceptionally large amount of broadening of the single ^{11}B peak was observed at low temperatures in samples which

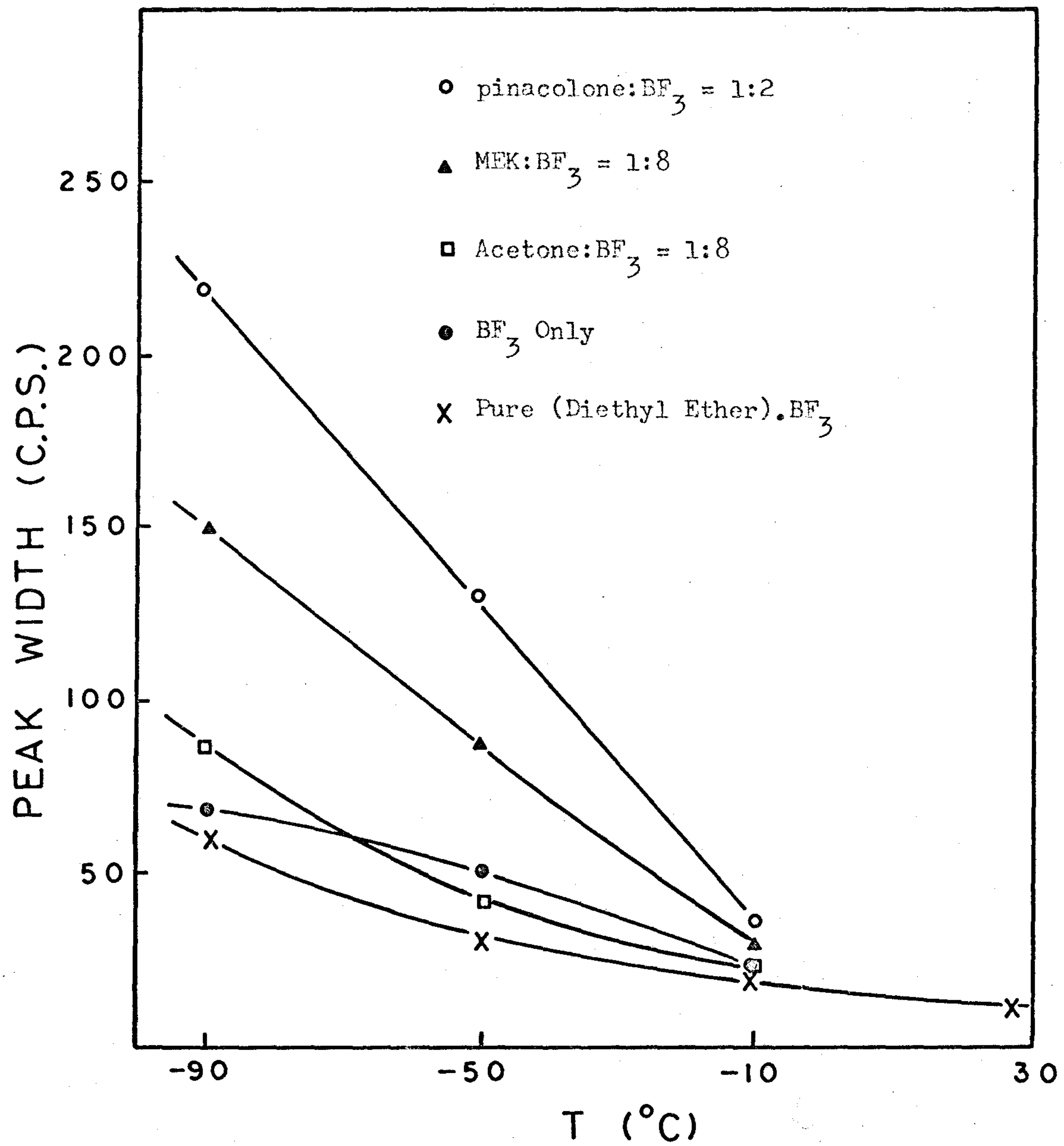


Fig. 20

Variation of boron-11 peak widths with temperature.

contained a two-fold excess of BF_3 over ketone. The additional broadening can probably be attributed to the effects of chemical exchange; samples containing an eight-fold excess of BF_3 did not give equally broad peaks.

The postulate of rapid quadrupole relaxation of boron is in accord with the absence of splittings due to boron-fluorine coupling in the ^{19}F spectra of the complexes. The smaller width at half-height at -10° of the ^{11}B peak of liquid (diethyl ether).BF_3, compared to the width of the peak in ketone-BF_3 solutions in which $[\text{ketone}] \geqslant [BF_3]$, indicates a more rapid quadrupole relaxation of the boron spin states in the ketone complexes. This is in accord with the observed sharper ^{19}F lines of the ketone complexes, which allowed the isotope shift to be seen clearly over a wide range of temperatures. The broader ^{19}F lines of the ether complexes do not always allow the isotope shift, which is of very similar magnitude, to be visible over the same temperature range. It apparently has not been observed in previous ^{19}F studies of ether.BF_3 complexes (46,50), although it was observed in a few solutions in the present work.

Figure 20 includes ^{11}B peak widths of a sample of BF_3 in methylene chloride solvent with only a small amount of trichlorofluoromethane present in addition. The ^{11}B spectrum is of interest in that, unlike the ^{11}B spectrum of pure liquid BF_3 (88), the quartet due to boron-fluorine coupling does not appear. The implications of the lack of boron-fluorine splittings are discussed in Chapter IX.

CHAPTER VII

EXCHANGE OF FLUORINE AMONG BORON ATOMS IN METHYLENE CHLORIDE SOLUTIONS OF KETONE.BF_3 COMPLEXES

INTRODUCTION

Low temperature ^{19}F spectra of solutions of ketones and BF_3 in methylene chloride in which $[\text{ketone}] > [BF_3]$ have two main peaks, of relative intensities 1:4 and relative chemical shift 0.066 p.p.m., arising from the $^{10}B-^{11}B$ isotope shift. This splitting of the ketone.BF_3 resonance into two peaks could not be observed at high temperatures; instead a single sharp peak was present. The implications of the collapse of the isotope shift are discussed in the present Chapter.

RESULTS AND DISCUSSION

(i) General

The NMR spectra of methylene chloride solutions of BF_3 and one of the four ketones acetone, MEK, MIK, and pinacolone have been discussed in Chapter VI; the disappearance of the isotope shift above -20° in ^{19}F spectra of solutions in which $[\text{ketone}] > [BF_3]$ was noted. The room temperature ^{19}F spectra of all solutions studied consisted of a single rather broadened peak, of different peak widths (2-8 c.p.s.) in different samples. The degree of broadening did not appear to be dependent on the ketone used or on the concentration or acid-base ratio of the sample. Spectra obtained at high temperatures consisted of a single peak, sufficiently sharp at 80° in all cases that an isotope shift of 0.066 p.p.m., if present, would have been clearly visible. It can be concluded that a rapid chemical exchange process occurs which averages the environments of the fluorine atoms. This implies a rapid scrambling of fluorine atoms among different boron atoms, and thus that a second exchange process occurs in these solutions, in addition to the process of breaking and re-forming of ketone donor-acceptor bonds, discussed in Chapter VI, which affects the ^1H spectra.

Figure 21 shows the collapse of the isotope shift in a solution of pinacolone (1.3M) and BF_3 (1.15M) containing isotopically substituted boron of approximately 52% ^{10}B and 48% ^{11}B. The spectra of the isotopically substituted sample shows the coalescence of the peaks more clearly than spectra of samples of natural abundance. It is evident from the spectrum at 54° that the isotope splitting is indeed absent at high temperatures. In this sample, unlike several others, there is little excess broadening of the signal in the coalescence region. Instead, the spectrum closely approximates the series of signal shapes expected for the collapse of two chemically shifted peaks.

The excess broadening found in the ^{19}F spectra of many samples in the temperature range of isotope shift coalescence is most easily explained by chemical exchange between the main ketone.BF_3 species and a second species which gives rise to a chemically shifted resonance. It has been pointed out (89) that the existence of a second species undergoing chemical exchange with the main species can cause a marked broadening of the resonance of the main species even if the second

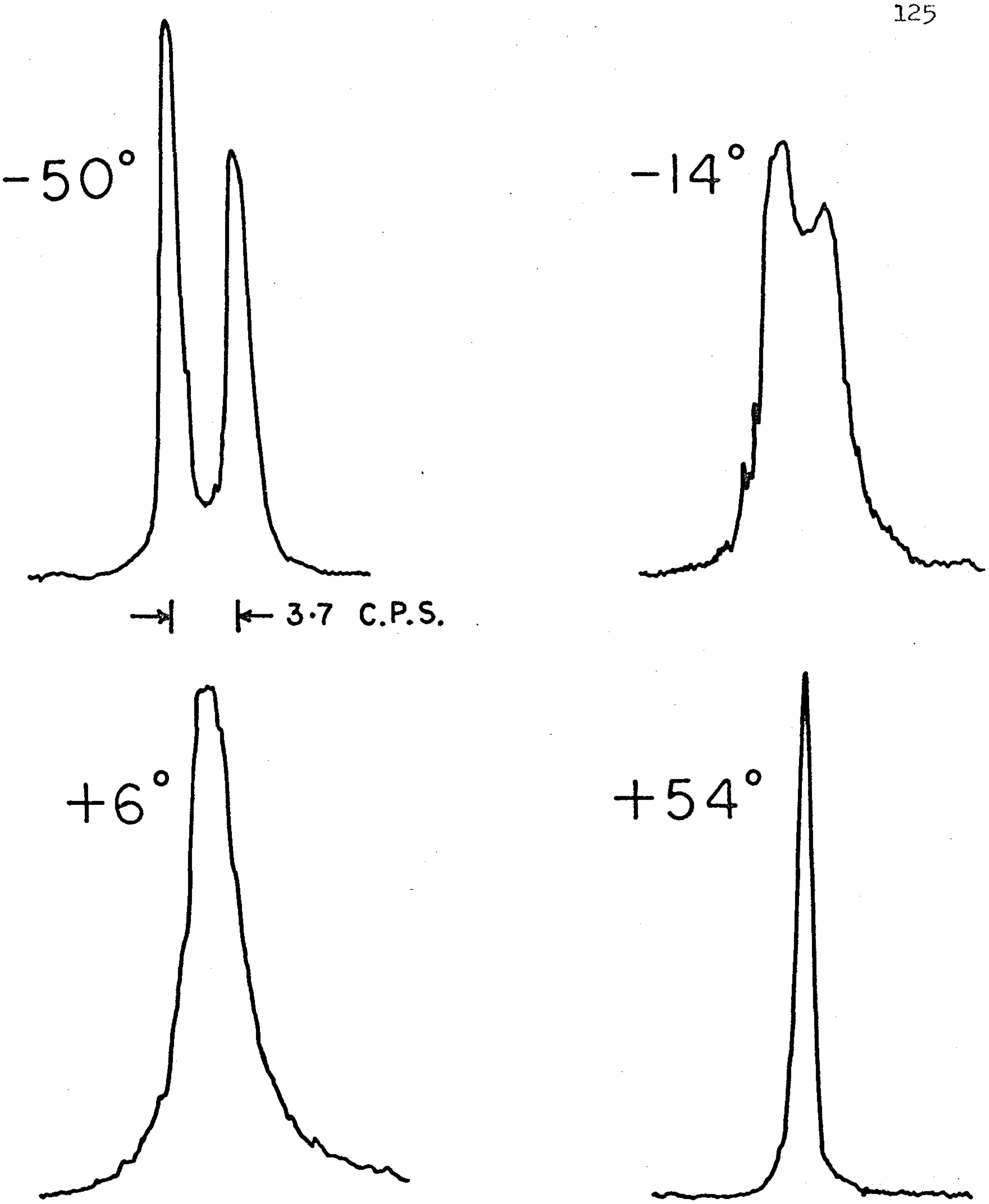


Fig. 21

Collapse of the isotope shift in a methylene chloride solution of pinacolone (1.3M), and BF_3 (1.15M), of isotope ratio $^{10}B:^{11}B=52:48$

species is present in such small amount that its own resonance absorption is not readily seen, even under conditions of slow exchange. In such cases the excess broadening of the main peak can provide a method of detecting the existence of the second species. The presence of extra broadening in the ^{19}F spectra of ketone.BF_3 solutions thus led to a search for a second small ^{19}F peak at low temperatures.

In all samples studied, a second small peak to high field of the ketone.BF_3 peak could be detected at low temperatures by the use of very high power levels. In a few samples the peak was of sufficient size that it could also be observed at normal power levels; the samples in which this peak was larger were those which had shown the greater degree of broadening of the ketone.BF_3 peaks near room temperature. At about -20° the small peak broadened to such an extent that it could not be observed above the noise level; it did not reappear at higher temperatures. This behaviour is in accord with a rapid chemical exchange of the fluorines of this species with those of the ketone.BF_3 species. In the few samples in which this peak was of a sufficient size to allow relative areas of it and of the main peak to be determined, it was found that the coalescence pattern agreed quite well with that calculated for collapse of two chemically shifted peaks by a rapid chemical exchange process.

It is evident that a fluorine-containing impurity is present, sometimes in very small amount, in all of the samples studied. Since the small peak collapses in the same temperature range as the isotope shift in the ketone.BF_3 resonance, it appears that a fairly general fluorine scrambling reaction occurs in solution. In a few samples in which the additional peak was especially large it was possible to detect fine structure. A skewed quartet structure, very similar to that of Figure 13c, Chapter IV, is strong evidence that the peak arises from $H_2O.BF_3$. The presence of differing amounts of moisture in different samples can explain the variable size of the peak. The assignment of the peak to $H_2O.BF_3$ was confirmed by the ^1H spectrum of one of the samples which gave a small 1:3:3:1 quartet, of splittings 2.78±0.1 c.p.s. and chemical shift 12.06, at -44°. The presence of $H_2O.BF_3$ in these solutions emphasizes the need for anhydrous conditions in studies of BF_3 complexes.

The temperature range of collapse of the $H_2O.BF_3$ and ketone.BF_3 peaks is quite similar to that observed in acetone solvent (Chapter III). In both acetone and methylene chloride solvents, the collapse of peaks due to exchange of BF_3 between different ketone molecules affects the spectra in a much lower temperature range (Chapters III and VI) so that a much faster reaction must be involved. Similar exchange processes are presumably involved in both solvents. The process which collapses the ketone.BF_3 and $H_2O.BF_3$ peaks may also be responsible for the collapse of the isotope shift.

Fluorine scrambling in the ketone.BF_3 complexes does not appear to be caused by $H_2O.BF_3$ since the collapse of the isotope shift occurs at about the same temperature regardless of the amount of $H_2O.BF_3$ in solution. It seems likely that a general rearrangement of fluorine occurs among all of the complexes in solution. If this is the case, the $H_2O.BF_3$ peak might be collapsed not by BF_3 exchange, as was assumed in Chapter III, but by the fluorine scrambling reaction. This would be in accord with a much greater donor-acceptor bond strength in $H_2O.BF_3$ than in the other complexes, so that the O-B bond is very nearly as strong as, or even stronger than, the B-F bonds.

(ii) Kinetic Studies

A few kinetic studies have been carried out. In a sample of MIK (0.7M) and BF_3 (0.3M), which gave an exceptionally large $H_2O.BF_3$ peak consisting of 17±4% of the total F-on-B peak area, approximate rates of fluorine exchange between the ketone.BF_3 and $H_2O.BF_3$ species were determined by comparison of observed and calculated spectra. A computer programme making use of equations (10.23) to (10.25) of (2), was used.* The calculations were complicated by the variation of the relative chemical shift of the peaks with temperature, shown in Figure 22.** Relative shifts in the coalescence region, required for the rate calculations, were obtained by extrapolation from Figure 22. The Arrhenius plot of the kinetic data is shown in Figure 23. Two parallel lines are obtained because species of unequal populations have unequal lifetimes with respect to mutual exchange. The activation energy for the exchange process was found to be 15.6 Kcal./mole. An error of up to ±2 Kcal./mole is likely as a result of the approximations involved. Comparison of Figure 23 with Figure 18, p. 111, which presents data for

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*The amounts of excess broadening of the large ketone.BF_3 peak caused by various rates of exchange of fluorines between ketone.BF_3 and $H_2O.BF_3$ were calculated. The programme then compared observed peak widths with the calculated ones, and by interpolation obtained lifetimes of fluorine on the nonequivalent sites at the temperatures of the observed spectra.

**A very similar temperature dependence of the relative shift was found in other solutions in methylene chloride. A similar effect was observed in acetone solution as well (e.g., Figure 11, p.69).

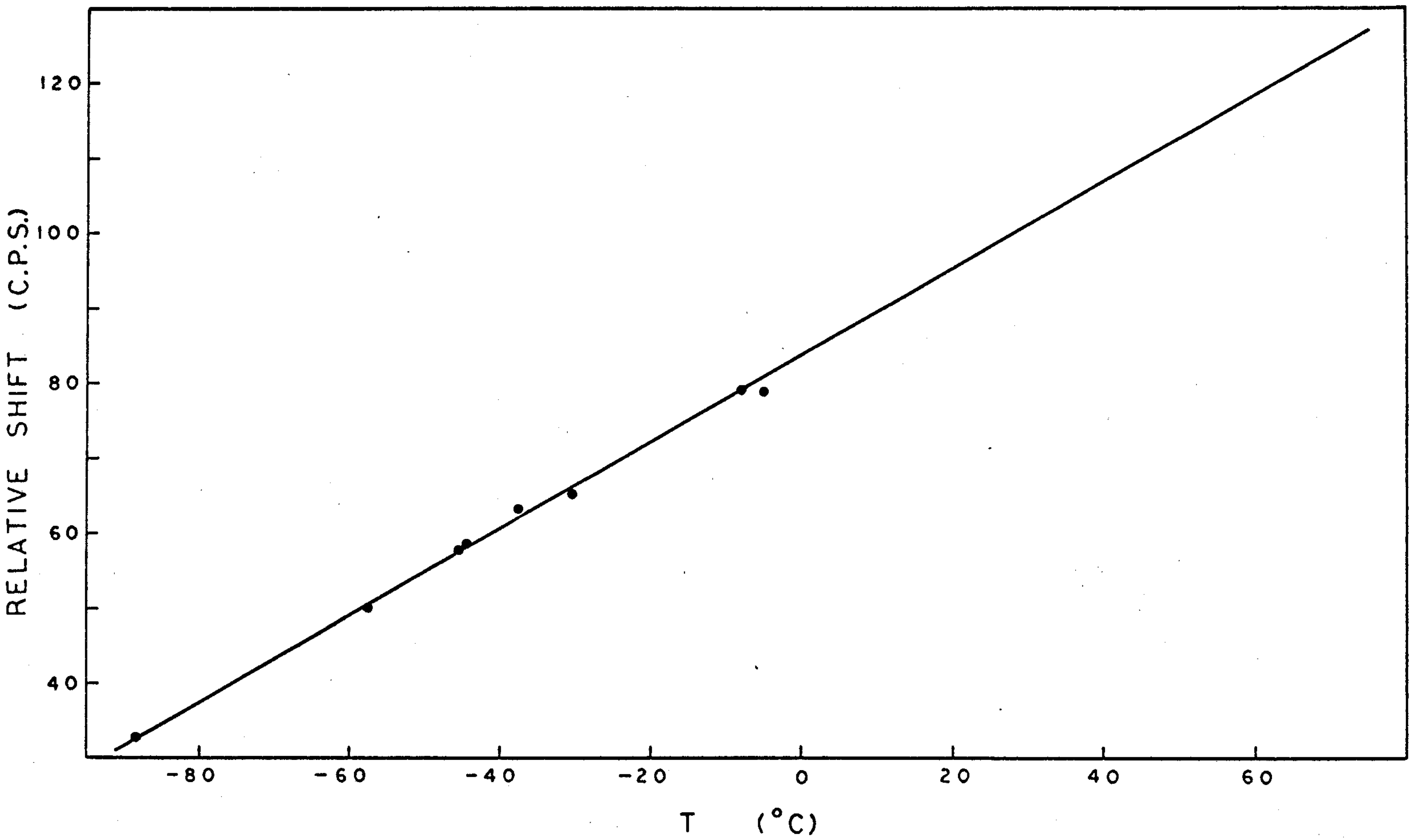


Fig. 22

Variation of relative ^{19}F chemical shift of $MIK.BF_3$ and $H_2O.BF_3$ with temperature.

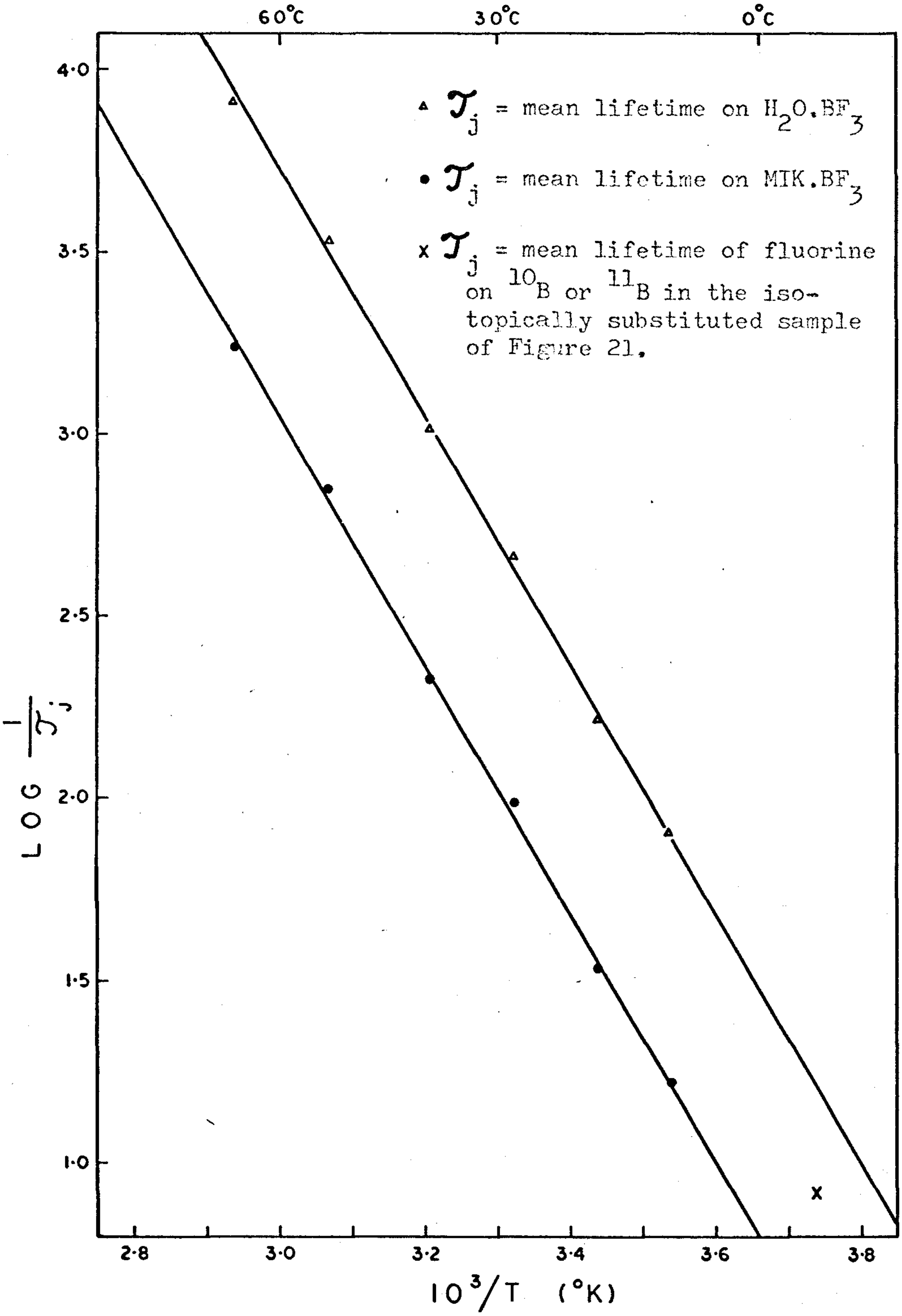


Fig. 23

Arrhenius plot for fluorine exchange between $MIK.BF_3$ (0.25M) and $H_2O.BF_3$ (0.05M) in methylene chloride.

BF_3 exchange among different donor sites in a solution of acetone.BF_3 and excess acetone, shows that the rate of the present reaction is less at a given temperature by a factor of about 1600, in spite of the lower concentration of the solution. This factor is in quite good agreement with that estimated for the same two exchange processes in acetone solvent (Chapter III).

The spectra of Figure 21, which illustrate the collapse of the isotope shift, are negligibly affected by broadening due to collapse of the ketone.BF_3 resonance with the $H_2O.BF_3$ resonance since very little $H_2O.BF_3$ is present in this solution. Thus the signal shapes obtained should approximate to those expected for the chemical exchange collapse of two peaks of equal areas and of relative chemical shifts 3.7 c.p.s. The lifetime 2τ of a fluorine atom attached to either ^{10}B or ^{11}B can be calculated at the coalescence temperature from

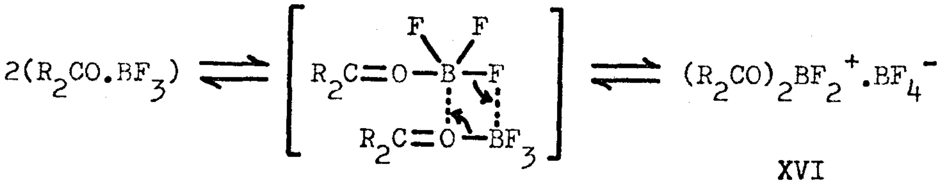
$$\tau = \frac{\sqrt{2}}{2\pi \nu_{AB}} , \qquad (27)$$

in which ν_{AB} = 3.7 c.p.s., the relative chemical shift of the peaks in the absence of exchange. The result is shown in Figure 23; the point falls between the two parallel lines obtained for fluorine exchange between $MIK.BF_3$ and $H_2O.BF_3$, at about the position through which the single line of the Arrhenius plot would pass if the concentration of $MIK.BF_3$ were equal to that of $H_2O.BF_3$. Thus the average lifetime of fluorine on a boron nucleus at this temperature is quite similar to the average lifetime of fluorine exchange between $MIK.BF_3$ and $H_2O.BF_3$ at the same temperature. Since different concentrations and different ketones are involved in the two samples compared, an exact fit to the Arrhenius plot is not expected; however, the fairly close agreement found suggests that the mechanism may be the same in both cases.

(iii) Possible Mechanisms for the Fluorine Scrambling

The experimental evidence described above establishes the existence of a fluorine scrambling reaction in methylene chloride solution. This appears to be analogous to the reported scrambling of halogen atoms of tetrahaloborate anions in methylene chloride solution (90), and to a similar scrambling of fluorine atoms in the tetrafluoroborate anion in acetonitrile solution, described in this thesis (Chapter X). Various mechanisms are possible for such a reaction.

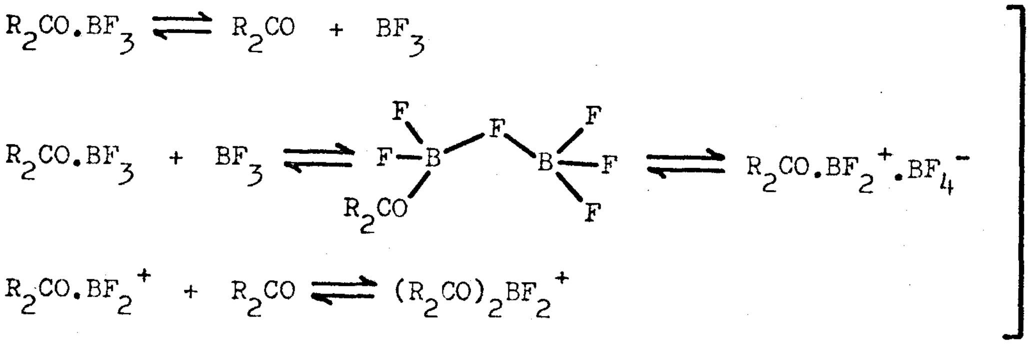
A rapid equilibration of the simple ketone.BF_3 complex with the ionic structure XVI would cause fluorine scrambling. This reaction might occur through a four-centre transition state:



XVI

(28)

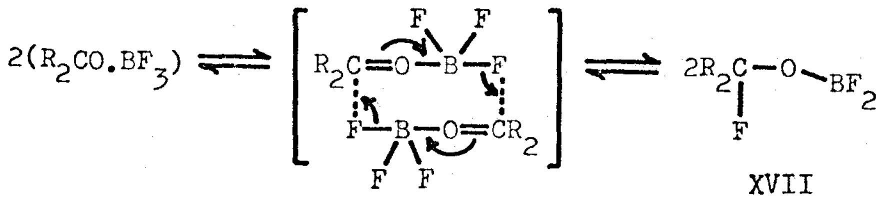
Alternatively, a preliminary dissociation of a mole of complex to give free BF_3 might be involved, as in the following reaction scheme:



(29)

Mixed species (donor)(donor')$BF_2^+.BF_4^-$, very similar to XVI, should be capable of existence as well, so that either of the above mechanisms should allow a general scrambling of fluorine among all BF_3 complexes. This would explain the collapse of the $H_2O.BF_3$ peak. The presence of less than 1% of the ionic species would likely not be detected by NMR, even in the slow exchange limit. Structures analogous to XVI seem to be rather common in solution. The 1:1 complex of acetonitrile and phosphorus pentafluoride has been reported to have the ionic structure $PF_4(CH_3CN)_2^+.PF_6^-$ in solution in excess acetonitrile (91). NMR studies have shown that solutions of niobium pentafluoride in DMF (92), ethanol (93) and dimethylsulphoxide (88) contain the NbF_6^- anion rather than the simple donor-acceptor complex. The structure IV (p. 29), proposed on the basis of NMR studies, is also analogous to XVI. Greenwood and Wade have proposed, on the basis of electrical conductivity measurements, that the fused complexes pyridine.BCl_3 and piperidine.BCl_3 are dissociated to the extent of about 1% to yield $(donor)_2.BCl_2^+.BCl_4^-$ (94).

A second possible mechanism, which would allow fluorine scrambling only among carbonyl donors, involves rapid reversible formation of the species XVII by a concerted mechanism involving two molecules of the simple 1:1 complex:



XVII

(30)

Structures analogous to XVII have been postulated by Kaplan and Weisleder (60) to explain the NMR spectra of the adducts of α-chloro- and α-bromopinacolone with BCl_3 and BBr_3, as has been described in Chapter I (p.31). The temperature dependence of the proton spectra of these adducts was attributed to reversible reactions involving the free acid and base. It should be noted that the formation of structures such as XVII need not involve the mechanism (30), but instead could proceed by a simple reversible addition of boron trihalide across the carbonyl double bond, a process especially likely in the presence of excess boron trihalide as in Kaplan and Weisleder's study. The simple addition mechanism would not cause fluorine scrambling. Mechanism (30) is limited in that it does not account for the collapse of the $H_2O.BF_3$ peak. It is possible that the collapse of this peak is due merely to breaking and re-forming of the donor-acceptor bond, which coincidentally has a rate similar to that of the fluorine scrambling reaction.

In connection with mechanism (30), it is of interest that some of Kaplan and Weisleder's results support an equilibrium between a simple donor-acceptor complex and a structure such as XVII. Solutions of α-bromopinacolone and excess BCl_3 were reported to give low temperature ^1H peaks in addition to those expected for the structure XVII; collapse of these extra peaks at higher temperatures indicates rapid equilibration of the species. The extra peaks consisted of sharp singlets corresponding to α-CH_2 and β-CH_3 resonances. Kaplan and Weisleder suggested that these peaks might arise from a 2:1 complex, ketone.$(BCl_3)_2$. However, it seems more likely that they arise from the simple 1:1 donor-acceptor adduct, since the complexation shifts (α-CH_2, 0.64 p.p.m., β-CH_3, 0.33 p.p.m.) are rather similar to those reported in Chapter VI for complexes of simple ketones with BF_3.* It seems reasonable that a similar equilibrium would exist in solutions of simple ketones and BF_3, but that the position of equilibrium would be so far in favour of the simple donor-acceptor adducts that the other structures do not give rise to observable NMR signals even in the slow exchange limit. A rate of interconversion similar to that indicated by the collapse of Kaplan and Weisleder's separate signals would, if mechanism (30) is involved, collapse the isotope shift as well, in about the observed temperature range.

Additional, less probable mechanisms, such as one involving a preliminary dissociation of the 1:1 complex to give $R_2CO.BF_2^+$ and F^-, could be written for the fluorine scrambling reaction. However, such mechanisms are much less likely than one involving breaking of the weaker donor-acceptor bond. Fluoride ion would not be expected to be split off readily in methylene chloride since no ionic fluoride is known which is soluble in methylene chloride (90). A similar but slower fluorine scrambling process which occurs in solutions of the tetrafluoroborate anion is discussed in Chapter X, pp.196-200; in this case dissociation of fluoride ion is obviously a required first step if reaction scheme (29) is involved.

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* Kaplan and Weisleder's complexation shifts quoted above do not correlate well with their much smaller shifts reported for the α-halogenopinacolone-BF_3 complexes, believed to be simple donor-acceptor adducts. The BF_3 complexes may be sufficiently weak, due to the electron-withdrawing α-halogen, that they are partially dissociated in solution; the observed chemical shifts would then be a weighted average of the free and complexed ketone, possibly with some of the structure XVII present as well.

Insufficient information is available to allow a choice between the possible mechanisms for the reaction causing fluorine scrambling in methylene chloride solutions of ketone and BF_3. It seems possible that both of the structures XVI and XVII might exist in small amounts in solution in equilibrium with the simple ketone. BF_3 complex.

CHAPTER VIII

BF_3-CATALYSED ALDOL CONDENSATION REACTIONS IN METHYLENE CHLORIDE SOLUTIONS OF ACETONE AND OF MESITYL OXIDE

INTRODUCTION

In the course of investigations of BF_3 exchange in solutions of ketones and BF_3 in methylene chloride solvent (Chapter VI) it was observed that dilute solutions of various relative proportions of ketone and BF_3 remain clear and only very slightly coloured even on heating to 100°, and that neither the ^1H or ^{19}F spectrum was much affected. This behaviour contrasts with the rapid darkening of dilute solutions of BF_3 in acetone on standing at room temperature, and the pronounced changes in the ^{19}F spectrum (Chapter III). A proton NMR investigation of the reactions of the complexes in methylene chloride is reported in the present Chapter. In the course of this work some interesting features of the spectra of solutions of mesityl oxide, water, and BF_3 in methylene chloride were observed.

RESULTS AND DISCUSSION

(i) Solutions of Simple Ketones and BF_3 in Methylene Chloride

Dilute solutions of acetone and BF_3, in methylene chloride, in which $[\text{acetone}] > [BF_3]$, were colourless when prepared at low temperatures but slowly became light yellow on standing for a few hours at room temperature; the colour change resembles the initial stage of the reaction of BF_3 solutions in acetone solvent. Room temperature proton spectra of the light yellow solutions showed that the combined peak of acetone and acetone.BF_3 remained the only large peak, although two very small peaks had appeared, unsymmetrically situated on either side of the acetone peak. Further standing at room temperature had no effect on the colour, nor did the small peaks near the acetone peak increase significantly in size. Other very small peaks at about 6.5 and 11.2δ were also not much affected by further standing at room temperature. After one hour of heating at 100°, little further darkening of the solution was evident; the size of the small impurity peaks near acetone, and the peak at 6.5δ, had not increased significantly. However, the peak at 11.2δ gained in intensity, and some new small peaks appeared to high field.

Similar solutions of BF_3 and the ketones MEK, MIK and pinacolone also did not react significantly at room temperature. MEK and MIK solutions discoloured slightly on standing at room temperature for a few hours, but no detectable discoloration occurred in pinacolone solutions even after heating at 100°. ^{19}F spectra at -80° confirmed that the ketone.BF_3 peak remained the only large peak. As described in Chapter VII, a second small peak arising from $H_2O.BF_3$ could be detected as well.

In solutions in which $[\text{ketone}] < [BF_3]$, the ketone condensation reaction apparently does not occur, since the characteristic yellow or straw colour does not appear, and in the case of acetone no small peaks appear near the acetone peak and in the 10-12δ region of the ^1H spectrum. In several solutions containing excess BF_3 which had been allowed to stand at room temperature for several days, a doublet centred at 0.23δ, with a splitting of 7.4±0.3 c.p.s., appeared in the proton spectrum and became larger on further standing. The observed pattern agrees closely with that reported for trimethylsilyl fluoride (0.20δ, J=7.48 c.p.s., (95)); it is apparent that a methyl group has been split off from the TMS present as an internal proton standard. Since the same doublet was obtained in a solution of phenol with excess BF_3, it is certain that it does not arise from any reaction of the ketone. No peaks arising from a second product of this reaction, which would presumably be methylboron difluoride, were identified.

The reaction of TMS, but not of ketone, when BF_3 is present in excess is in accord with the known stability of protonated ketones in strong proton acids such as sulphuric acid (71). The condensation-dehydration reaction of the ketones apparently takes place only in the presence of some free ketone. The reaction of TMS with BF_3 is analogous to the loss of a methyl group of TMS in strong proton acids such as concentrated sulphuric acid (96), in which ketones are protonated but do not react further. This emphasizes that TMS must be used with caution as an internal standard in highly acidic mixtures, either of Brønsted acids or of Lewis acids.

(ii) <u>Solutions of Mesityl Oxide, Water, and BF_3 in Methylene Chloride</u>

Some of the very small peaks which appear in acetone-BF_3 solutions are likely to arise from mesityl oxide, the first product of the aldol condensation of acetone. To test this possibility, proton spectra of mesityl oxide solutions were studied. A solution of mesityl oxide alone in methylene chloride gave the -80° spectrum of the methyl region shown in Figure 24a, and a peak to lower field arising from the olefinic

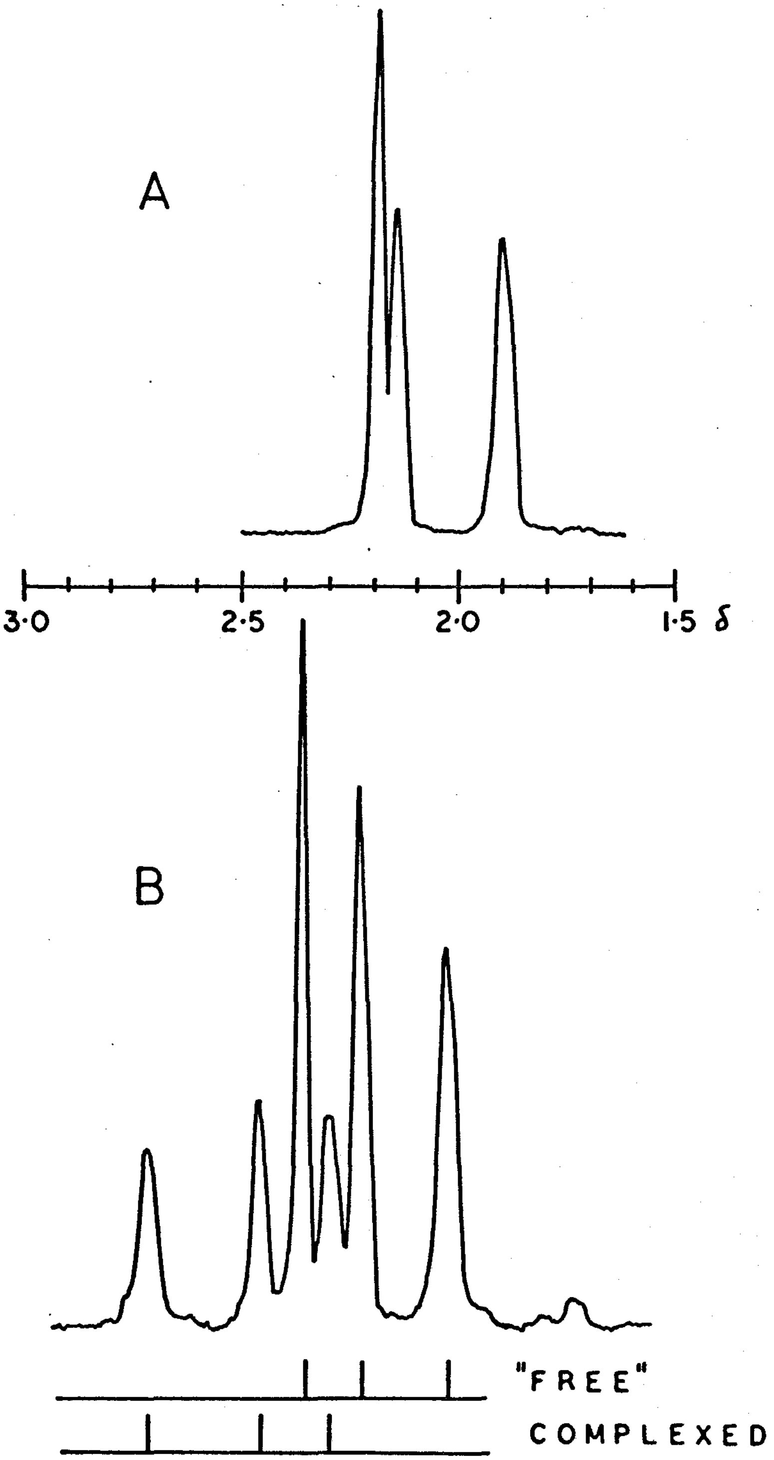


Fig. 24. -80° proton spectra of the methyl region of solutions of mesityl oxide in methylene chloride. A. without BF_3; B. with added BF_3

α-proton. The methyl peaks at 1.90 and 2.14δ, which are considerably broader than the third at 2.18δ, presumably arise from methyl groups in environments which allow similar small spin-spin couplings and are tentatively assigned to the two γ-methyl groups. The sharper peak would then arise from the α-methyl group, which would be broadened only slightly by α,α' coupling. The -80° chemical shifts of this sample are given in Table V (sample 1).

The room temperature spectrum of a methylene chloride solution of mesityl oxide and BF_3 in which [mesityl oxide]>[BF_3] was similar to the spectrum of mesityl oxide alone, except that all the peaks were considerably shifted to lower field. Also none of the methyl peaks were as close together, as a result of different complexation shifts of the different peaks. In the -80° spectrum six peaks instead of three were present in the methyl region (Figure 24b) and two instead of one were present in the region of the olefinic α-hydrogen. Thus BF_3 exchange is rapid at room temperature but slow at -80° on the NMR time scale, as in the case of the simple saturated ketones discussed in Chapter VI. Peaks in the -80° spectrum could from their relative sizes be assigned to either the free or the complexed ketone. The chemical shifts of the peaks as thus assigned are given in Table V (sample 2). A small, broadened peak at 13.2δ was present in addition to the mesityl oxide peaks, indicating the presence of a strongly acidic species.

Table V includes chemical shift data obtained from methylene chloride solutions of mesityl oxide, water, and BF_3, such that [mesityl oxide] + [water]>[BF_3]. Sample 3, which had been allowed to stand at room temperature for a week before spectra were obtained,

TABLE V

-80° PROTON CHEMICAL SHIFTS IN METHYLENE CHLORIDE SOLUTIONS OF MESITYL OXIDE

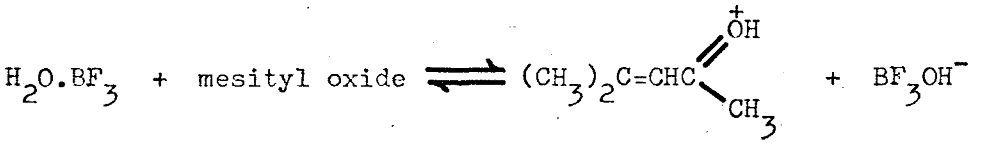
Sample No.	Solute	Chemical Shifts (δ)								
		"free" mesityl oxide				mesityl oxide.BF_3				acidic species
1	mesityl oxide	6.14	2.18	2.14	1.90					
2	mesityl oxide and BF_3	6.30	2.36	2.24	2.03	6.63	2.72	2.48	2.31	13.18
3*	mesityl oxide, water, and BF_3					6.62	2.69	2.43	2.27	12.03
4	mesityl oxide, water, and BF_3	6.44	2.51	2.32	2.15	6.64	2.70	2.45	-	11.40
5	mesityl oxide, water, and BF_3	6.55	2.58	2.37	2.14	6.68	2.67	2.41	2.21	13.10
average chemical shifts of (mesityl oxide).BF_3						6.64	2.70	2.44	2.26	
BF_3 complexation shifts						0.50	0.52	0.30	0.36	
shift of "free" mesityl oxide peaks between samples 1 and 5						0.41	0.40	0.23	0.24	

* allowed to stand one week at room temperature

gave no peaks at -80° which could be assigned to free mesityl oxide, indicating that a considerable amount of the mesityl oxide had reacted; other peaks arising from reaction products in this sample are discussed in a later section. The fresh samples 4 and 5 gave spectra quite similar to that of sample 2. It is seen in Table V that the chemical shifts of the peaks assigned to the 1:1 complex remain essentially constant in the different samples. From the average values of these, and from the chemical shifts of the peaks in the sample containing no BF_3 (sample 1), the BF_3 complexation shifts were determined for mesityl oxide, as shown in Table V. The complexation shifts of the γ-methyl peaks are about two-thirds as large as those of the α-methyl and olefinic α-hydrogen peaks. These γ-methyl shifts are much greater than would be expected from the inductive effect alone; this provides strong evidence for delocalization of charge along the conjugated system by a mesomeric effect.

While the chemical shifts of the peaks assigned to (mesityl oxide).BF_3 remain constant in the different samples, the shifts of the peaks assigned to free mesityl oxide are shifted considerably to lower field of corresponding peaks in the sample which contained no BF_3. The magnitude of the shifts to low field appears to vary with the amount of water in the sample. Thus sample 2, to which no water was deliberately added but which nevertheless had a small low field peak probably due to moisture in the solvent, showed the smallest low field shift of the "free" peak. In a given sample, the largest shifts of the "free" peaks to low field are found for the α-methyl and olefinic α-hydrogen resonances; as in the case of the BF_3 complexation shifts, the shifts of the γ-methyl peaks are about two-thirds as large.

The methyl peak of "free" methanol shows a similar shift to low field in methanol-BF_3 solutions in sulphur dioxide (Chapter V); the same type of process probably occurs in solutions of mesityl oxide, water, and BF_3 in methylene chloride. If mesityl oxide is a sufficiently strong base that a significant fraction of it is protonated in the presence of $H_2O.BF_3$, an increase in the protonated form with increasing proportions of H_2O and BF_3 would cause an increasing low field shift of the "free" peaks. The "complexed" peaks of mesityl oxide would not be expected to shift significantly, as does the "complexed" peak of methanol (Chapter V), because mesityl oxide cannot similarly lose a proton. Thus the following rapid proton exchange reaction apparently occurs in solution:



$$H_2O.BF_3 + \text{mesityl oxide} \rightleftharpoons (CH_3)_2C{=}CHC(=\overset{+}{O}H)CH_3 + BF_3OH^- \qquad (31)$$

In support of this, the single hydroxyl peak is in some samples considerably to low field of the position previously found for $H_2O.BF_3$ (10.5-12.0δ). Some ketonic $= OH^+$ resonances have been reported to occur at 12.5-15.5 p.p.m. with respect to external (capillary) TMS (80,97). It appears that an averaging of peaks arising from (mesityl oxide).H^+, $H_2O.BF_3$, and BF_3OH^- should give rise to the observed peak, at 11.4-13.2δ in different samples. The various degrees of broadening and the absence of fine structure are further indications of a rapid exchange process. Protonation of mesityl oxide under conditions which apparently do not protonate acetone implies that mesityl oxide is a stronger Brønsted base than acetone, in keeping with its stronger Lewis basicity with respect to BF_3 (Chapter III).

The above interpretation satisfactorily explains the proton spectra. However, some of these solutions gave an unexpectedly large number of ^{19}F peaks in the region of fluorine on tetrahedral boron. Samples 3, 4 and 5 gave four peaks in this region, the relative areas and relative chemical shifts varying between samples in a complex manner. Reaction of sample 3 at high temperatures gave a few new peaks as well. Sample 2 had two major peaks of relative chemical shift 0.70 p.p.m., one of which probably arises from $H_2O.BF_3$. There is insufficient information available to identify all of the ^{19}F peaks; the existence of several species in solution should be kept in mind. Possibly the enol form of mesityl oxide, or complexes of higher ketones, are involved.

(iii) The Presence of Identical Species in Solutions of Acetone and BF_3, and of Mesityl Oxide, Water, and BF_3: Forward and Reverse Aldol Reactions

The methyl chemical shifts of mesityl oxide and (mesityl oxide).BF_3 cover the range 1.90 to 2.70δ (Table V) and are not markedly temperature-dependent. This range includes practically the entire range of chemical shifts expected for mixtures of acetone and acetone.BF_3 (Chapter VI). Thus small amounts of mesityl oxide present in solutions of acetone and BF_3 should give small peaks near the acetone peak and likely on both sides of it; such peaks have been observed in several samples. Normally two peaks, of relative chemical shift about 0.42 p.p.m., are visible; this shift is in agreement with the observed separation of the outermost two methyl groups in the spectrum of the (mesityl oxide).BF_3 complex. Presumably the central methyl peak is obscured by the large acetone peak. Further evidence for the presence of mesityl oxide in solutions of acetone and BF_3 in methylene chloride is provided by the presence of a small peak at about 6.5δ, which presumably arises from the olefinic α-hydrogen.

The methyl region of the room temperature proton spectrum of a solution of mesityl oxide, water, and BF_3 which had been allowed to stand at room temperature for a week (sample 3 of Table V) is shown in Figure 25a. A peak is present in addition to the three peaks of equal size which are assigned to mesityl oxide. In order to observe further reaction the sample was heated at 100^o for 10 minutes; Figure 25b shows the resulting spectrum. The reaction is obviously fairly rapid at 100^o, since the mesityl oxide peaks have greatly decreased in intensity while the new sharp peak is much larger. A second new peak is visible as well. After heating at 100^o for a further 15 minutes the spectrum shown in Figure 25c was obtained. Less mesityl oxide remains; both new peaks have increased in size. The chemical shifts of the mesityl oxide peaks remained essentially constant throughout the reaction while the chemical shift of the large new peak shifted to lower field, as is indicated in Figure 25. As the reaction at 100^o proceeded, much of the absorption intensity of the spectrum shifted away from the "ketone methyl" region shown in the Figure and appeared as broad irregular absorptions to high field of this region. This indicates extensive condensation to yield amorphous

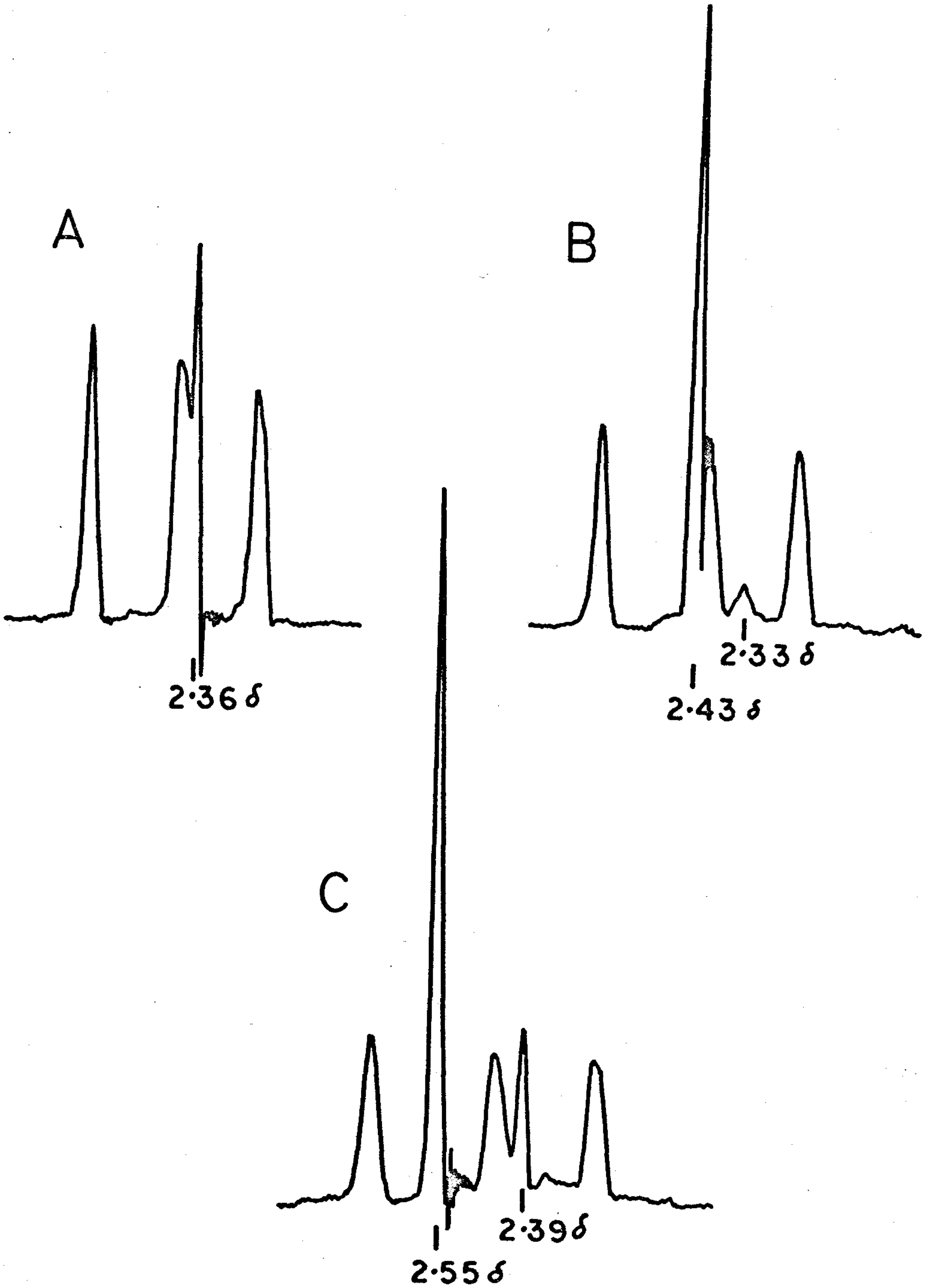


Fig. 25. Room temperature proton spectra of the methyl region of a solution of mesityl oxide, water, and BF_3 in methylene chloride. Reaction times:
A. one week at room temperature
B. + 10 minutes at 100°
C. + 15 minutes (total 25 minutes) at 100°

high molecular weight products, a reaction competitive with the reactions forming the definite chemical compounds giving rise to sharp peaks in the "ketone methyl" region. The darkening of the solution on standing for a day at room temperature had already shown that some decomposition had occurred.

Table VI illustrates the close correspondence of peaks in the proton spectra of methylene chloride solutions of acetone and BF_3, and of mesityl oxide, water, and BF_3, after reaction at 100°. The similarities in the patterns are especially significant since the two samples initially had no species in common except BF_3, TMS, and methylene chloride.

TABLE VI

ROOM TEMPERATURE PROTON CHEMICAL SHIFTS IN METHYLENE CHLORIDE SOLUTIONS AFTER REACTION AT 100°

Solute	Time at 100° (min.)	Chemical Shifts (δ)[*]							
acetone and BF_3	60	11.23	6.47	2.64		2.42 (sh)	$\underline{2.36}$	2.22	(1.70, etc.)[**]
mesityl oxide, water and BF_3	25	$\underline{10.43}$	$\underline{6.53}$	$\underline{2.66}$	2.55	$\underline{2.44}$	2.39	$\underline{2.25}$	(1.67, etc.)[**]

[*] initial peaks underlined

[**] small peaks arising from condensation products appear at high field.

In the sample of acetone and BF_3 the high temperature did not significantly increase the relative size of the small peaks near acetone, but did increase the size of the peak at 11.23δ, and also caused the appearance of some broad irregular absorptions to high field, as were found in the mesityl oxide sample.

The presence, in proton resonance spectra of methylene chloride solutions of acetone and BF_3, of small peaks which closely match the peaks of mesityl oxide, as is demonstrated in Table VI, provides evidence for the formation of mesityl oxide. The absence of a significant increase in the size of the mesityl oxide peaks on heating for one hour at 100° strongly suggests that an equilibrium is reached between acetone and mesityl oxide. However, an increase in the size of the low field peak, assigned to $H_2O.BF_3$, and of the broad absorptions at high field shows that a very slow reaction occurs which yields higher condensation products. This reaction likely requires mesityl oxide and is slow because of the low concentration of mesityl oxide in solution. Thus the following equilibria appear to explain the results:

$$\left.\begin{array}{l} 2(\text{acetone}) \xrightleftharpoons{BF_3} \text{mesityl oxide + water} \\ \text{mesityl oxide + acetone} \xrightleftharpoons{BF_3} \text{higher condensation products + water} \end{array}\right] \quad (32)$$

If acetone is strongly favoured in the first equilibrium the mesityl oxide peaks would never become large in a solution of acetone and BF_3.

It should be noted that exact correspondence of room temperature chemical shifts in different samples is not to be expected. The room temperature chemical shifts are weighted averages of the shifts of free and complexed species, the relative proportions of which vary between samples. Comparison of the chemical shifts of the mesityl oxide peaks of both samples in Table VI with the values for the 1:1 complex, shown in Table V, indicates that in both samples most of the mesityl oxide is complexed. However, in the solution of acetone and BF_3 in Table VI, sufficient BF_3 is present to complex with only half of the acetone. Thus mesityl oxide is a stronger donor to BF_3 than is acetone, as was proposed in Chapter III.

The existence of a BF_3-catalysed equilibrium between acetone, and mesityl oxide and water, would imply that solutions of mesityl oxide, water, and BF_3 in methylene chloride should react to yield acetone by a reverse aldol condensation, which should be competitive with the formation of higher condensation products. It seems reasonable that the large sharp peak at 2.55δ (Table VI and Figure 25c) might arise from acetone; this is supported by the difficulty in proposing any other compound which might arise from mesityl oxide under mild conditions and which could give rise to a proton spectrum consisting of only a single sharp peak. The shift of this peak to lower field on reaction of the sample at 100° (Figure 25) is in accord with the expected behaviour of acetone. In this sample, in which $[\text{mesityl oxide}] + [\text{water}] > [BF_3]$, the first acetone to form would not be able to displace the stronger bases water or mesityl oxide from their complexes and should give a proton signal near the position of free acetone, 2.14δ. However, by the time the first spectrum (Figure 25a) was obtained, after a week of reaction at room temperature, all of the excess free mesityl oxide had reacted, as was shown by the absence of -80° peaks due to free mesityl oxide (sample 3 in Table V). Further reaction to give more acetone would consume complexed mesityl oxide and water; BF_3 would be displaced as these stronger donors are consumed and would complex with the weaker donor acetone, formed in the reaction. Thus the sharp peak due to acetone should show the observed shift to lower field as it gains in intensity, since it is a weighted average of peaks arising from free and complexed acetone; the relative proportion of acetone.BF_3, with respect to free acetone, is increasing.

The -80° spectrum corresponding to the room temperature spectrum of Figure 25a contained, in addition to the (mesityl oxide).BF_3 peaks, two additional peaks instead of the single sharp room temperature peak. This appears to further confirm that acetone is formed, since at this temperature separate peaks are expected for acetone and acetone.BF_3. However, the chemical shifts of these were 2.39 and 2.63δ, instead of the 2.10 and 2.72δ expected (Chapter VI). This discrepancy is not explained. The pronounced shift of the "free" acetone peak to low field is similar to the shift of the "free" mesityl oxide peak discussed previously, and suggests partial protonation of acetone. However, this explanation seems unlikely as it was shown in Chapter IV that $H_2O.BF_3$ is unable to donate a proton to acetone when acetone is the solvent.

The assignment of the principal new "ketone methyl" peak to a weighted average of acetone and acetone.BF_3 was confirmed by studies on a very similar solution (sample 5 in Table V). This sample gave a similar small sharp peak at 2.60δ in the "ketone methyl" region, in addition to the mesityl oxide peaks, after standing at room temperature. The addition of small amounts of acetone to the sample caused this peak to increase greatly in size and to shift to higher field (to 2.23δ), as is expected if the peak is a weighted average of peaks arising from free and complexed acetone.

Although the formation of acetone from mesityl oxide and water seems well established by the above evidence, considerably less than half of the mesityl oxide reacts in this way; the rest apparently forms higher condensation products. This was shown by the appearance of broad, poorly defined resonances to high field of the "ketone methyl" region, which increased in size quite rapidly at 100° so that after 25 minutes of reaction they had a total area about equal to the total area of the peaks in the "ketone methyl" region. The changes in the relative areas of the hydroxylic peak and the mesityl oxide peaks also demonstrate the predominance of the condensation reaction. Since $[\text{mesityl oxide}] > [\text{water}]$ in this sample, reversion to acetone as the dominant reaction would lead to a decrease in the relative intensity of the hydroxylic peak with respect to the mesityl oxide peaks. Instead the hydroxylic peak gained in intensity, showing that dehydration yielding higher condensation products occurred to a greater extent than hydration and breaking of the carbon chain to give acetone.

The observed more rapid formation of higher condensation products when mesityl oxide rather than acetone is present initially is in accord with the equilibria (32). Since observable amounts of the higher products form even in solutions of acetone and BF_3 in which the concentration of the intermediate mesityl oxide remains small, these products should form much more rapidly when mesityl oxide is present initially in large amount. These conclusions are in accord with the observed pronounced discolouration of solutions of mesityl oxide and BF_3 on standing at room temperature, whereas similar solutions of acetone and BF_3 discolour only very slowly.

The small peak present at 2.39δ in the "ketone methyl" region of Figure 25c might arise from mesitylene, another product of acid-catalysed condensation of acetone, for which the methyl chemical shift is reported to be 2.25δ. The aromatic peak of this compound, only one-third as large and reported to appear at 6.78δ, could have been missed.

The evidence presented in this Chapter strongly supports the postulate that the same series of compounds, interconvertible by forward and reverse BF_3-catalysed aldol reactions, exists in methylene chloride solutions of either acetone and BF_3, or mesityl oxide, water, and BF_3, which have been allowed to react for a sufficient length of time. It seems unlikely that a true equilibrium was attained in any of the solutions studied, as some of the reactions appear to be quite slow. It is not clear whether the reactions are much slower than those in acetone solvent (Chapter III) or whether the presence of a large excess of acetone merely makes the changes more visible by displacement of the equilibrium position in favour of BF_3 complexation with the condensation products, which strongly affects the ^{19}F spectrum. Further experiments would be desirable to verify the postulated equilibria (31) and (32), and the origin of some of the observed NMR peaks.

CHAPTER IX

WEAK COMPLEXES OF BORON TRIFLUORIDE

INTRODUCTION

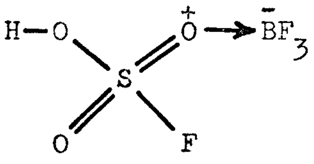
Broadening of a large NMR peak can occur as a result of exchange of magnetic nuclei between the major species and a minor species present in solution; the degree of broadening can be significant even if the resonance peak due to the minor species cannot be detected (89). In a few systems, in which no complexation of BF_3 was expected because of previous reports in the literature that such complexation does not occur, a temperature-dependent broadening of the single ^{19}F peak assigned to free BF_3 could not be readily explained other than by the assumption that the fluorine of free BF_3 exchanges with a minor species in solution. This minor species is probably a weak complex of BF_3; the formation constant is apparently low, so that the complex is largely dissociated into the free components. Also the absence of fine structure due to B-F coupling in the ^{19}F spectrum of BF_3 in methylene chloride and similar solvents is interpreted in terms of rapid reversible formation of a weak complex between BF_3 and the solvent.

RESULTS AND DISCUSSION

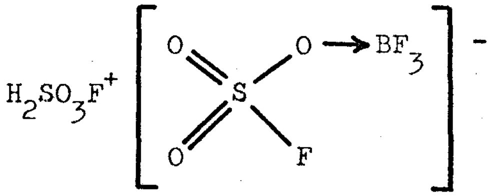
(i) Boron Trifluoride in Fluorosulphuric Acid

A solution of boron trifluoride in fluorosulphuric acid gave a

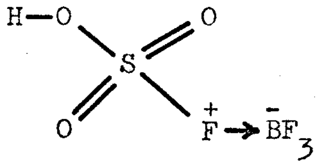
^{19}F peak, assigned to free BF_3, at 128.2 p.p.m. at room temperature, and at 127.0 p.p.m. at -90°, to high field of capillary trichlorofluoromethane. The absence of a marked temperature dependence of the chemical shift of the peak contrasts with the strong temperature dependence of the peak width at half-height, shown in Figure 26. The remarkable broadening of the peak in the intermediate temperature range of the Figure is most easily explained by the postulate that a small fraction of the BF_3 is complexed with the solvent. Various types of complex might form, such as XVIII - XX:



XVIII



XIX



XX

Rapid reversible abstraction of fluoride ion from the solvent to form BF_4^- cannot be involved as the ^{19}F resonance of fluorosulphuric acid remains separate and sharp.

The great excess broadening of the BF_3 peak, up to almost 30 c.p.s., is presumably a result of a large relative chemical shift between the exchanging species. The equation for the excess broadening of a strong peak due to exchange with a minor species, developed and used in a more general form by Meiboom (89) and used in the form given below by Cocivera (98), is

$$\Delta = \frac{p\,\delta^2\,\tau}{1 + \delta^2\tau^2} \qquad (33)$$

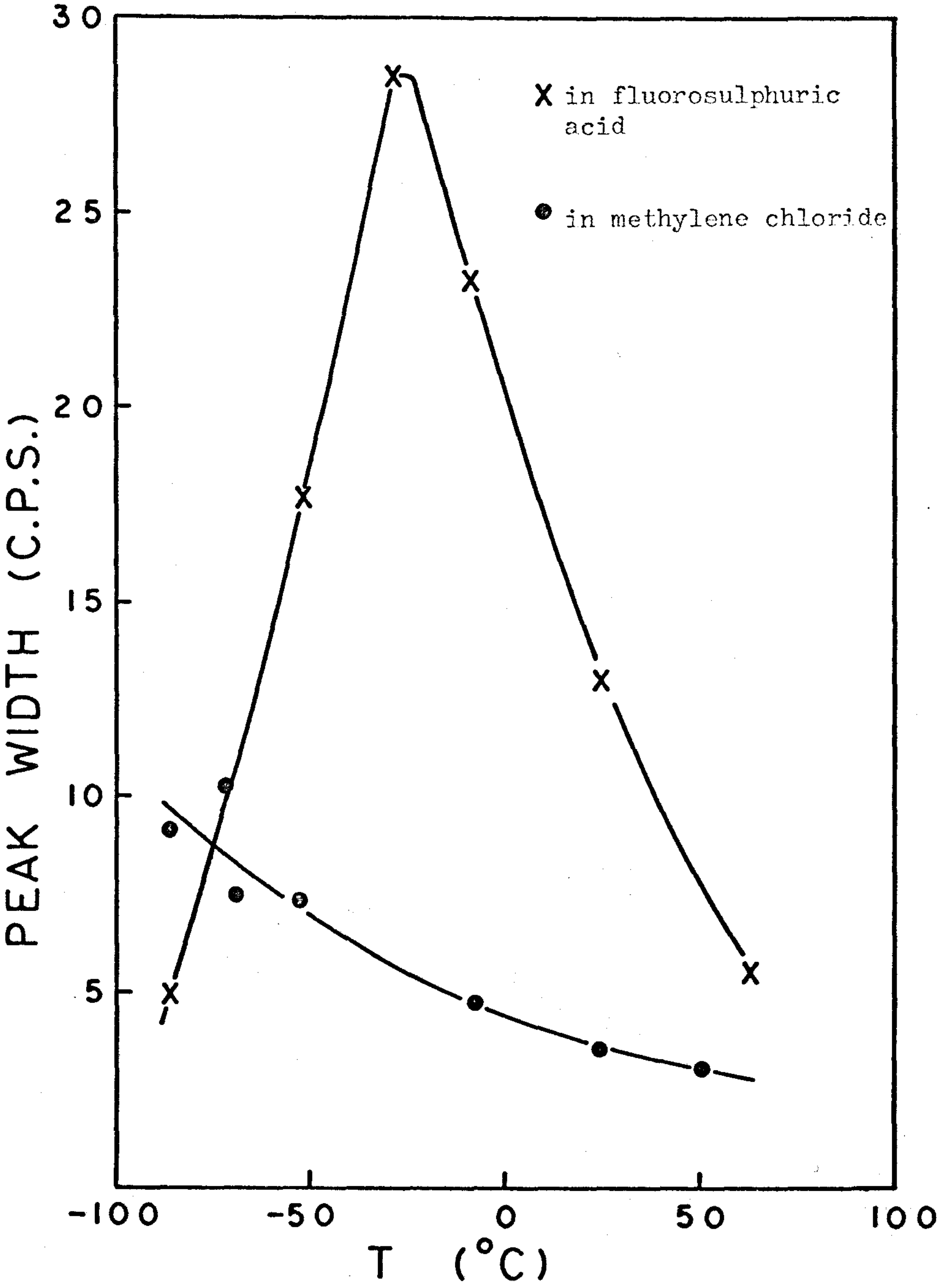


Fig. 26. Variation of ^{19}F peak width at half-height with temperature in BF_3 solutions

in which Δ is the excess broadening in radians per second, p is the fraction of the resonating nuclei which are in the minor environment, δ is the relative chemical shift in radians per second, and $\mathcal{T}$ is given by

$$\mathcal{T}^{-1} = \mathcal{T}_{major}^{-1} + \mathcal{T}_{minor}^{-1} , \qquad (34)$$

in which $\mathcal{T}_{major}$ and $\mathcal{T}_{minor}$ are the average lifetimes of the magnetic nuclei in the major and minor environments. Calculations based on equation (33), assuming that 5% of the BF_3 is complexed and that the complex has a chemical shift similar to that of other BF_3 complexes of oxygen or fluorine donors, (i.e., the relative chemical shift is about 1000 c.p.s.) gave a maximum width at half-height of about 23 c.p.s. for the major peak, in quite good agreement with experiment.

Even at -90° no small peak arising from the proposed complex of BF_3 could be detected. This does not conflict with the postulate of a second species in solution. If the minor species gives rise to 5% of the total fluorine-on-boron peak area, the average lifetimes of fluorine on the major and minor species would be in the ratio 19:1. This would result in a broadening of the minor peak many times greater than the broadening of the major peak in the slow exchange limit, according to equation (9) (p. 8). Since at -90° the main peak has a width of 4 c.p.s., the much greater amount of broadening of the minor peak would prevent it from being visible above the noise level.

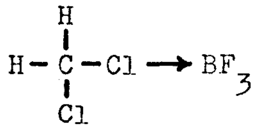
The chemical shift of BF_3 in fluorosulphuric acid is within a few p.p.m. of that of BF_3 in methylene chloride, and thus is in agreement with an earlier study which showed the insolubility, and hence the absence of strong interactions, of BF_3 in fluorosulphuric acid (81). The lack of a strong interaction is in accord with the low solubility of BF_3 in sulphuric acid, which contrasts with the ready reaction of the related compounds BCl_3 and $B(OH)_3$ with sulphuric acid (99), i.e.,

$$BCl_3 + 5H_2SO_4 \longrightarrow H_3SO_4^+ + B(HSO_4)_4^- + 3HCl \qquad (35)$$

Although BF_3 is apparently insoluble in fluorosulphuric acid at room temperature and a pressure of one atmosphere (81), it appears that the solubility may be increased by the BF_3 pressure of several atmospheres which should be present in the sealed sample tube. Although much of the BF_3 would presumably be in the vapour phase above the solution, a sufficient amount is dissolved to give a large NMR peak.

(ii) Boron Trifluoride in Methylene Chloride and other "Inert" Solvents

A solution of boron trifluoride in methylene chloride gave a single ^{19}F peak, assigned to free BF_3, at 124.7 p.p.m. at 0°, and at 122.2 p.p.m. at -90°. No fine structure was visible on this peak at any temperature from -90° to +50°; this contrasts with the ^{19}F spectrum of pure liquid BF_3 which shows partially collapsed fine structure due to coupling with boron (65). The peak width was found to vary with temperature as is shown in Figure 26. The increased broadening as the temperature is lowered cannot be attributed to the effects of quadrupole relaxation of boron, which would cause greater broadening at higher temperatures. Instead, this effect seems most easily explained by rapid reversible formation of a very weak complex between BF_3 and the solvent, such as XXI, or possibly between BF_3 and the internal trichlorofluoromethane standard, such as XXII or XXIII.



$$H-\overset{H}{\underset{Cl}{C}}-Cl \rightarrow BF_3$$

XXI

$$Cl_3C-F \rightarrow BF_3$$

XXII

$$Cl_2FC-Cl \rightarrow BF_3$$

XXIII

The broadening would then be analogous to that of BF_3 in fluorosulphuric acid, also shown in Figure 26, except that only part of the temperature range in which the main peak is broadened can be observed.

There is some evidence from ^{11}B NMR that methylene chloride can complex with other boron trihalides (45). Any such complex with BF_3 would be very weak since the differential heat of solution of BF_3 in methylene chloride is only 2.8 Kcal./mole (87). The possibility of interaction between BF_3 and trichlorofluoromethane is supported by the observation, in the course of other work carried out for this thesis, that the stronger Lewis acid antimony pentafluoride forms a solid complex with trichlorofluoromethane[*]; interaction of BF_3 as well thus seems plausible.

The absence of splittings due to coupling with boron can be attributed to rapid quadrupole relaxation of boron. This would require a lowering of the symmetry of the electric field at boron, which can best be explained by a strong interaction with the solvent, such as formation of the weak complex postulated above. Even if only a small proportion of the BF_3 were complexed at any given time, rapid reversible complexation, with rapid quadrupole relaxation while the BF_3 is incorporated in the complex, could account for the absence of splittings due to B-F coupling. The ^{11}B spectrum of this sample confirms that

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[*] A white, amorphous solid, m.p. 75-80°, stoichiometry and structure not known;can be sublimed slowly under high vacuum; ^{19}F NMR on the liquid at 86° gave a single broad resonance of width at half-height 480 c.p.s.

quadrupole relaxation is rapid; Figure 20 (p. 121) shows the width at half-height of the single ^{11}B peak. The very large peak width increases as the temperature is lowered, as is expected if the broadening is caused by rapid quadrupole relaxation. Considerably narrower resonances, showing splitting into a 1:3:3:1 quartet of spacings 22.6±2 c.p.s. by coupling with fluorine, have been observed for pure liquid BF_3 (88). If the coupling constant is approximately the same in BF_3 dissolved in methylene chloride, the splittings would be obscured by the broadening of the resonance.

The postulate that the broadening of the ^{19}F resonance of BF_3 in methylene chloride is due to exchange between free BF_3 and a weak complex appears to be supported by some results obtained by Brownstein and co-workers (52), who reported ^{19}F peak widths at half-height of solutions of BF_3 in chloroform and in toluene over a range of temperatures. Their results are plotted in Figure 27, together with the peak widths found in the present work for the solution of BF_3 in methylene chloride. Brownstein and co-workers observed no fine structure in the ^{19}F resonance in either chloroform or toluene; this indicates that some type of interaction with the solvent, lowering the symmetry, must occur in these solvents as well. The complex with toluene must be extremely weak, and exchange must be rapid even at -90°, as there is no broadening of the ^{19}F peak as the temperature is lowered.* The complex with chloroform, on the other hand, would appear to be stronger than that with methylene chloride, since the

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*The formation of related complexes, apparently quite weak, of benzene with BBr_3 and BI_3 has been reported by Finch, Gates, and Steele (100); see p. 165.

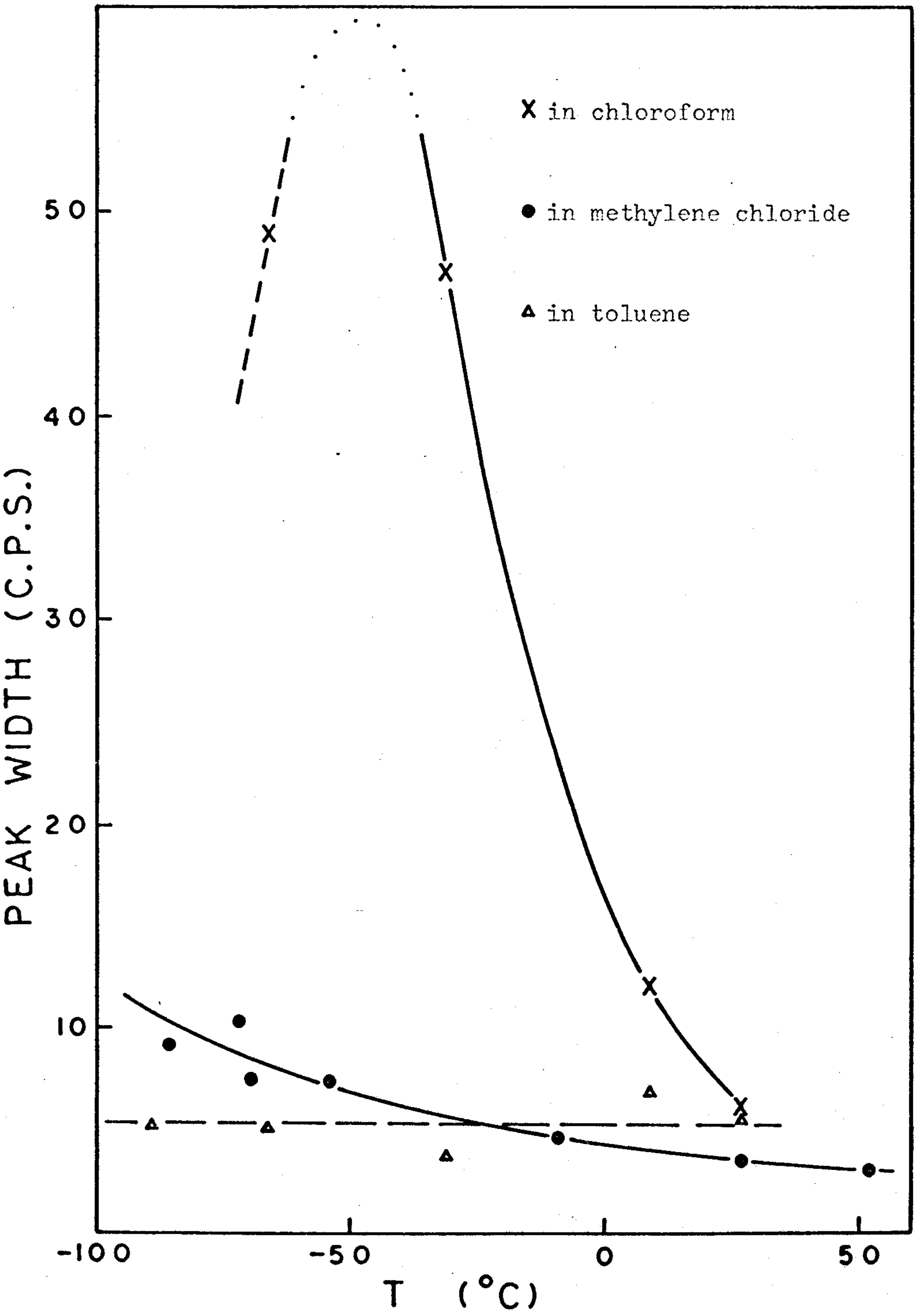

Fig. 27. Variation of ^{19}F peak widths at half-height with temperature in BF_3 solutions.

peak width apparently reaches a maximum at about -50°. It may decrease as the temperature is lowered further, as is indicated in the Figure, but this has not been verified.

In the course of studies of solutions of ketones and BF_3 in methylene chloride, a few solutions containing an eightfold excess of BF_3 over ketone were made up. At low temperatures these contained two immiscible liquid layers, presumably due to liquid BF_3 and to methylene chloride solution. Two ^{19}F peaks, separated by about 5.8 p.p.m., were observed in the "free BF_3" region at -90°, as well as the peak due to the 1:1 complex which occurred at much higher field. The relative areas of the two "free BF_3" peaks varied widely in the same sample at the same temperature, apparently depending on the amount of each liquid layer in the region of the sample near the receiver coil, so that one signal must have arisen from each of the two immiscible layers. Since the smaller layer was in some cases entirely out of the region of the receiver coil, in which case only the higher field peak was visible, and since from the relative amounts added to the sample tube the larger layer must arise from the methylene chloride solution, it can be concluded that the lower field peak arises from liquid BF_3, possibly containing some dissolved species.

The large relative shift of 5.8 p.p.m. between "free" BF_3 in the two different environments suggests a considerable degree of intermolecular interaction of the BF_3 in one or both of the environments. Self-association through fluorine bridging is a possibility in liquid BF_3; this would probably shift the ^{19}F peak to lower field by analogy with the ^{19}F spectrum of antimony pentafluoride, in which fluorine bridging has been definitely established and the bridging fluorines have their resonance to low field of the non-bridging fluorines (101). Weak donor-acceptor interaction of BF_3 with methylene chloride, as discussed previously, would shift the ^{19}F resonance to higher field in this solvent. Either effect, or a combination of the two, could account for the considerable chemical shift between neat BF_3 and BF_3 in methylene chloride solvent.

(iii) Diphenyl Ether and Boron Trifluoride in Methylene Chloride

Earlier workers have reported that diphenyl ether does not complex with boron trifluoride (19). In accord with this, solutions of diphenyl ether and BF_3 in methylene chloride were found to give a single ^{19}F peak at all temperatures studied between room temperature and -90°; its chemical shift at room temperature was 126.5 ± 0.5 p.p.m. to high field of trichlorofluoromethane, within a few p.p.m. of that of "free" BF_3 in this solvent. The peak width, however, was greater than that observed for a solution of BF_3 alone in methylene chloride, and increased to a maximum above -90° as is shown in Figure 28. This behaviour is analogous to that of the ^{19}F spectrum of the solution of BF_3 in fluorosulphuric acid discussed earlier. It thus appears that a small proportion of the BF_3 is able to complex with diphenyl ether; although this does not have much effect on the chemical shift of the single large peak, it does have an observable effect on the peak width. As in the case of BF_3 in fluorosulphuric acid, it appears that the exchange is still too rapid at -90° to allow a separate peak arising from the (diphenyl ether).BF_3 complex to be detected.

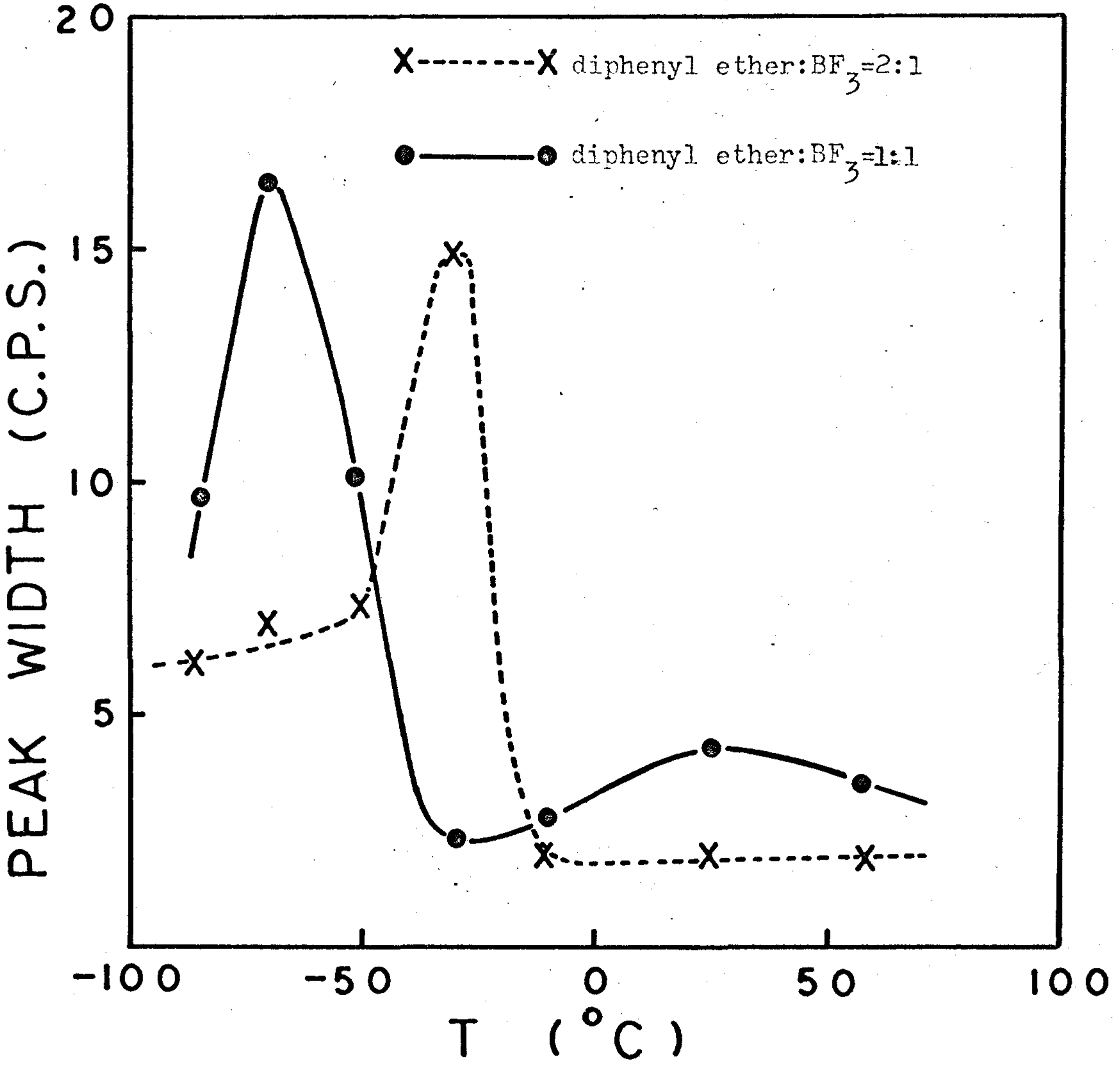

Fig. 28. Variation of ^{19}F peak widths at half-height with temperature in methylene chloride solutions of diphenyl ether and BF_3.

The broadening of the peak is good indirect evidence for the existence of a BF_3 complex in solution. The possibility remains, however, that a trace of water present in the solution could be responsible for the observed broadening; further experiments using samples dried under especially rigorous conditions would be required to verify that the complex present is between diphenyl ether and BF_3, rather than between water and BF_3. However, the excess broadening definitely indicates that some type of complex is present.

CONCLUSION

NMR methods which have been developed for the study of various types of weak association, including hydrogen bonding, in solution have in general been dependent on chemical shift changes as a measure of the interaction (e.g., (2), Chapters 15 and 16; (102)). Such methods have the disadvantage that, if only very slight changes in chemical shift are observed, it is difficult to determine that interaction or complexation has occurred. Thus Finch, Gates, and Steele (100), who established from ultraviolet spectroscopic evidence that benzene complexes weakly with BBr_3 and BI_3, were unable to obtain convincing evidence from ^{11}B NMR for the existence of the complexes. The very small "complexation shifts" which they reported on changing the relative proportions of acid and base could reasonably be assigned to a solvent shift.

The new method, proposed in the present Chapter, of detecting the existence of a weak complex is dependent on the existence of a large chemical shift between free and complexed species, but such a shift does not have to be observed directly; the broadening which is observed results from the complexation shift according to equation (33). This method seems suitable only in cases in which very large complexation shifts are observed, and would probably not be very useful in proton resonance studies of complex formation because of the much smaller complexation shifts obtained.

CHAPTER X

SOLVENT EFFECTS ON THE BORON-FLUORINE COUPLING CONSTANT IN THE TETRAFLUOROBORATE ANION*

INTRODUCTION

Spin-spin interactions within a molecule in solution are normally not highly dependent on solvent, concentration, or temperature. Because of this, the remarkable variation with concentration of the ^{11}B-^{19}F coupling constant of sodium tetrafluoroborate in aqueous solution, recognized by Kuhlmann and Grant (66) only after mutually inconsistent values had appeared in the literature (90,103), has aroused considerable interest. Kuhlmann and Grant, in a detailed ^{19}F NMR study of the BF_4^- ion in aqueous solution, have found that $J_{^{11}B-^{19}F}$** is dependent not only on the concentration as in $NaBF_4$ solutions, but also on the cation and on the presence of other ions in solution. In $NaBF_4$ solutions the value of the coupling constant varied from an estimated 1.1 c.p.s. at infinite dilution to 4.8 c.p.s. in a saturated solution. An equilibrium between free BF_4^- and BF_4^- associated with Na^+ in an ion pair was postulated to explain the results. Since the coupling constant in ammonium tetrafluoroborate was

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*Some of this work has been published (67).

**In this chapter, $J_{^{11}B-^{19}F}$ is abbreviated to J.

found to be 1.1 c.p.s., essentially independent of concentration, it was concluded that the NH_4^+ ion does not form an ion pair with BF_4^-.

The ion pair hypothesis has not been readily accepted since it seems to imply a considerable asymmetry of charge about boron; hence rapid quadrupole relaxation of the boron nuclei should collapse the splitting due to boron-fluorine coupling. In a recent paper Haque and Reeves (68) have discussed the evidence against the ion pair hypothesis. This evidence includes an X-ray diffraction study by Ryss and Radchenko (104) which shows that in solutions of $NaBF_4$ (2-9 M) the Na^+ ion is hexacoordinated with water; thus there can be no direct contact of Na^+ and BF_4^-. This study excludes an intimate, or inner sphere, ion pair, but a solvent separated ion pair, in which the interactions of anion and cation would be much less and which might not greatly disturb the symmetrical charge distribution about boron, remains a possibility. Further evidence against an intimate ion pair has been provided by a study of ^7Li resonance in aqueous solutions of $LiBF_4$ (105); narrow resonance lines were obtained. The absence of considerable broadening due to quadrupole relaxation of ^7Li ($I = 3/2$) implies that the environment is highly symmetrical; yet Li^+, like Na^+, was shown by Kuhlmann and Grant to have a specific ion effect on the B-F coupling constant.

Kuhlmann and Grant noted that the anomalous variation of the coupling constant is accompanied by an anomalously small size with respect to the isoelectronic molecules $BeF_4^=$ ($J_{^9Be-^{19}F} = 33.7$ c.p.s. (106)) and CF_4 ($J_{^{13}C-^{19}F} = 259$ c.p.s. (107) or 257 c.p.s. (108)). Haque and Reeves (68) have expressed these values in terms of reduced coupling constant j, which correct for variations in the magnetogyric ratios γ_X of the element X bonded to fluorine and thus give a measure solely of the ability of the electron cloud to transmit spin-spin interactions.

$$\left| j_{X-F} \right| = \left| \frac{J_{X-F}}{\gamma_X} \right| . \qquad (36)$$

This yields the reduced coupling constants j_{Be-F}, j_{B-F}, and j_{C-F} as 8.16, 0.16, and 34.9, respectively, with the anomalously small B-F interaction still evident. Further evidence of this anomaly is provided by the larger B-F coupling constants in the closely related species BF_3OH^- (66,77) and $CF_3BF_3^-$ (103), which are 12.7 and 39.0 c.p.s., respectively. In aqueous solutions of $NaBF_3OH$ the B-F coupling constant was found to be dependent on concentration and specific cationic effects (66), much like the B-F coupling constant in aqueous solutions of $NaBF_4$.

Pople and Santry, who carried out calculations of nuclear spin-spin coupling constants by molecular orbital theory (109), proposed that the anomalously small size of J in BF_4^- is a result of a close balance between large coupling terms of opposite sign, arising from different coupling mechanisms. This explanation was also put forward by Kuhlmann and Grant to explain both the variations in J and the low values of J; although they considered that ion pair formation causes the variations in J, some other minor effect might be responsible. The existence of large coupling terms of opposite sign is supported by work of Tiers which strongly suggests that directly bonded $^{13}C-^{19}F$ couplings are negative (110). The Fermi contact term which is usually considered to be predominant in spin-spin coupling would render the coupling constant positive; thus a second major term of opposite sign appears to be present. This interpretation has recently been further confirmed by additional calculations, by the Pople-Santry method, of directly bonded coupling of fluorine to a series of first row elements (111). The assumption of zero coupling in BF_4^- due to the cancellation of two coupling terms led to a predicted large negative coupling in CF_4, the magnitude of which agrees quite closely with the experimental value. Since the calculated magnitudes of the coupling constants in other first row fluorides also agreed quite well, it can reasonably be assumed that the signs are correct as well. Thus the available evidence strongly supports the postulate that the small size of the boron-fluorine coupling constant of the tetrafluoroborate anion is a result of the near-cancellation of large coupling terms of opposite sign. A result of this, pointed out by Kuhlmann and Grant, is that the large relative changes in the observed J can be caused by changes of only a few percent in one or more of the large opposing terms. Evidence that this is indeed the cause of the changes in J is presented in this Chapter.

Haque and Reeves (68) proposed, as an alternative to ion pair formation, that the large relative changes in J are the result of hydrogen bonding between BF_4^- and water, in the bonding arrangement $F_3B{-}F^{-}\cdots\cdots H{-}OH$ which has not been previously observed. They measured J and the ^{19}F chemical shift of $NaBF_4$ as a function of concentration and solvent composition in water-acetone, water-dioxane, and water-dimethyl sulphoxide mixtures. Coupling constants and chemical shifts at infinite dilution and the variation of these with concentration, found to depend on the solvent mixture, were interpreted in terms of changes in the hydrogen bonding between water and BF_4^-. Changes in chemical shifts were found to parallel the changes in J. The anomalously small size of J was noted but not explained.

^{19}F NMR spectra of solutions of $NaBF_4$ in water-diglyme solvent mixtures were studied by Quail in this laboratory (77). In a series of samples of equal concentrations, varying in composition from pure water to 70% diglyme, the coupling constant decreased from 3.5 c.p.s. to 1.3 c.p.s.; the trend appears to be similar to that obtained by Haque and Reeves in water-dimethyl sulphoxide solvent mixtures. No splitting could be observed in solutions of lower concentration in 90% and 100% diglyme; the absence of splitting was attributed to quadrupole relaxation of the boron nuclei.

To date, no single explanation of the variations in J in the tetrafluoroborate anion has appeared which is capable of satisfactorily explaining all the results. New data obtained in the present work has provided further evidence for the origin of the variations of J and has led to a modified interpretation which combines features of two previous interpretations and appears more feasible that either of these separately.

RESULTS

(i) General

The ^{11}B-^{19}F coupling constant J of silver tetrafluoroborate was investigated by ^{19}F NMR in the solvents water, acetonitrile, and acetone, and in intermediate solvent mixtures. A few BF_4^- solutions with other cations and in other solvents were also studied, but in less detail.

In the pure solvents water and acetonitrile, but not in acetone, the 1:1:1:1 quartet caused by coupling with boron-11 ($I = 3/2$) could be observed. The peak due to fluorine on boron-10, which was shifted 0.050 p.p.m. to lower field as was previously reported (66,77) did not have observable multiplet structure except in concentrated solutions in water, where a splitting corresponding to $J_{^{10}B-^{19}F} = 0.4 \pm 0.1$ c.p.s. was observed; this value agrees well with the corresponding $J_{^{11}B-^{19}F}$ value of 1.07 ± 0.07 c.p.s.* In most other solutions of the silver salt the expected $^{10}B-^{19}F$ splittings were below the limit of resolution of the spectrometer which was about 0.35 c.p.s.

The chemical shift of $AgBF_4$ with respect to trichlorofluoromethane increased by about 1.8 p.p.m. in a regular fashion as the mole fraction of water in the solvent decreased from pure water to either pure acetone or acetonitrile. These results are similar to those of Haque and Reeves (68) for solutions of $NaBF_4$ in water-acetone mixtures.

(ii) Variation of J in $AgBF_4$ with Solvent Composition in the Water-Acetonitrile System

^{19}F spectra of carefully degassed solutions of $AgBF_4$ in water and acetonitrile, and in intermediate solvent mixtures, are shown in Figure 29. The solute dissolved readily, with the evolution of considerable heat, even in pure acetonitrile.** The very closely

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* Because of the smaller magnetogyric ratio of ^{10}B with respect to that of ^{11}B,

$$\frac{J_{^{10}B-^{19}F}}{J_{^{11}B-^{19}F}} = 0.33 .$$

** In a few samples in the mixed solvents a precipitate of well-formed crystals appeared after standing for a few days with evaporation of part of the solvent. These presumably are a coordinated species, $Ag(CH_3CN)_n{}^+BF_4{}^-$.

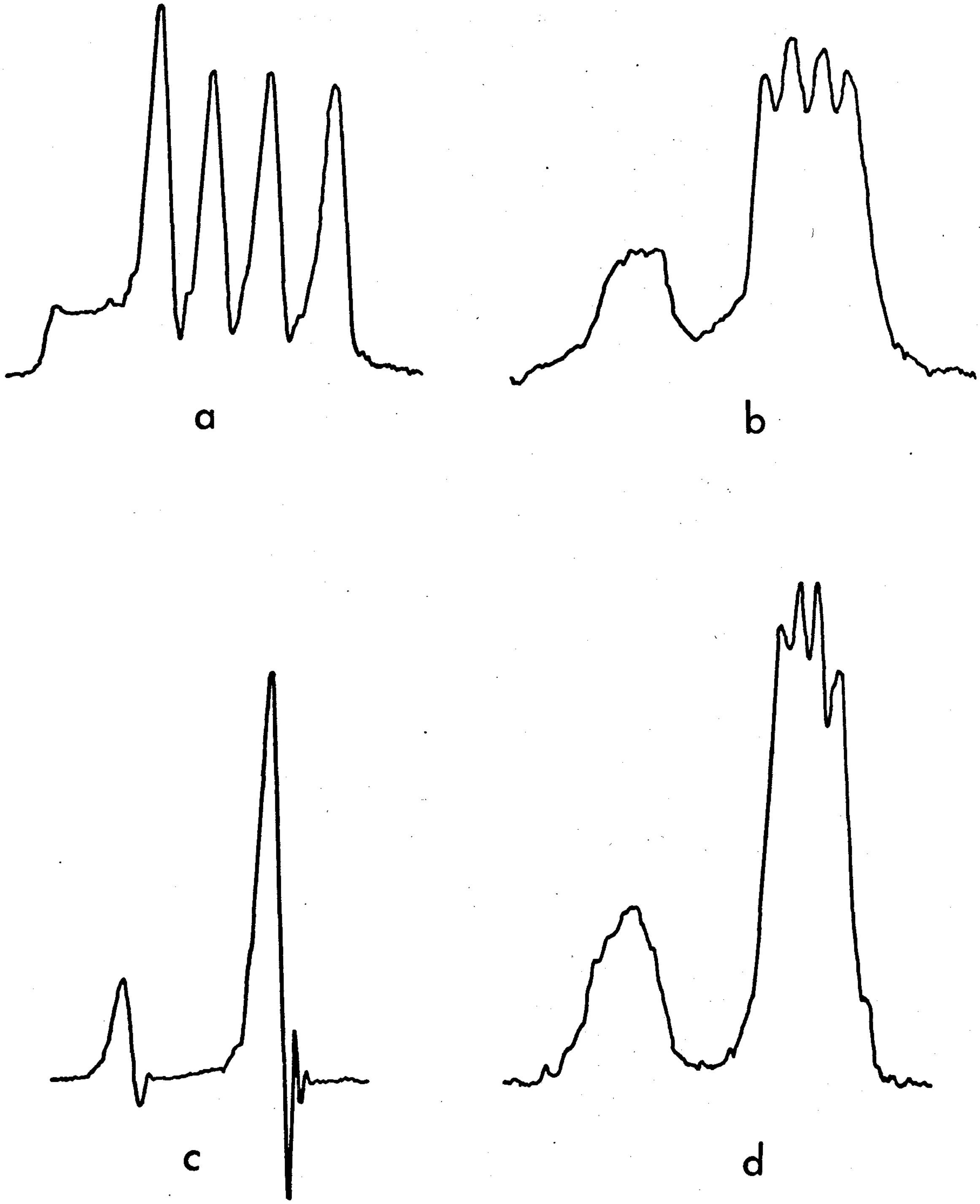

Fig. 29. Fluorine-19 spectra of silver tetrafluoroborate solutions. (a) in water; (b) in 50 mole percent acetonitrile; (c) in 80 mole percent acetonitrile; (d) in acetonitrile.

spaced quartet observed for the F-on-^{11}B peak in pure acetonitrile corresponds to a coupling of 0.39±0.07 c.p.s; it was difficult to observe and could not be seen in one sample.

Values of $J_{^{11}B-^{19}F}$ for solutions of various concentrations in the pure solvents water and acetonitrile, and in the 50:50 mole percent solvent mixture, are shown in Table VII. The absence of any marked dependence of J on concentration indicates that the BF_4^- ion is unaffected by specific cationic interactions in the water-acetonitrile system when the Ag^+ cation is used, and simplifies the present investigation of the effects of changing the solvent. The value of J in aqueous solution, 1.07±0.07 c.p.s., is the same value, within experimental error, as was obtained by Kuhlmann and Grant for NH_4BF_4 solutions (66); this is further evidence that the same species, free BF_4^-, is present when either the Ag^+ or NH_4^+ cations are used. The silver salt is especially suitable for use in non-aqueous solvents because of the high complexing ability of Ag^+ with many of the common solvents, and especially with acetonitrile (112), which increases the otherwise rather low solubility of the BF_4^- ion.

Figure 30 shows the variation of J with the mole fraction of acetonitrile in the solvent. A smooth curve is obtained if it is assumed that the sign of J changes when the solvent contains about 80 mole percent acetonitrile. A solution of $AgBF_4$ in this solvent mixture yielded two sharp peaks with the expected relative areas for F-on-^{10}B and F-on-^{11}B and with no indication of boron-fluorine coupling (Figure 29c). It can reasonably be concluded that J has opposite signs in water and acetonitrile.

TABLE VII

$J_{^{11}B-^{19}F}$ VALUES IN $AgBF_4$ SOLUTIONS IN WATER, ACETONITRILE, AND THE 50:50 MOLE PERCENT SOLVENT MIXTURE

Solvent	$[AgBF_4]$ (mole percent)	J at room temperature	Additional temperature	J at additional temperature
water	0.19	1.05		
	1.03	1.13		
	1.03		69°	1.13
	1.03		96°	0.98
	4.06	1.04		
50:50 mole percent water-acetonitrile	0.25	0.53		
	1.68	0.50		
	4.23	0.43		
acetonitrile	0.64	0.36		
	0.64		0°	0.33
	4.55	0.37		
	4.55		5°	0.42
	4.55		45°	-

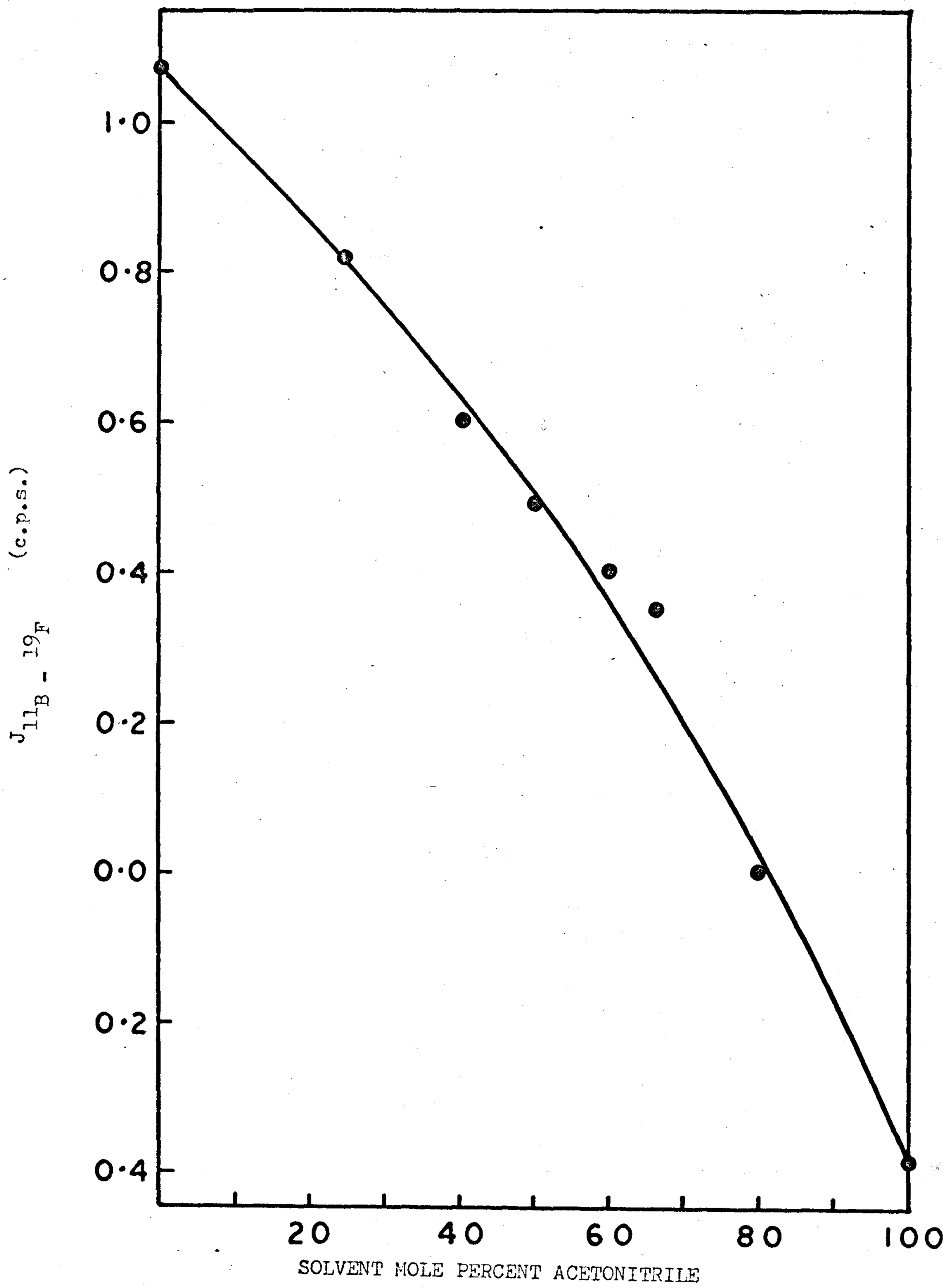

Fig. 30. Plot of $J_{^{11}B - ^{19}F}$ in $AgBF_4$ vs. composition of water-acetonitrile solvent mixtures.

(iii) Variation of J in $AgBF_4$ with Solvent Composition in the Water-Acetone and Acetonitrile-Acetone Systems

Although the solubility of $AgBF_4$ appears to be less in acetone than in acetonitrile, with less heat being evolved on solution, solutions of concentrations adequate for NMR measurements could be obtained. The trend of the spectra with solvent composition was quite similar to that obtained in the water-acetonitrile system. The 1.07 c.p.s. coupling constant in water decreased as the proportion of acetone was increased; a solution in 77 mole percent acetone yielded two fairly sharp separate peaks for F-on-^{10}B and F-on-^{11}B, with no indication of boron-fluorine coupling. Further increasing the mole fraction of acetone caused the peaks to broaden again, but splittings due to coupling did not reappear in pure acetone solvent. This is rather surprising as the widths of the peaks in pure acetone are quite similar to those in pure acetonitrile, indicating a similar coupling constant. It seems unlikely that concentration effects or poorer resolution of the spectrometer when the spectra of the acetone samples were obtained could account for the absence of splitting, as several different samples of different concentrations were used, their spectra being obtained at different times; in all cases a similar broadening was obtained. It appears more likely that a slight extra broadening of the peaks making up the 1:1:1:1 quartet, perhaps as a result of quadrupole relaxation of boron due to some form of association in the solvent of lower dielectric constant, is involved. If this is the case, it would appear that the change in J and the quadrupole relaxation are caused by two different effects.

Figure 31 shows the variation of J with the mole fraction of acetone in the water-acetone system. The points on the right-hand side of the plot represent estimates of J, obtained from the widths of the peaks by comparison with corresponding spectra of similar peak widths in the water-acetonitrile system. The similarity to Figure 30 is evident, and suggests that J changes sign in this system as well.

Further evidence that J does indeed change sign in the water-acetone system is provided by solutions of $AgBF_4$ in mixtures of acetonitrile and acetone. As the mole fraction of acetone is increased, the small splittings observed in acetonitrile become less well resolved and eventually disappear. However, as long as the splittings are visible they do not change appreciably in size from those obtained in pure acetonitrile. The width at half-height of the peaks also appears similar across the entire range of solvent compositions. Figure 31 shows the lack of variation of J with solvent composition in this case, and provides convincing evidence that J has the same sign in acetonitrile and in acetone. Since J has opposite signs in water and in acetonitrile, the signs in water and in acetone must also be opposite, as is indicated by Figure 31.

(iv) Variations in J with Temperature

(a) Aqueous $NaBF_4$, $AgBF_4$ and $(CH_3)_4NBF_4$ Solutions

Aqueous solutions of $NaBF_4$ in water show a small but distinct decrease in J at higher temperatures. A brief investigation showed that one sample with $J = 4.37 \pm 0.1$ c.p.s. at room temperature yielded $J = 3.61 \pm 0.2$ c.p.s. at 98°. A second sample with $J = 2.03 \pm 0.1$ c.p.s.

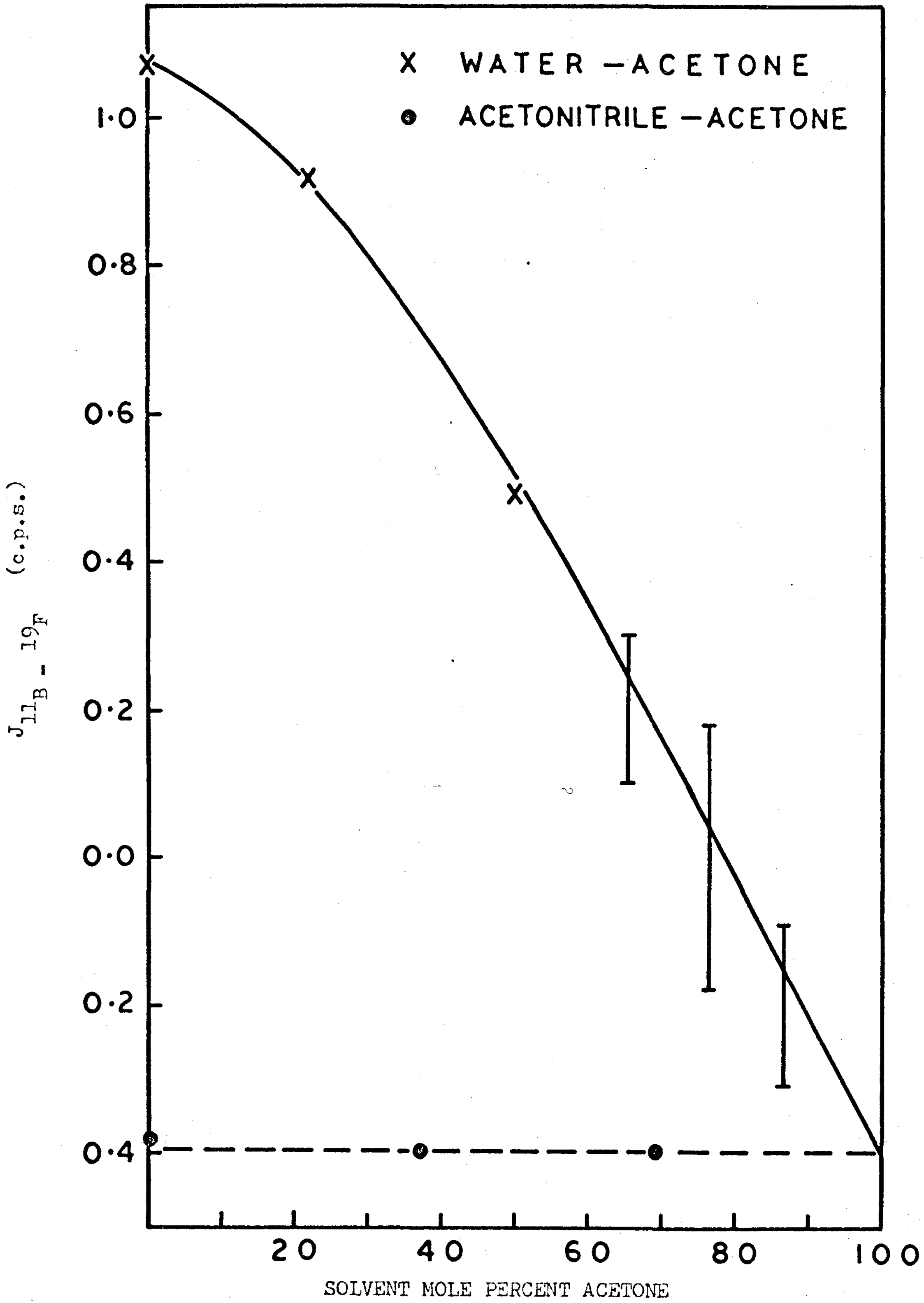

Fig. 31. Plot of $J_{^{11}B - ^{19}F}$ in $AgBF_4$ vs. composition of water-acetone and acetonitrile-acetone solvent mixtures.

at room temperature yielded J = 1.7±0.1 c.p.s. at 83°. This effect was not due to any irreversible reaction since the original room temperature value could be obtained again on cooling. These results indicate that the effect of the specific cationic interaction of Na^+ is decreased as the solutions become more disordered at higher temperatures. This would fit either an ion pair or a hydrogen bonding interaction.

Aqueous solutions of silver and tetramethylammonium tetrafluoroborates, on the other hand, do not show marked changes in J with temperature. Table VII shows that the J values obtained for a solution of $AgBF_4$ at 69° and 96° were within 0.1 c.p.s. of the average room temperature value of 1.07 c.p.s. The absence of marked changes in J with temperature, such as are observed in the sodium salt, is a further indication of the lack of similar cationic interactions. Similar behaviour was observed in an aqueous solution of $(CH_3)_4NBF_4$;J was 1.11±0.1 c.p.s. at room temperature and 0.92±0.1 c.p.s. at 83°. Again the variation in J is less than the sum of the estimated experimental errors; the good agreement of J at room temperature with the values obtained for solutions of the ammonium and silver salts is good evidence that the tetramethylammonium ion also is unable to take part in specific cationic interactions.

In spite of the absence of marked changes in J with temperature in the silver and tetramethylammonium ions, it may nevertheless be significant that J in both cases is rather smaller at the highest temperature studied than at room temperature. If the decrease in J is a real effect, it is sufficiently small that it might result from changes with temperature in the vibrational motions of the atoms (113).

(b) $AgBF_4$ in Acetonitrile

The very closely spaced quartet structure due to boron-fluorine coupling was difficult to observe at room temperature. Slightly better resolution, with no change in the size of the small splittings, was obtained at rather lower temperatures; the spectrum shown in Figure 29d was obtained at +6°.

Above room temperature the small splittings due to J disappeared completely. At high temperatures the separate peaks arising from F-on-^{10}B and F-on-^{11}B collapsed to yield a single sharp peak, which showed no further change at higher temperatures up to 150°. Obviously no information about B-F coupling at high temperatures is obtainable. However, the collapse of the isotopically shifted peaks at higher temperatures is strong evidence for rapid exchange of fluorine among boron atoms at these temperatures. The coalescence temperature in most samples was close to 90°. There was little broadening of the peaks in the region of coalescence,as is expected if only the closely spaced isotopically shifted peaks are involved in the exchange process (Chapter VII). Because of the small relative shifts of the peaks and the narrow temperature range in which coalescence occurred, a wide range of signal shapes was not obtained and it did not seem worthwhile to attempt to obtain kinetic data for the process. It appeared, however, that in more concentrated solutions the peak coalescence occurred at somewhat lower temperatures; this is in accord with an exchange mechanism which is second order in tetrafluoroborate anion.

In one sample coalescence occurred at considerably lower temperatures, and there was considerably more broadening of the peaks than would result from coalescence of only the isotopically shifted peaks. It appears that in this sample a fluorine-containing impurity was present which catalysed and took part in the fluorine exchange. Even a peak too small to be readily observable in the spectrum can, if it coalesces with a main peak, cause a considerable broadening of the large peak in the coalescence region, as is discussed in Chapters VII and IX.

(c) $AgBF_4$ in Acetone

Spectra were not obtained above room temperature. Such spectra would likely show collapse of the isotope shift as in acetonitrile solutions. Low temperature spectra were obtained to determine if the absence of observable splittings due to B-F coupling at room temperature could be due to exchange of fluorine among boron atoms. Since spectra essentially identical to those at room temperature were obtained at several temperatures down to -56°, the absence of splittings must be attributed to some other effect.

(d) $AgBF_4$ in Dimethylsulphoxide (DMSO)

Splittings due to B-F coupling were clearly visible at several temperatures between room temperature and 91°. J remained constant at 1.24 ± 0.1 c.p.s. over the entire temperature range. These results show the absence of rapid fluorine exchange; the constant value of J indicates the absence of any specific cationic interaction.

A single sample of $AgBF_4$ in mixed water-DMSO solvent of 28 mole percent DMSO yielded two well-separated peaks for F-on-^{10}B and F-on-^{11}B, with no splitting evident. Since solutions in both pure solvents clearly show splittings due to J, it can be tentatively concluded that the signs of J are opposite in water and in DMSO.

(e) $AgBF_4$ in Pivalonitrile and in Diglyme

A saturated solution of $AgBF_4$ in pivalonitrile (t-butyl cyanide) yielded a single broad peak with no fine structure. Half-widths of between 3 and 7.5 c.p.s. were obtained at various temperatures between room temperature and 91°; the sharpest spectrum, obtained at 45°, showed the isotope shift only as a shoulder.

$AgBF_4$ appears to take part in an unexpected reaction with diglyme (bis(2-methoxyethyl)ether); a solution which was heated to dissolve the $AgBF_4$ yielded a ^{19}F spectrum consisting of a broad, doublet-like structure with the two maxima separated by 34 c.p.s. These results have not been explained. A second sample, prepared at room temperature, yielded a single broad peak with widths at half-height of 6.0±0.6 c.p.s. at a series of temperatures between room temperature and 90°. These spectra in diglyme are very different from those of solutions of the sodium salt, reported by Quail (77), which consisted of two well-separated peaks due to F-on-^{10}B and F-on-^{11}B.

DISCUSSION

(i) Change of Sign of J

Figures 29 and 30 yield conclusive evidence that the sign of J changes as the solvent is changed from water to acetonitrile. Similar reasoning has shown that the sign of J_{P-C-H} in trimethylphosphine changes between free trimethylphosphine and its 1:1 complex with triethylaluminum (114); rapid exchange of the free and complexed species at room temperature led to the observation of an averaged J_{P-C-H} which, as the relative proportions of acid and base were changed, passed through zero. The small P-C-H couplings had previously been postulated to arise from the near cancellation of larger terms (115); the sign change was thus postulated to result from a difference in the sensitivity of these terms to the rehybridization occurring on coordination.

The suggestion of Kuhlmann and Grant that the small values of J in BF_4^- are due to a close balance between large coupling terms of opposite sign is strongly supported by the evidence for a change of sign between water and organic solvents. A change of solvent is not expected to seriously affect the structure or charge density in the ion. Only a small solvent effect should be observed; such effects often cause changes of a few percent in coupling constants. A change as striking as is observed in the present case is to be expected only if the contributing terms are large, so that a change of no more than a few percent in one or more of these could change the sign of J. It can be concluded that the abnormally small coupling in the tetrafluoroborate ion is the result of near-cancellation of large opposing terms.

Since the large relative changes in J can be attributed merely to changes of a few percent in large opposing coupling terms, it is apparent that no gross changes in structure with solvent or, in the case of the sodium salt, with concentration, are required. Haque and Reeves apparently lost sight of Kuhlmann and Grant's postulate of large opposing coupling terms and thus sought a source for what they considered to be anomalously strong solvent and concentration effects. Instead, it is more likely that the interactions of BF_4^- with solvent and cation in solution are fairly normal. If this is the case, the BF_4^- ion provides a particularly favourable opportunity to study interactions in solution by NMR. The small values of J allow the effects of changes in the large coupling terms to be determined to a small fraction of a cycle per second. Equally small changes are not likely to be observed in a more normal directly bonded X-F coupling constant of a few hundred c.p.s. Although the percentage error in measuring J should be less when J is larger, the absolute error in c.p.s. should be much more, due to the faster sweep rate used or, if a very slow sweep rate is used, to the increased amount of drift.*

To illustrate that the magnitude of the observed changes in J in BF_4^- is not unusually large, the values of J obtained for liquid BF_3 are of interest. The change in $J_{^{11}B-^{19}F}$ in liquid BF_3 with temperature between -105° and -50°, verified by the values of $J_{^{10}B-^{19}F}$ obtained from liquid $^{10}BF_3$ (Chapter XI), is 2.1 c.p.s. This is considerably greater than the change in J in BF_4^- as the solvent is changed from water to acetonitrile. The smaller change in J in BF_4^- is of special interest because it has the more spectacular effect of changing the sign of J.

(ii) Structural Interpretation of the Variations in J

In previous studies, variations of coupling constants in other compounds with solvent and concentration have been attributed to molecular complex formation or association (references 11-16 of (68)).

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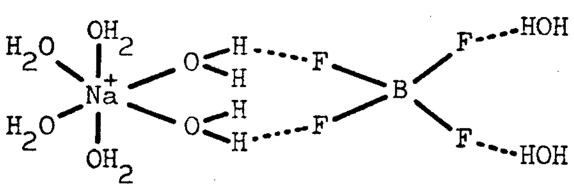
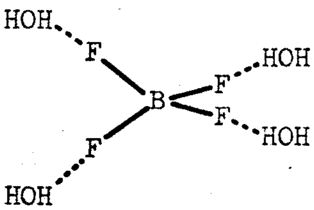
* Errors due to drift would be eliminated by the use of a spectrometer with a frequency lock.

The closest analogies in the case of BF_4^-, which has no accessible vacant orbitals or lone pairs of electrons, would be ion pair formation or hydrogen bonding with the solvent. Haque and Reeves rejected Kuhlmann and Grant's ion pair hypothesis, apparently on the assumption that any significant interaction would have to involve an inner sphere ion pair. Their reasons for discarding an inner sphere ion pair in aqueous solutions are convincing; however, a more loosely bound solvent separated ion pair is also a possibility, and is not excluded by any of their evidence. It is conceivable that even an ion pair so weakly held together that it does not decrease the symmetry at boron sufficiently to collapse the splitting due to boron-fluorine coupling could still affect the coupling constant, especially since the postulate of opposing coupling terms provides that small interactions can strongly affect the observed small J.

The ion pair postulate of Kuhlmann and Grant thus remains tenable if an inner sphere ion pair is excluded. Structure XXIV appears



XXIV



XXV

possible for the ion pair in aqueous solution; the very small differences in the fluorine environments between it and structure XXV which is feasible for the free (but solvated) anion could cause changes of several c.p.s. in J and considerable changes in the chemical shift. Structure

XXIV is in accord with a very small electric field gradient about boron, and also with hexacoordination of water molecules about Na^+ as has been demonstrated by Ryss and Radchenko (104). Both of the structures XXIV and XXV are in reasonable agreement with Ryss and Radchenko's estimate that each fluorine of BF_4^- has 1.1 nearest neighbour water molecules. An equilibrium between XXIV and XXV is feasible; equilibrium constants for free and ion paired BF_4^-, determined by Kuhlmann and Grant, could thus be valid. Structure XXIV combines the ion pair hypothesis of Kuhlmann and Grant with the hydrogen bonding hypothesis of Haque and Reeves, and appears to be better than either postulate separately.

Hydrogen bonding alone as an explanation for the changes in J, as suggested by Haque and Reeves, suffers from serious limitations. The changes in J when Na^+ or Li^+ are used are attributed to strong ion-dipole forces disrupting the hydrogen-bonded structure of water, removing water molecules which in dilute solutions can form weaker hydrogen bonds to BF_4^-. However, the considerable concentration effect even in quite dilute solutions casts doubt on this hypothesis. In a 1M solution of $NaBF_4$ the coupling constant is 1.9 c.p.s., a considerable increase from the value of 1.1 c.p.s. at infinite dilution. In this solution there are over 50 molecules of water per mole of $NaBF_4$. The work of Ryss and Radchenko has shown that only 6 of the water molecules are in the inner solvation sphere of Na^+. Additional water molecules in outer solvation shells should be held more weakly by hydrogen bonding to the inner sphere. It seems unlikely that as many as 50 water molecules could be bonded so tightly to Na^+ that they could not take part in weak hydrogen bonding with the anion. This argument becomes stronger when the lack of concentration dependence of NH_4BF_4 is considered. The chief difference between Na^+ and NH_4^+ would appear to be the inner coordination of 6 water molecules to Na^+, which are presumably held by sp^3d^2 hybridization about Na^+ and hence are held much more tightly than any of the molecules in the solvation shell of NH_4^+, which has no similar set of orbitals available to tightly bind water. Outer solvation shells of NH_4^+ should be much the same as those of Na^+. A structure such as XXIV, in which closely held inner sphere water molecules are required for ion pair formation, would explain the lack of similar ion pair formation,and hence of similar concentration effects on J, in aqueous solutions of NH_4BF_4. Thus Haque and Reeves' explanation of the differences in behaviour of the sodium and ammonium salts based only on differences in hydrogen bonding is not convincing.

The considerable variation, of up to 5 p.p.m., of the ^{19}F chemical shift of $NaBF_4$ with concentration and solvent (68) might be explained in terms of structures such as XXIV. The changes with concentration could result from the shifting of the equilibrium between the free and ion paired species, as proposed by Kuhlmann and Grant. The shift to higher field as the solvent is changed from water to acetone could result from a greater tendency to form ion pairs,or from the formation of more tightly held ion pairs, in solvents of poorer solvating ability. Thus in acetone ion pair formation might occur even with the silver salt, which remains in the form of free ions in water. The decrease in shielding as the solvent is changed from water to DMSO (68) might be due to a specific interaction of either the ion pair or the free anion with this solvent, so that some of the water molecules surrounding the Na^+ as in XXIV might be replaced by DMSO molecules. An interaction of BF_4^- with the conjugate acid of DMSO would be an alternate possibility; this was proposed by Haque and Reeves although such a complex constitutes an ion pair and thus contradicts their opposition to the postulate of ion pairs in solution.

The choice of the sodium salt for studies of the dependence of J on solvent (68,77) was unfortunate as the specific cationic effects of Na^+, as well as simple solvation effects, are likely to be affected by the solvent. The observed changes in J could thus arise from either of these two effects, or from some combination of the two, and thus interpretations based on these results must remain somewhat ambiguous. The sodium salt was probably chosen because its solubility in water is greater than that of the ammonium salt. In the present work it was found that the silver salt does not show specific cationic effects in water or in acetonitrile, and also that this salt is quite soluble in many organic solvents as well as in water. The high solubility in organic donor solvents is in accord with the high complexing ability or Ag^+ (112) and makes the silver salt ideal for studies of the effects of solvent on J. Because of the simplification in the interpretation of the results due to the absence of specific cationic effects of Ag^+, at least in the higher dielectric constant solvents, the interpretation of the present results is believed to be more meaningful than interpretations of the results of Quail (77) or of Haque and Reeves (68).

It is of interest that the use of the sodium salt rather than the silver salt appears to always cause a change in J in the same direction. Thus assuming for convenience, without evidence, that J is positive in aqueous solutions, and obtaining values of J for Haque and Reeves' fixed concentration of $NaBF_4$ in pure organic solvents by extrapolating Figure 4b of (68), we can compare J for the Na^+ and Ag^+ salts:

	J_{Na^+}	J_{Ag^+}	$\Delta J_{(Ag^+ \rightarrow Na^+)}$
acetone	+1.7	-0.4	+2.1
DMSO	+0.3	-1.2	+1.5
water	+2.0	+1.1	+0.9

If the presence of ion pairs causes the high field shift in all the solvents studied, it seems possible that ΔJ may give a measure of the strength of the $(Na^+ BF_4^-)$ ion pair.

(iii) Correlation with the Solvent Dielectric Constant

The presence of splittings in the ^{19}F resonance due to B-F coupling, and of NMR evidence for a rapid exchange of fluorine among boron atoms, appears to be strongly dependent on the dielectric constant of the solvent. Table VIII indicates this dependence; the data for solutions in methylene chloride was obtained by Sharp and co-workers who studied solutions of triphenylmethyl tetrafluoroborate (90). It is seen that solvents of low dielectric constant do not give rise to splittings due to boron-fluorine coupling. This is apparently not due to a coupling constant of zero since the peaks are not sharp; the absence of splittings is likely a result of quadrupole relaxation of boron. Poorer solvation

TABLE VIII

CORRELATION OF ^{19}F NMR SPECTRAL FEATURES WITH SOLVENT DIELECTRIC CONSTANT

Solvent	Dielectric Constant at 20° (116)		Visibility at Room Temperature of Splittings due to J	NMR Evidence of Fluorine Exchange	
				Room Temperature	90°
Water	80	high	yes	no	no
DMSO	47	↓	yes	no	no
acetonitrile	38		yes	no	yes
acetone	21		no	no	-
pivalonitrile	(18)*		no	no	-
methylene chloride	9	low	no	yes**	-

*Isovaleronitrile (isobutyl cyanide) has a value of 18; the tertiary butyl compound is not listed

**Exchange between BCl_4^- and BF_4^- is indicated by ^{19}F and ^{11}B NMR (90).

in these solvents would probably result in association of the solute, very likely in the form of ion pairs. These ion pairs would be more strongly associated than those proposed in aqueous solution when the sodium salt is used, due to the absence of a stable solvation shell about the cation capable of hydrogen bonding to BF_4^-, and could cause a sufficiently large field gradient at boron to collapse the small splittings.

It is interesting that some lower dielectric constant solvents also appear to facilitate fluorine exchange, as is evidenced by collapse of the isotope shift at high temperatures in acetonitrile. The fluorine exchange thus may result from poorer solvation of the anion. The two effects, collapse of the splittings and fluorine exchange, are discussed separately in the next sections.

(iv) Collapse of B-F Splittings in Solvents of Low Dielectric Constant: Evidence for Quadrupole Relaxation

A study by Packer and Muetterties (117) of ^{19}F spectra of solutions of potassium hexafluoroarsenate provides strong support for the postulate that the absence of splittings due to B-F coupling in solutions of the tetrafluoroborate ion in solvents of low dielectric constant is due to quadrupole relaxation. The AsF_6^- ion is similar to the BF_4^- ion in that it is a highly symmetrical species with a central spin-3/2 nucleus, and in aqueous solution it gives rise to a ^{19}F spectrum consisting of a 1:1:1:1 quartet. However, its much larger spin-spin coupling constant($J_{^{75}As-^{19}F}$ = 933 c.p.s. (118)) allows the characteristic ^{19}F signal shapes expected (65) for intermediate rates of quadrupole relaxation of ^{75}As to be distinguished. ^{19}F spectra of $KAsF_6$ in the series of solvents of decreasing dielectric constant, acetonitrile, acetone, and glyme, showed increasing amounts of quadrupole relaxation. In these solvents it was possible to obtain the entire range of line shapes for a spin-1/2 nucleus coupled to a spin-3/2 nucleus. A further study by Arnold and Packer (118), using ^{75}As resonance, was interpreted as indicating association of AsF_6^- with cations rather than with solvent molecules.

In solutions of the tetrafluoroborate ion the B-F splittings are so small that even a small degree of quadrupole relaxation of boron should be sufficient to prevent resolution of the ^{19}F quartet. In the present study of $AgBF_4$ complexes, the absence of splitting due to B-F coupling in acetone solutions provides the best evidence for quadrupole relaxation of boron in a solvent of low dielectric constant. Studies with mixed solvents containing acetone, as described previously, provide very strong evidence that J is not zero in acetone but that a broadening process obscures the splittings. This process cannot be a moderately fast fluorine exchange as the same broadened spectrum was obtained down to -56°. The effect is not dependent on concentration as essentially identical spectra were obtained over a considerable range of concentrations. The most reasonable explanation is association of the solute; ion pairs are the most likely type of association. In the acetonitrile-acetone system, as the solvent changes from acetonitrile to acetone the decreasing ability to solvate the ions could cause an increasing proportion of them to exist in the form of ion pairs, with resultant broadening and disappearance of the closely spaced 1:1:1:1 multiplet. The degree of solvation of Ag^+

appears to vary with the solvent in the order acetone $<$ acetonitrile $<$ DMSO (119). The tendency of Ag^+ to form ion pairs should be in the reverse order; this would allow ion pair formation to obscure the splittings due to boron-fluorine coupling in acetone but not in acetonitrile or DMSO.

Equally good evidence for the presence of ($Ag^+BF_4^-$) ion pairs was not obtained in other low dielectric constant solvents. In pivalonitrile a broad peak was obtained at room temperature; this narrowed to some extent at 45°, so that an isotope shift could just be distinguished, and broadened again at higher temperatures. A possible explanation is that the broad line at room temperature resulted from quadrupole relaxation of boron; at 45° fluorine exchange was fast enough to eliminate the effects of coupling to boron so that the signal became sharper. At higher temperatures additional broadening could be caused by rapid exchange of fluorine with a fluorine-containing impurity. The results obtained from a single sample in this solvent are inadequate, however, to allow definite conclusions to be drawn.

Brownstein and Paasivirta (87), in a low temperature study of the uptake of BF_3 by methylene chloride solutions of silver and tetra-_n_-butylammonium tetrafluoroborates, presumably to form the complex ions $B_2F_7^-$ and $B_3F_{10}^-$, observed that the uptake depends on the cation present. This effect of the cation on the stability of anionic complexes seems to require that the various fluoroborate complexes be present as ion pairs in methylene chloride solution.

Some solutions of $NaBF_4$ in non-aqueous solvents have shown effects which have been attributed to quadrupole relaxation of boron. Quail (77) observed that in solutions in 50% and 70% diglyme solvent B-F couplings were visible but showed evidence of partial quadrupole relaxation. Thus as the solvent dielectric constant decreases the ion pair appears to be held more tightly, with a reduction in symmetry about boron. A spectrum of a solution of $NaBF_4$ in DMF also indicated such a pattern (120) whereas a similar solution studied in the course of the present work yielded only a broad peak; the discrepancy in these results seems to suggest differing magnitudes of J and differing amounts of quadrupole relaxation, possibly depending on concentration.

Haque and Reeves (68) have referred to unpublished experiments on aqueous solutions of tetrafluoroborates of the large polarizable cations Sn^{2+}, Cd^{2+}, Sb^{3+}, and Pb^{2+}, in which broadening effects were observed in the ^{19}F spectrum. They proposed inner-sphere ion pairs in these cases, ion pair formation being favoured by the large polarizable cations.

Ion pair formation should be favoured by the absence of a stable solvation shell about the cation. In solutions of $NaBF_4$ the collapse of splittings due to J during the transition from water to a lower dielectric constant solvent does not appear to allow the observation of splittings due to J when these are much smaller then 1 c.p.s. (68,77), whereas much smaller splittings (down to 0.3 c.p.s.) can be observed when $AgBF_4$ is used. This is a further indication, in addition to the specific cationic effects found for Na^+ but not for Ag^+ in aqueous solution, that ion pairs form more readily with Na^+ than with Ag^+, and that quadrupole relaxation of boron is greater in Na^+ solutions.

In non-aqueous solvents the lower degree of quadrupole relaxation when Ag^+ is the cation may be related to the more ready complexation of Ag^+ with solvent molecules; the resultant large coordinated species should be less suitable for formation of an ion pair with BF_4^-.

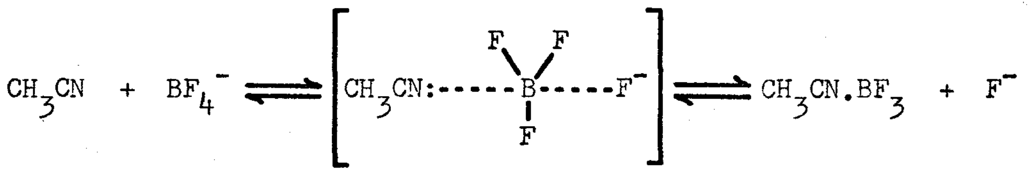
(v) The Exchange of Fluorine among Boron Atoms

Rapid exchange of fluorine among boron atoms has been proved by the collapse of the ^{10}B-^{11}B isotope shift at high temperatures in solutions of $AgBF_4$ in acetonitrile. The absence of such exchange in water and in DMSO was shown by NMR spectra at high temperatures which clearly showed both the isotope splitting and the splittings due to J. Acetone solutions were not studied above room temperature. The results obtained for the single solution in pivalonitrile are not conclusive. No solutions of BF_4^- in methylene chloride were studied in the present work; the results of Sharp and co-workers are relevant and are included in Table VIII. However, these results are not strictly analogous as the observed exchange was between fluorine and chlorine, rather than among fluorines. The data available is sufficient to suggest that the exchange of halogens among boron atoms is facilitated by low dielectric constant solvents.

A similar fluorine scrambling process occurring in ketone.BF_3 complexes has been discussed in Chapter VII. Of the mechanisms proposed for this process, only the reaction scheme (29) (p. 132), which involves the dissociation of a donor molecule, is likely in the case of the tetrafluoroborate anion. Even this reaction should be considerably slower for BF_4^- than for ketone.BF_3 since a B-F bond, which is considerably stronger than the ketone.BF_3 donor-acceptor bond, must be broken in the first step. The reaction scheme can be simplified in the case of BF_4^- exchange to give:

$$2BF_4^- \rightleftharpoons F^- + BF_3 + BF_4^- \rightleftharpoons F^- + B_2F_7^- \qquad (37)$$

The details of the process should be different in different solvents. Thus in acetonitrile free BF_3 does not exist to any significant extent but forms a 1:1 complex with the solvent. The dissociation of fluoride ion in this solvent could result from a concerted (S_N2) mechanism involving attack on BF_4^- by a solvent molecule:

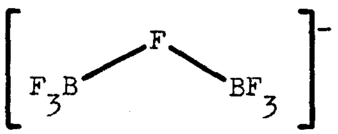


$$CH_3CN + BF_4^- \rightleftharpoons \left[CH_3CN{:}\text{-----}\underset{F}{\overset{F\quad F}{B}}\text{-----}F^-\right] \rightleftharpoons CH_3CN.BF_3 + F^- \qquad (38)$$

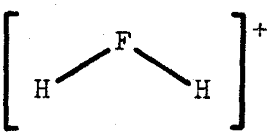
Such a mechanism would favour the reaction since the 1:1 complex is of considerably lower energy than free BF_3. The 1:1 complex could then attack a second molecule of BF_4^-, with dissociation of the solvent molecule which is more weakly bound than fluorine. Exchange in a low dielectric constant solvent such as methylene chloride, on the other hand, should not involve an intermediate complex with the solvent as strong complexes do not form.

Evidence for the existence of the proposed intermediate $B_2F_7^-$ as a definite chemical compound has been provided by Brownstein and Paasivirta, by vapour pressure measurements of BF_3 over solutions of tetrafluoroborate ion in methylene chloride at low temperatures (87). Considerably more BF_3 was taken up than was expected from solubility considerations alone; the solutions gave a single ^{19}F peak indicating rapid exchange of all the fluorines. The existence of the ions $B_2F_7^-$ and $B_3F_{10}^-$ in ion pairs in solution was postulated. A very similar study involving reaction of BF_3 with BF_4^- salts, carried out later by Harris (121), duplicated the conclusion of Brownstein and Paasivirta that the $B_2F_7^-$ ion can exist; investigation of the BF_4^- salts of a larger number of cations showed that the $B_2F_7^-$ ion can be stable at room temperature only if the cation is sufficiently large. Tetrafluoroborate salts of smaller cations do not absorb BF_3; even with large cations the instability of the $B_2F_7^-$ ion is shown by the fact that all of the added BF_3 could be pumped off at reduced pressures. Harris also reported that the ^{19}F spectrum consists of a single peak, indicative of rapid exchange.

The $B_2F_7^-$ ion would be expected to have the bent fluorine bridged structure XXVI. Brownstein and Paasivirta pointed out that this species is isoelectronic with bis(trifluoromethyl) ether, for which the bent structure is known (122). Structure XXVI is the BF_3 analogue of the diprotonation product of fluoride ion XXVII, known to exist in small concentrations in liquid HF (123).*



XXVI



XXVII

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*Other examples of two-coordinate fluorine are known, such as the anion XXVIII (124) and the closely related neutral compound XXIX (125). In XXVIII the central atoms Al-F-Al are linear; the structure is apparently stabilized by pπ-dπ bonding.

$[F_3Al\text{-}F\text{-}AlF_3]^-$

XXVIII

$F_3Al\text{-}F\text{-}SiF_3$

XXIX

The dissociation of a fluoride ion can with confidence be considered to be the slow step in the fluorine exchange reaction. A solution of both $AgBF_4$ and BF_3 in acetonitrile, which gave separate ^{19}F peaks for BF_4^- and BF_3 at -17°, each having an isotope shift, gave partially collapsed spectra near 0° and a single broad peak at room temperature which became sharper as the temperature was raised. The collapse of the peaks and of the isotope shift at much lower temperatures when BF_3 is present indicates that the ionization of F^- is the slow step in the BF_4^- exchange reaction in the absence of BF_3; this step is bypassed when BF_3 is added to the solution.

The relationship of these results to those obtained by Sharp and co-workers (90) for methylene chloride solutions of triphenylmethyl tetrafluoroborate is of interest. These workers found that added chloride ion would not exchange with BF_4^-, whereas added BCl_3 exchanged readily. It was not possible to test fluoride ion since there appears to be no ionic fluoride which is soluble in methylene chloride (90); however, covalent triphenylmethyl fluoride was found not to undergo rapid exchange since separate ^{19}F peaks were observed for the fluoride and for BF_4^-. BCl_4^- and BF_4^- must exchange readily since the ^{11}B and ^{19}F chemical shifts of the observed single peak were found to vary greatly with relative proportions of chlorine and fluorine. Sharp and co-workers proposed the dissociation of a chloride ion from BCl_4^-, and attack of the resulting BCl_3 on the BF_4^- ion. An equilibrium between BCl_4^-, and BCl_3 and Cl^-, in methylene chloride was also proposed by Thompson and Davis (45) as an explanation of the variation of the ^{11}B chemical shift of the BCl_4^- ion with concentration of chloride ion in this solvent. BF_4^- apparently does not dissociate appreciably in a similar fashion to give fluoride ion. It should be noted that any ionic species in methylene chloride would probably exist as ion pairs (87); this should not affect the above discussion.

The above considerations indicate that BF_4^- alone in methylene chloride might not be able to exchange fluorine among boron atoms because of the inability of the first step in the reaction scheme (37) to proceed. A study of the ^{19}F spectra of BF_4^- solutions in methylene chloride over a range of temperatures would thus be of interest, to determine whether the collapse of the isotope shift could be observed.

Scrambling of halogen atoms among boron atoms occurs in a wide variety of cases, probably by widely differing mechanisms. In addition to the examples discussed in this thesis, at least two other cases have been reported. Fluorine exchange between HBF_4 and HF in aqueous solutions has been investigated by ^{18}F tracer studies (126); dissociation of fluorine from HBF_4 was found to be 10^{10} times faster than dissociation of fluorine from BF_4^- in neutral solutions. Mixtures of different boron trihalides exchange halogen atoms to give the mixed trihalides, in a process which is slow on the NMR time scale at room temperature so that separate ^{19}F or ^{11}B signals may be detected for the separate species (127,128).

CHAPTER XI

QUADRUPOLE RELAXATION IN A NUCLEUS OF SPIN I=3. THE ^{19}F NMR SPECTRUM OF $^{10}BF_3$

INTRODUCTION

The temperature dependence of the ^{19}F NMR spectrum of liquid boron trifluoride has been studied in detail by Bacon, Gillespie and Quail (65). The shape of the spectrum varied from four broadened lines at -21° to a broad, doublet-like structure at -100° (Figure 2 of (65)). These shapes were satisfactorily explained in terms of coupling of the fluorine atoms to the boron-11 nucleus (I=3/2, 81.17% natural abundance), which is undergoing electric quadrupole relaxation, the rate of the relaxation process varying inversely with the temperature. An overlapping spectrum due to the fluorine atoms attached to boron-10 (I=3, 18.83% natural abundance) distorted the F-on-^{11}B signal to some extent; nevertheless it was possible to compute theoretical spectra for different rates of quadrupole relaxation of ^{11}B and to fit these to the observed spectra. Good agreement of observed and calculated spectra was obtained. From the skewing of the F-on-^{11}B spectrum, it was estimated that the F-on-^{10}B spectrum was centered approximately 0.05 p.p.m. to low field of the dominant F-on-^{11}B spectrum. This value is in accord with the magnitude and direction of ^{10}B-^{11}B isotope shifts reported elsewhere in this thesis.

Good agreement between observed and calculated spectral shapes has been obtained for the spectra of spin-1/2 nuclei coupled to high-spin nuclei of spin I=1 (129), I=3/2 (65), I=5/2 (130), I=7/2 (88), and I=9/2 (88). Similar good agreement is reported in the present work for a case in which the high-spin nucleus has spin I=3.

The preparation of $^{10}BF_3$, of isotopic purity about 97%, in the course of studies reported elsewhere in this thesis made it convenient to carry out a study of the ^{19}F NMR spectrum of liquid $^{10}BF_3$. Such a study is of special interest since boron-10 is the only stable nuclide with a spin of 3, and $^{10}BF_3$ appears to be one of very few compounds suitable for a study of the effect of partial quadrupole relaxation of a spin-3 nucleus on the spectrum of a spin-1/2 nucleus coupled directly to it. Suzuki and Kubo (131) were the first to calculate the line shapes for a spin-1/2 nucleus coupled to a spin-3 nucleus. Their method is quite similar to that used by Bacon, Gillespie and Quail for the spin-3/2 case, and their line shapes agree very well with those calculated in the present work. They did not, however, compare their theoretical spectral shapes with observed shapes. The present chapter describes the first comparison of observed and theoretical spectra for the I=3 case.

THEORY

(i) Pure Quadrupole Relaxation

The general expression for signal shapes of a spin-1/2 nucleus coupled to a high-spin nucleus undergoing electric quadrupole relaxation has been derived by Pople (129), who discussed in detail the case of spin I=1. At intermediate rates of relaxation the separate components of the multiplet were predicted to coalesce, passing through a series of distinctive signal shapes, until only a single broadened line can be observed at high rates of relaxation. The case of spin I=3/2 has been studied in detail by Bacon, Gillespie and Quail (65), who summarized the derivation in a convenient form; a similar derivation is used in the present discussion. Further details of the derivation are available ((1), pp. 447-451, 501-505).

A closely related, rather more general method of calculation has been used by Suzuki and Kubo (131), who obtained theoretical spectra for the I=3/2 and I=3 cases, among others. The derivation of the line shape equations, summarized here, is only slightly different from that used by Suzuki and Kubo, and leads to identical line shapes.

Seven spin states, m = 3,2,.....-3, are possible for a nucleus of spin I=3. In the absence of quadrupole relaxation the spectrum of a nucleus of spin 1/2 coupled to a nucleus of spin 3 would consist of seven peaks of equal intensities and spacings. When a high-spin nucleus undergoes quadrupole relaxation, transitions are induced between spin states in which m differs by 1 or 2; other transitions are forbidden. The transition probabilities, as derived by Pople, are

$$P_{m,m\pm1} = \frac{3}{20} \frac{(2m\pm1)^2(I\pm m+1)(I\mp m)}{4I^2(2I-1)^2} \left[\frac{e^2qQ}{\hbar}\right]^2 \mathcal{T}_q \qquad (32)$$

$$P_{m,m\pm2} = \frac{3}{20} \frac{(I\mp m)(I\mp m-1)(I\pm m+1)(I\pm m+2)}{4I^2(2I-1)^2} \left[\frac{e^2qQ}{\hbar}\right]^2 \mathcal{T}_q \qquad (33)$$

in which e is the electronic charge, eq is the electric field gradient at the nucleus, eQ is the quadrupole moment of the nucleus, and $\mathcal{T}_q$

is the correlation time for molecular reorientation. The inverse lifetime of each state m is given by

$$\frac{1}{\tau_m} = \sum_{\substack{n \\ n \neq m}} P_{m,n} \quad . \qquad (34)$$

It has been shown (1) that the spin-lattice relaxation time T_1, due to quadrupole coupling with a high-spin nucleus, is given to a good approximation by

$$\frac{1}{T_1} = \frac{3}{40} \, \frac{(2I+1)}{I^2(2I-1)} \left[\frac{e^2qQ}{\hbar} \right]^2 \tau_q \quad . \qquad (35)$$

Substitution of this expression in equations (32) and (33) leads to expressions for $P_{m,n}$ and $\frac{1}{\tau_m}$ in terms of $\frac{1}{T_1}$.

For intermediate rates of quadrupole relaxation the line shape of a spin-1/2 nucleus coupled to a high-spin nucleus is given by

$$I(\omega) \propto \mathrm{Re}\left\{ \mathbf{W} \cdot \mathbf{A}^{-1} \cdot \mathbf{1} \right\}, \qquad (36)$$

in which Re$\{\ \}$ denotes the "real part of",

$$\mathbf{W} \text{ is the vector } \left[1 \ldots\ldots\ldots 1 \right],$$

$$\mathbf{1} \text{ is the vector } \begin{bmatrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{bmatrix},$$

and $\mathbf{A}^{-1}$ is the inverse of the complex matrix $\mathbf{A}$, defined by

$$A_{m,m} = i\left[(\omega_0 - \omega) + m.2\pi J \right] - \frac{1}{\tau_m} \quad , \qquad (37)$$

$$A_{m,n} = P_{m,n} \, , \quad m \neq n, \qquad (38)$$

where ω_o is the centre of the unperturbed multiplet, and J is the coupling constant in c.p.s. It turns out that for pure quadrupole relaxation, other mechanisms of relaxation being negligible, the shape of the spectrum depends only on the dimensionless parameter

$$\eta = 2\pi JT_1 . \qquad (39)$$

Frequencies relative to the centre of the multiplet can be measured by the dimensionless quantity

$$x = \frac{\omega_o - \omega}{2\pi J} . \qquad (40)$$

Substitution of η and x into the matrix elements, and removal of the factor $\frac{1}{T_1}$, which is common to all terms of the matrix and hence has no effect on the line shape, yields a form of the **A** matrix which is suitable for numerical solution. For spin I=3 the **A** matrix is given on the following page (equation (41)).

Numerical solutions of the line shape equation (36) were obtained using the computer programme shown in the Appendix, Figure 38. Some calculated line shapes are shown in Figure 32. The changes of shape with changes in η are the same as those obtained by Suzuki and Kubo (131).

(ii) Quadrupole Relaxation and Chemical Exchange

The determination of line shapes of a spin-1/2 nucleus coupled to a high-spin nucleus undergoing quadrupole relaxation, and of line shapes due to chemical exchange as in Chapter III, both make use of essentially the same general expression, equations (11) and (36), which involves a matrix containing off-diagonal elements $P_{m,n}$. As a result of this it turns out that slight modiciations of

$$A = \begin{bmatrix} i\eta(x+3) - \frac{7}{3} & \frac{5}{3} & \frac{2}{3} & 0 & 0 & 0 & 0 \\ \frac{5}{3} & i\eta(x+2) - 4 & 1 & \frac{4}{3} & 0 & 0 & 0 \\ \frac{2}{3} & 1 & i\eta(x+1) - \frac{17}{5} & \frac{2}{15} & \frac{8}{15} & 0 & 0 \\ 0 & \frac{4}{3} & \frac{2}{15} & i\eta x - \frac{44}{15} & \frac{2}{15} & \frac{4}{3} & 0 \\ 0 & 0 & \frac{8}{5} & \frac{2}{15} & i\eta(x-1) - \frac{17}{15} & 1 & \frac{2}{3} \\ 0 & 0 & 0 & \frac{4}{3} & 1 & i\eta(x-2) - 4 & \frac{5}{3} \\ 0 & 0 & 0 & 0 & \frac{2}{3} & \frac{5}{3} & i\eta(x-3) - \frac{7}{3} \end{bmatrix} \qquad (41)$$

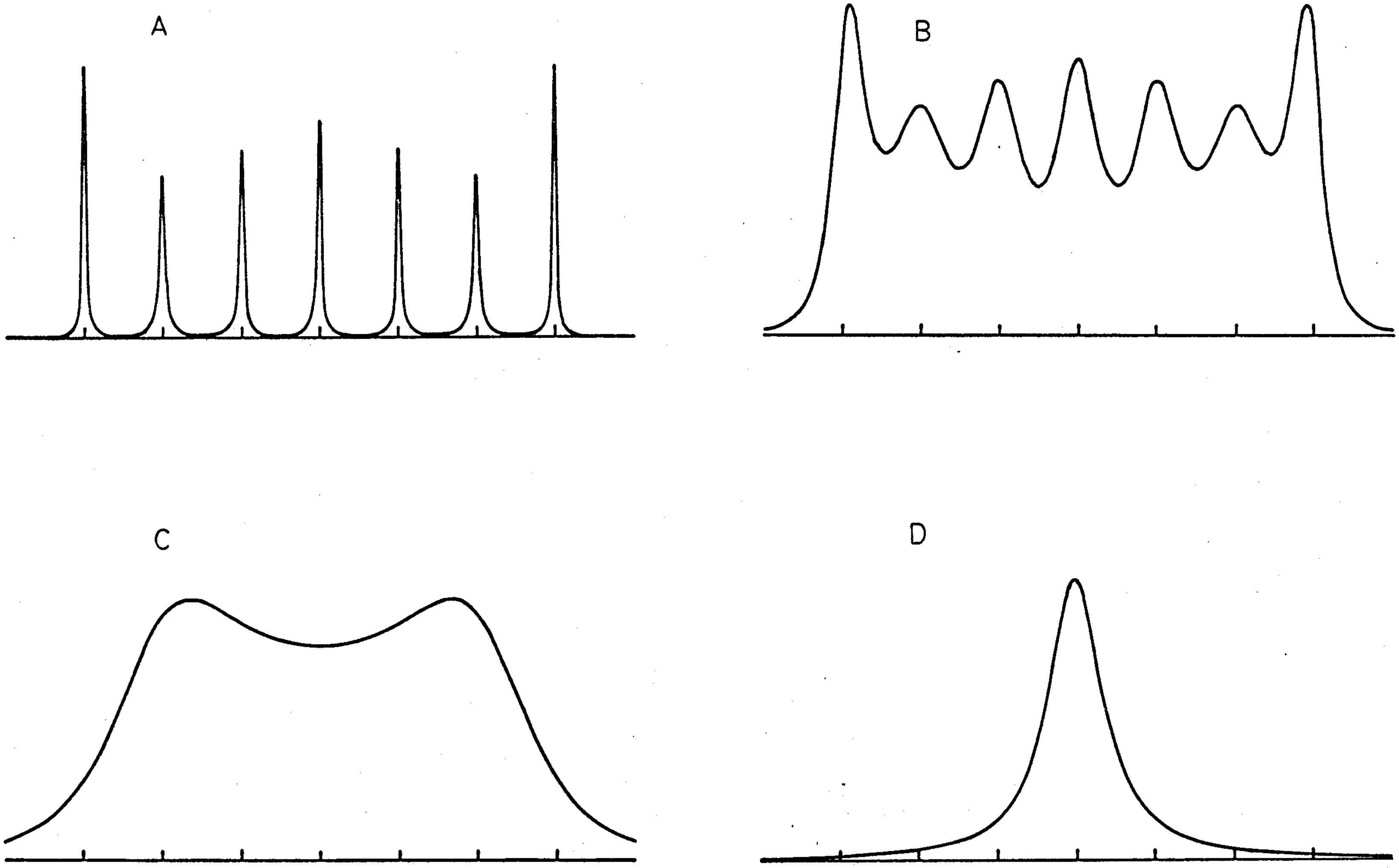

Fig. 32. Theoretical line shakes for the spectrum of a nucleus of spin 1/2 coupled to a nucleus of spin 3. A. $\eta = 100$; B. $\eta = 10$; C. $\eta = 1$; D. $\eta = 0.1$. The vertical lines indicate the peak positions in the absence of quadrupole relaxation.

the computer programme for line shapes due to quadrupole relaxation can allow for chemical exchange of fluorine atoms between different ^{10}B atoms within the $^{10}BF_3$ system, in addition to quadrupole relaxation of ^{10}B.

The desired line shape expression must allow for both a change in the spin state of the boron atom directly attached, as in part (i), and an exchange of fluorine between different boron atoms, such that the average boron-fluorine bond lifetime is τ' seconds. To include the latter effect, an additional term must be added to the $P_{m,n}$ terms appearing in the **A** matrix:

$$\begin{aligned} P_{m,n} &= (P_{m,n})_{\text{quadrupole relaxation}} + (P_{m,n})_{\text{chemical exchange}} \\ &= (P_{m,n})_{QP} + (P_{m,n})_{EX} \qquad (42) \end{aligned}$$

A fluorine atom leaving a boron atom of spin state m must become attached to another boron atom in one of seven equally probable spin states, and since $\sum_{n=1}^{7} (P_{m,n})_{EX} = \frac{1}{\tau'}$,

then $(P_{m,n})_{EX} = \dfrac{1}{7\tau'}$, for all n. (43)

Thus $$P_{m,n} = (P_{m,n})_{QP} + \frac{1}{7\tau'} \; . \qquad (44)$$

In removing the common term $\frac{1}{T_1}$ from the matrix, the new term $\frac{1}{7\tau'}$ becomes $\dfrac{T_1}{7\tau'}$, or $\dfrac{\eta}{14\pi J\tau'}$. This quantity is added to each off-diagonal matrix element of equation (41), and the τ_m terms recalculated according to equation (34). Numerical solutions of the **A** matrix thus modified lead to modified line shapes which include the effects of chemical exchange for given input J and τ' values, as well as the effects of quadrupole relaxation for a given input η.

RESULTS AND DISCUSSION

^{19}F NMR spectra of pure liquid $^{10}BF_3$ at four representative temperatures are shown in Figure 33. These spectra differ greatly in appearance from those of natural abundance BF_3, obtained over a similar range of temperatures by Bacon, Gillespie and Quail (65). The natural abundance BF_3 spectra showed a considerable range of line shapes corresponding to theoretical shapes for ^{19}F coupled to the spin-3/2 nucleus ^{11}B. In contrast, the spectra of $^{10}BF_3$ are much more collapsed. A broad doublet-like structure, resembling the calculated spectrum of Figure 32c for which $\eta = 1$, persists throughout the temperature range studied. Since the species differ only in isotopic substitution, the correlation time τ_q and the electric field gradient eq should be practically identical. The great difference in appearance is explained by differences in the properties of the ^{10}B and ^{11}B nuclei, in addition to their different nuclear spins. The quadrupole moment eQ of ^{10}B is greater than that of ^{11}B by a factor of 3.13; this allows the ^{10}B nucleus to interact much more strongly with the electric field gradient, resulting in an increased probability of transitions between spin states according to equations (32) and (33). Also the magnetogyric ratio of ^{10}B is only 0.335 times that of ^{11}B, so that $J_{^{10}B-^{19}F} = 0.335\ J_{^{11}B-^{19}F}$. Both of these factors increase the degree of collapse of the F-on-^{10}B multiplet with respect to the F-on-^{11}B multiplet.

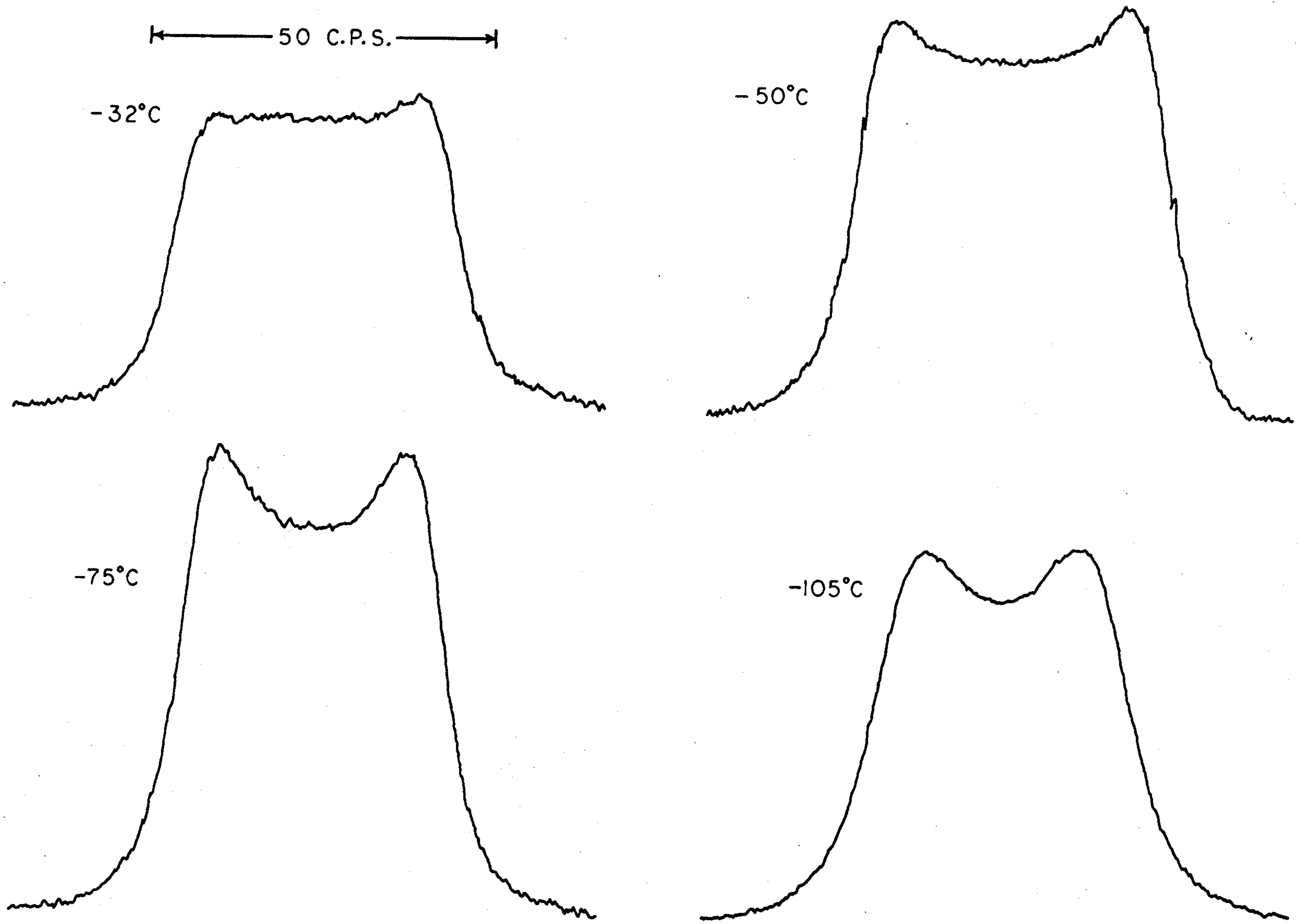

Fig. 33. ^{19}F spectra of liquid $^{10}BF_3$.

The shape of the broad doublet-like structure was found to change significantly over the range of temperatures studied (Figure 33). The central trough became shallower, the maxima positions moved farther apart, and the slope of the sides became steeper as the temperature was raised. Although the changes in signal shape are not as striking as those observed with $^{11}BF_3$, they are sufficient to allow a moderately accurate determination of η values for the various temperatures. At temperatures below -50° the two η values, obtained at a given temperature by calculations from two different line shape parameters as described on p.219, agreed quite well. This is in accord with the similarity of the appearance of experimental spectra obtained in this temperature range to that of the calculated spectra. Above -50°, however, agreement of experimental and calculated spectra is less satisfactory.

Values of the ^{10}B-^{19}F coupling constant, obtained by comparison of the experimental and computer calculated spectra, show a definite trend with temperature, as is evident in Figure 34, although anomalous values were obtained above -50°. A similar trend was observed in the ^{11}B-^{19}F coupling constant of $^{11}BF_3$, as determined by ^{11}B resonance (88); the values of $J_{^{11}B-^{19}F}$ obtained from the ^{11}B spectra agree quite well with the values of $J_{^{10}B-^{19}F}$ obtained in the present study, when the relationship, $J_{^{10}B-^{19}F} = 0.335\ J_{^{11}B-^{19}F}$, is applied.

It is of interest that the change in $J_{^{10}B-^{19}F}$ between -50° and -105°, 0.7 c.p.s., corresponds to a change in $J_{^{11}B-^{19}F}$ of 2.1 c.p.s. This illustrates that boron-fluorine coupling constants can change considerably as a result of minor changes in environment. Such changes

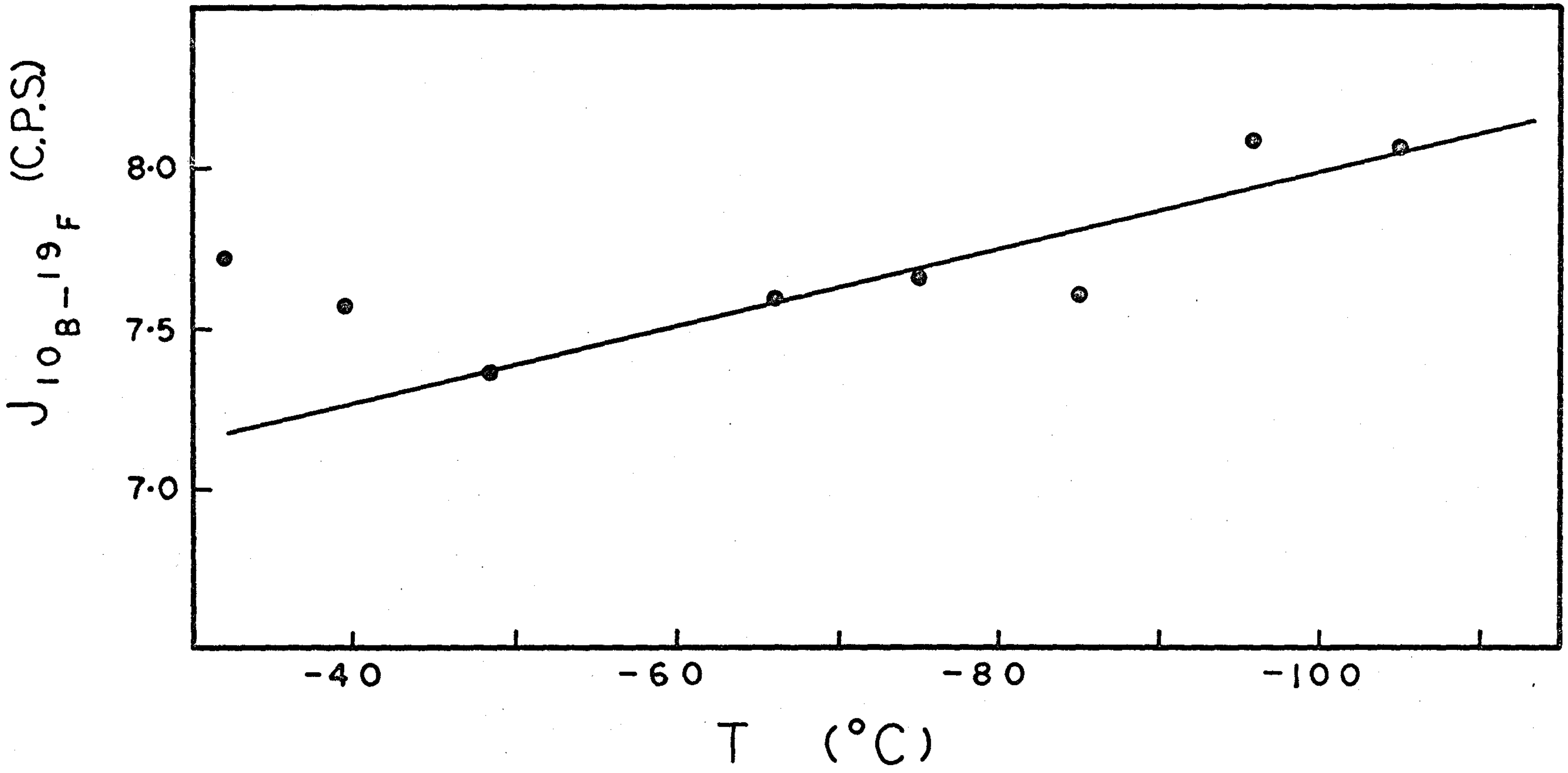

Fig. 34. Variation of $J_{^{10}B-^{19}F}$ of liquid $^{10}BF_3$ with temperature.

have been discussed at length in Chapter X for the case of tetrafluoroborate anion, in which a smaller change of 1.5 c.p.s. in $J_{^{11}B-^{19}F}$ caused a change of sign of the coupling constant. Here a larger change is J has much less apparent effect.

In the derivation of the line shape equation, the lifetimes $\mathcal{T}_m$ of the boron spin states are seen to be directly related to T_1 by constant factors consisting of simple fractions, and to be inversely related to $\mathcal{T}_q$, the correlation time for molecular reorientation. If the reorientation is a thermally activated process, the usual rate equation

$$\mathcal{T}_q = \mathcal{T}_q^{o} \; e^{E_a/RT} \qquad (45)$$

should apply. A plot of log T_1 vs. 1/T should thus give a straight line of slope $-E_a/2.303R$. Previous studies of $^{11}BF_3$ have yielded linear plots of log T_1 vs. 1/T, thus confirming that a normal thermally activated process is involved in quadrupole relaxation. Arrhenius activation energies of 1.4 Kcal./mole and 1.43 Kcal./mole were obtained from ^{19}F and ^{11}B spectra of natural abundance BF_3 (65,88). An Arrhenius plot of the data obtained in the present study is shown in Figure 35. A fairly good linear plot is obtained for temperatures below -50°. From the slope an Arrhenius activation energy of 1.36 Kcal./mole was calculated for the molecular "tumbling" or reorientation process, in substantial agreement with the values obtained for $^{11}BF_3$. The decreased accuracy of matching ^{19}F spectra in the ^{10}B case, because of smaller changes in line shape, may be compensated by the greater isotopic purity of the sample.

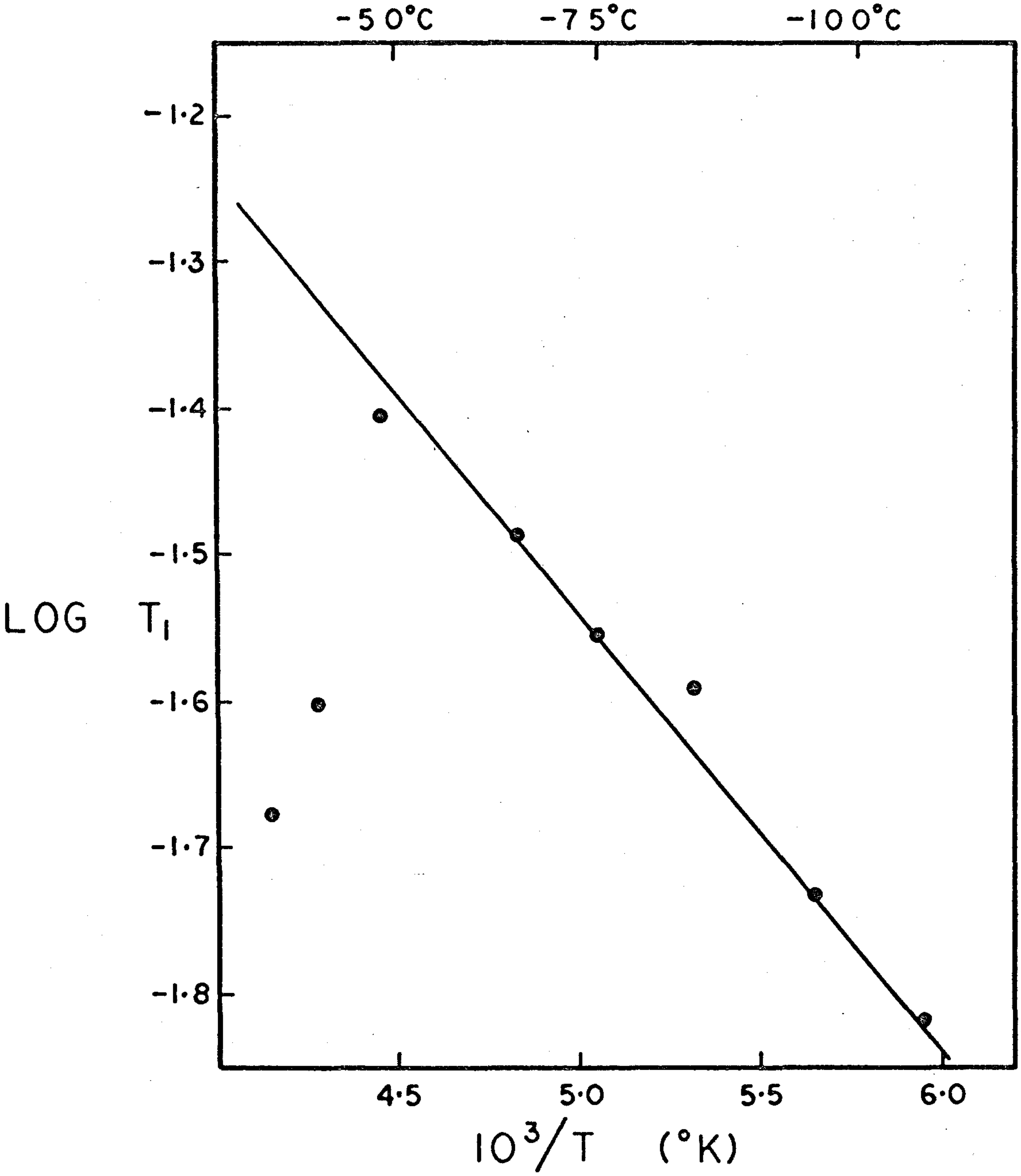

Fig. 35. Arrhenius plot for ^{10}B spin reorientation due to quadrupole relaxation in liquid $^{10}BF_3$.

The observed spectrum at -32° (Figure 33) could not be closely reproduced by computer calculated spectra by assuming that quadrupole relaxation of boron-10 is the only factor determining the signal shape. η values for a given temperature above -50°, obtained from the two independent line shape parameters used, were inconsistent. This effect was most marked at -32°, the highest temperature studied. Values of T_1 calculated from the η values obtained in this temperature range did not fall on the linear Arrhenius plot (Figure 35). Even the expected trend of η with temperature was reversed, so that the η values obtained at -32° from the two spectral parameters were less than those obtained at -75°. Values of $J_{^{10}B-^{19}F}$, as estimated from the line shape at temperatures above -50°, did not fit the linear trend of $J_{^{10}B-^{19}F}$ with temperature, established at lower temperatures (Figure 34). These discrepancies show that some additional factor besides quadrupole relaxation in the F-on-^{10}B system affects the spectrum above -50°.

The spectrum at -32° is expected, by extrapolation of Figures 34 and 35, to yield an η value of 2.33 and a coupling constant of 7.18 c.p.s. The computer calculated line shape is shown in Figure 36a. A comparison with the observed spectrum at -32° (Figure 33) shows that the anomalous change in shape consists of a flattening of the top of the spectrum, a decreased slope of the sides, and a distortion so that only the high field maximum is plainly visible.

The only obvious cause of asymmetry, as distinct from anomalous shape, is interference from the small amount of F-on-^{11}B present; the spectrum of F-on-^{11}B is shifted about 0.05 p.p.m. to higher field (65).

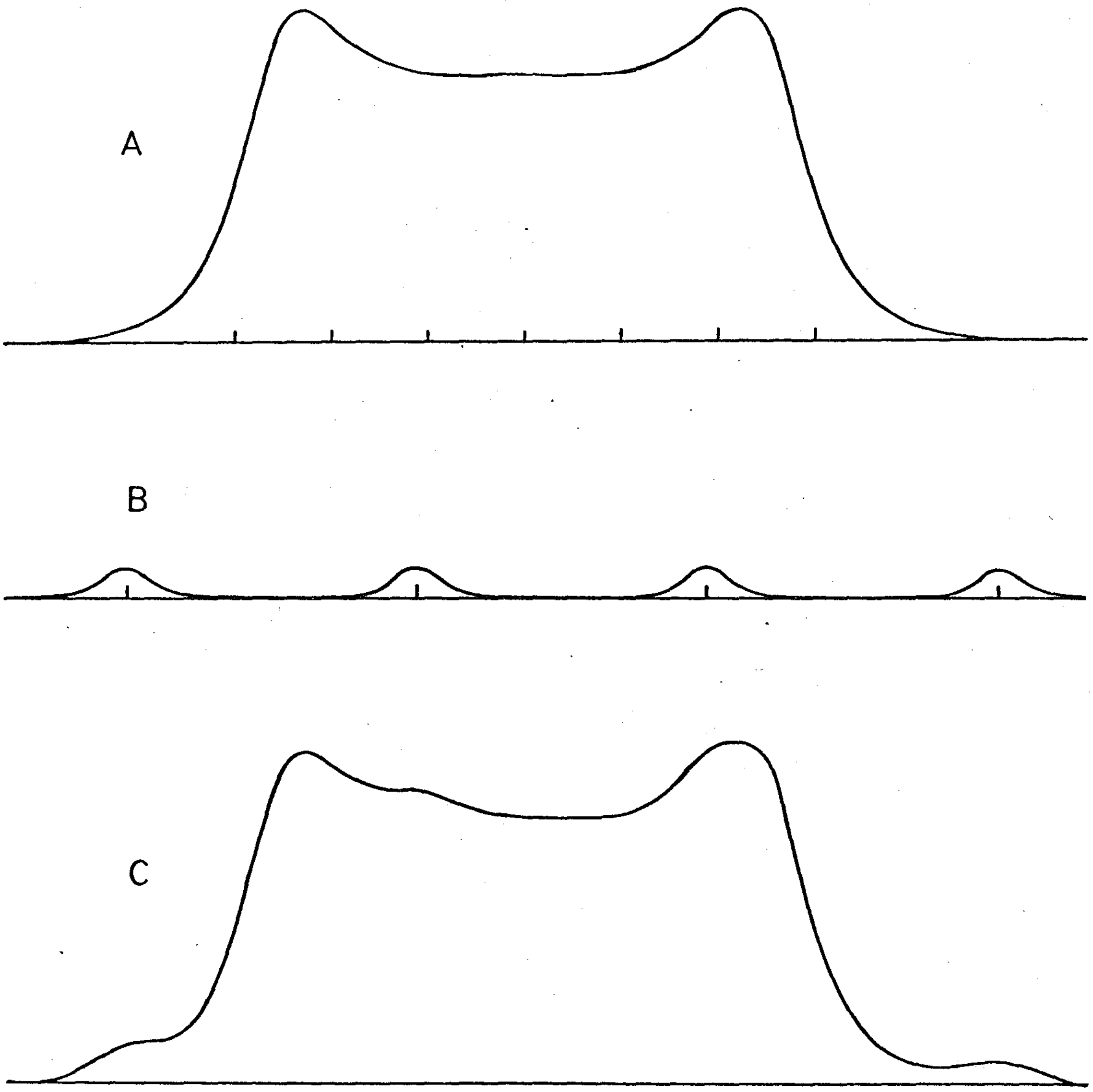

Fig. 36. Calculated ^{19}F spectra of liquid $^{10}BF_3$ at -32°.

a) line shape of F-on-^{10}B undergoing quadrupole relaxation.
b) estimated contribution from F-on-^{11}B isotopic impurity.
c) the sum of a) and b).

An effect due to F-on-^{11}B seems unlikely at first glance, since only about 3% of ^{11}B isotopic impurity is present. Bacon, Gillespie and Quail were able to obtain satisfactory matching of computer calculated spectra with the ^{19}F spectra of $^{11}BF_3$ in spite of the 18.83% of $^{10}BF_3$ present at natural abundance. However, the spectrum of $^{10}BF_3$ should be more sensitive to isotopic impurity, especially at temperatures above 50°, because of the relative sharpness of the F-on-^{11}B quartet in this temperature range (Figure 2 of (65)). In $^{11}BF_3$ only a small degree of collapse occurs at -32°. The broad, doublet-like structure of F-on-^{10}B, with an almost flat region on top, should readily show the effects of small but fairly sharp impurity peaks.

Figure 36b shows the expected F-on-^{11}B quartet. Peak positions and relative areas correspond to those of the F-on-^{10}B spectrum directly above, for 3% ^{11}B isotopic impurity, an isotope shift of 0.05 p.p.m., and $J_{^{11}B-^{19}F} = 21.4$ c.p.s. The total spectrum including the F-on-^{11}B isotopic impurity is shown in Figure 36c. The distortions caused by F-on-^{11}B do not in themselves appear sufficient to cause the observed line shape of Figure 33. However, the existence of small peaks outside the broad doublet-like F-on-^{10}B spectrum is very likely to lead to incorrect phasing of the spectrum. Phasing is normally adjusted until the base line is at equal height on both sides of the spectrum. In this case an equal "base line" level on both sides of the F-on-^{10}B spectrum would distort the spectrum, since immediately to low field of the F-on-^{10}B is a small F-on-^{11}B peak; the corresponding F-on-^{11}B peak to high field is considerably further removed from the

F-on-^{10}B spectrum because of the isotope shift. An attempt to obtain equal "base line"levels on both sides of the F-on-^{10}B spectrum would thus depress the low field side and raise the high field side, relative to the true absorption mode spectrum. Such distortion could account for the observed line shape.

Chemical exchange of fluorine among different boron atoms was considered as an alternative possible cause of the distortion of the spectrum. It is known, from studies of mixtures of two or more boron trihalides by NMR (127,128) and other methods (e.g., (132)) that such exchange does occur. However, the process is slow on the NMR time scale even at room temperature since chemical shifts (127,128) and spin-spin splittings (65,127) can be observed. The possibility of a more rapid exchange process was not ruled out in the present case as it seemed possible that a trace impurity such as hydrogen fluoride might be present and catalyse exchange.

The computer programme for line shapes due to quadrupole relaxation was modified to allow for chemical exchange of fluorine between different ^{10}B atoms (pp. 205-209). Line shape calculations using the modified programme, for $\eta = 2.33$ and $J_{^{10}B-^{19}F} = 7.18$ c.p.s., showed that for an average B-F bond lifetime τ' of about 0.07 seconds the top of the spectrum flattened out so that the calculated spectrum resembled the experimental spectrum at -32°, except for the high field maximum. However, it was not possible to obtain a calculated spectrum in which both spectral parameters r_1 and r_2 (p. 219) were close to the experimental values. Since the observed spectrum at -32° could not be matched satisfactorily with chemical exchange included in the calculations, the observed anomalies in the spectral shape do not arise from chemical exchange and can be attributed to interference by fluorine on boron-11.

The agreement of the observed and calculated line shapes below -50°, and the agreement of the Arrhenius plot for $^{10}BF_3$ with those obtained for $^{11}BF_3$, provides further evidence that the line shape expressions derived by Pople (129) are generally applicable. Modification of the expressions to include the effects of chemical exchange within the multiplet is not useful in the present case, but may find application in other cases.

CALCULATIONS

In order to match experimental and calculated spectra, a series of computer calculated spectra was first obtained at closely spaced η values over the range of line shapes found in the experimental spectra. The spectral parameters r_1 and r_2 were defined as

$$r_1 = \frac{HS}{\omega_{1/2}} \quad \text{and} \quad r_2 = \frac{HS}{\omega_{3/4}} \quad , \tag{46}$$

in which HS is the head separation, i.e., the separation of the two maxima in the observed broad, doublet-like structure, $\omega_{1/2}$ is the peak width at half-height, and $\omega_{3/4}$ is the peak width at three-quarters height. These parameters were determined from the calculated spectra and tabulated. Values of the parameters were then obtained from the experimental spectra and were used to obtain interpolated η values for the experimental spectra. At temperatures below -50°, η values for a given temperature, calculated from the two different ratios, agreed quite well.

The coupling constant, $J_{^{10}B-^{19}F}$, was estimated at each temperature by comparing the experimental spectrum, calibrated in c.p.s., with the theoretical spectrum, calculated in units of J using the appropriate η value determined as above. Comparison of experimental and calculated values of the three quantities HS, $\omega_{1/2}$, and $\omega_{3/4}$ yielded three estimates of $J_{^{10}B-^{19}F}$, in c.p.s., at each temperature. Below -50° the estimates at a given temperature agreed quite closely.

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APPENDIX

COMPUTER PROGRAMMES

Fig. 37. Computer programme for calculating NMR spectral shapes resulting from chemical exchange among six nonequivalent sites, five of the six sites having equal bond lifetimes.

```
C     PRØGRAM TØ CALCULATE SPECTRA FØR EXCHANGE IN PARTIALLY DECØMPØSED
C     SØLUTIØNS ØF BF3 IN ACETØNE
C     NØT THE GENERAL CASE---REQUIRES EQUAL D-A BØND LIFETIMES FØR FIVE
C     ØF THE SIX SPECIES
C     ASSUMES NATURAL LINEWIDTH ØF 1.0 CPS
      DIMENSIØN A(12,12),NI(48),C(6),SIGMA(10,13),Y(10),YY(130),
     1SHIFT(6),FRACT(6)
  100 READ 2, (SHIFT(I),FRACT(I),I=1,6)
      READ 3, ALIF,FACT4,FACT,MA
      READ 4,WCST,CINCR,NØ
    2 FØRMAT(3(2X,F8.2,2X,F6.4))
    3 FØRMAT(F12.7,F9.3,F6.3,I2)
    4 FØRMAT(F8.2,F8.2,I3)
      DØ 40 NZ=1,MA
      PRINT 601
  601 FØRMAT(X,65HLINE SHAPES FØR 6 SITE EXCHANGE, PARTIALLY DECØMPØSED
     1ACETØNE.BF3)
      PRINT 602,ALIF,FACT4,ALIF
  602 FØRMAT(X,33HD-A BØND LIFETIMES -ØRGANIC.BF3 =,F12.7,
     115H SEC, H2Ø.BF3 =,F9.3,6H TIMES,F12.7,3HSEC)
      PRINT 603,WCST,CINCR
  603 FØRMAT (X,19HFIRST CALC PØINT AT,F8.2,29H CPS WRT H2Ø.BF3, INCREME
     1NT =,F8.2,4H CPS,//)
      PRINT 604
  604 FØRMAT(5X,14HSPECTRAL DATA ,5X,11HPEAK NUMBER,5X,20HCHEMICAL SHIFT
     1 (CPS),5X,18HRELATIVE PEAK AREA)
      PRINT 605, (IU,SHIFT(IU),FRACT(IU),IU=1,6)
  605 FØRMAT(30X,I1,15X,F8.2,17X,F10.4)
      PRINT 606, CINCR
  606 FØRMAT(///,5X,6HW(CPS),6X,4H0.00,F8.2,7H   ETC.)
      YMAX=0.
      WC=WCST-CINCR
      DØ 15 L=1,13
      DØ 14 K=1,10
      DØ 19 IA=1,12
      DØ 19 JA=1,12
   19 A(I,J)=0.
      WC=WC+CINCR
      Y(K)=WC
      DØ 21 JZ=1,6
      DØ 21 KZ=1,6
   21 A(JZ,KZ)=FRACT(KZ)/ALIF
      DØ 22 LZ=1,6
   22 A(LZ,4)=A(LZ,4)/FACT4
      DØ 23 MZ=1,6
   23 A(4,MZ)=A(4,MZ)/FACT4
      DØ 24 NQ=1,6
   24 A(NQ,NQ)=0.
      DØ 26 II=2,6
   26 A(1,1)=A(1,1)+A(1,II)
      A(2,2)=A(2,1)
      DØ 27 JJ=3,6
   27 A(2,2)=A(2,2)+A(2,JJ)
      A(3,3)=A(3,1)+A(3,2)+A(3,4)+A(3,5)+A(3,6)
```

(continued on next page)

Fig. 37. (continued)

```
   A(4,4)=A(4,1)+A(4,2)+A(4,3)+A(4,5)+A(4,6)
   DØ 28 KK=1,4
28 A(5,5)=A(5,5)+A(5,KK)
   A(5,5)=A(5,5)+A(5,6)
   DØ 29 LL=1,5
29 A(6,6)=A(6,6)+A(6,LL)
   DØ 31 IA=1,6
31 A(IA,IA)=-1.*A(IA,IA) -6.28318
   DØ 32 IB=1,6
   DØ 32 IC=1,6
32 A(IB+6,IC+6)=A(IB,IC)
   DØ 53 ND=1,6
   A(ND,ND+6)=(     SHIFT(ND)-WC)*6.28318
53 A(ND+6,ND)=-A(ND,ND+6)
   CALL INVMAT(A,12,12,1.E-8,IERR,NI)
   DØ 33 IK=1,6
33 C(IK)=0.
   DØ 13 IH=1,6
   DØ 13 IG=1,6
13 C(IH)=C(IH)+A(IH,IG)
   CC=0.
   DØ 34 IL=1,6
34 CC=CC+C(IL)*FRACT(IL)
   SIGMA(K,L)=-1.*CC
14 YMAX=AMAX1(YMAX,SIGMA(K,L))
15 PRINT 16 , Y(1),(SIGMA(M,L),M=1,10)
16 FØRMAT (2X,F9.2,10F10.4)
   XMAX=FLØAT(NØ)
   DØ 79 L=1,13
   DØ 79 K=1,10
   IW=10*(L-1)+K
79 YY(IW)=SIGMA(K,L)
   CALL PLØT1(YY,YMAX,0.,XMAX,0.,54,NØ,5)
   PRINT 68,ALIF,FACT4
68 FØRMAT (X,42HF-19 ØF BF3 IN ACETØNE, D-A BØND LIFETIMES,F12.7,
  18H SEC AND,F9.3,10HTIMES THIS)
   PRINT 99
99 FØRMAT (1H1)
40 ALIF=FACT*ALIF
   GØ TØ 100
   END
```

Fig. 38. Computer programme for calculating spectral shapes of a spin-1/2 nucleus coupled to a spin-3 nucleus which is undergoing quadrupole relaxation.

```
C     NMR SPECTRUM ØF FLUØRINE CØUPLED TØ BØRØN 10.
      DIMENSIØN A(14,14),NI(56),TEM(14),Y(10),SIGMA(10,20),FUN(125)
       DIMENSIØN B(14,14),AA(196),BB(196)
       EQUIVALENCE (A,AA),(B,BB)
      DØ 5 I=1,14
      DØ 5 J=1,14
    5 A(I,J)=0.
      A(1,1)=-7./3.
      A(2,2)=-4.
      A(3,3)=-51./15.
      A(4,4)=-44./15.
      DØ 6 I=1,4
      MARY=8-I
    6 A(MARY,MARY)=A(I,I)
      A(1,2)=5./3.
      A(2,3)=1.
      A(3,4)=2./15.
      DØ 7 ILA=1,3
    7 A(ILA+1,ILA)=A(ILA,ILA+1)
      DØ 8 JUDY=1,3
      MARG=8-JUDY
      LYN=7-JUDY
      A(LYN,MARG)=A(JUDY,JUDY+1)
    8 A(MARG,LYN)=A(LYN,MARG)
      A(1,3)=2./3.
      A(2,4)=4./3.
      A(3,5)=8./5.
      DØ 9 JILL=1,3
    9 A(JILL+2,JILL)=A(JILL,JILL+2)
      DØ 10 JUNE=1,2
      J1=8-JUNE
      J2=6-JUNE
      A(J1,J2)=A(JUNE,JUNE+2)
   10 A(J2,J1)=A(J1,J2)
      DØ 11 I1=1,7
      DØ 11 J1=1,7
   11 A(I1+7,J1+7)=A(I1,J1)
      READ(5,1) N
    1 FØRMAT(I2)
      II=1
   22 IF(II.GT.N) GØ TØ 20
      READ(5,2) ETA
    2 FØRMAT(F10.4)
      WRITE(6,3) ETA
    3 FØRMAT(10X, 79HNMR SPECTRAL INTENSITIES ØF FLUØRINE CØUPLED TØ BØR
     2ØN-10 IN TRIFLUØRIDE AT ETA=,F10.4//)
      WRITE(6,4)
    4 FØRMAT(1X,105H  X           .00        .02        .04        .06
     2.08        .10        .12        .14        .16        .18)
      YMAX=0.
      X=-0.02
      DØ 15 L=1,20
      DØ 14 K=1,10
      X=X+0.02
```

(continued on next page)

Fig. 38. (continued)

```
      Y(K)=X
      Z1=Y(K)+3.
       DØ 1234 KKK=1,196
1234   BB(KKK)=AA(KKK)
       B(1,8)=ETA*Z1
       DØ 123 KKK=1,6
123    B(KKK+1,KKK+8)=B(KKK,KKK+7)-ETA
       DØ 12 I2=1,7
12     B(I2+7,I2)=-B(I2,I2+7)
       CALL INVMAT(B,14,14,1.E-8,IERR,NI)
      C=0.
      DØ 13 III=1,7
      DØ 13 JJJ=1,7
13     C=C-B(III,JJJ)
      SIGMA(K,L)=C
   14 YMAX=AMAX1(YMAX,SIGMA(K,L))
   15 WRITE(6,16) Y(1),(SIGMA(M,L),M=1,10)
   16 FØRMAT(1X,F6.3,10F10.4)
      YMAX=1.1*YMAX
      DØ 17 L=1,20
      DØ 17 K=1,10,2
      I=(10*(L-1)+K+1)/2
   17 FUN(I)=SIGMA(K,L)
      CALL PLØT1(FUN,YMAX,0.0,3.98,0.0,54,130,5)
      WRITE(6,18) ETA
   18 FØRMAT(10X, 31HNMR SPECTRUM ØF B-10 F3 AT ETA=,F10.4)
      II=II+1
      WRITE(6,19)
   19 FØRMAT(1H1)
      GØ TØ 22
   20 STØP
      END
```