Enthalpies of Reaction of Amines with Group III and IV Halides

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ABSTRACT

Enthalpies of reaction of BF_3 with amines have been measured calorimetrically by a displacement technique in acetronitrile solution. Enthalpies are in the order; 4->5-~7->6->3-membered ring, for the cyclicimines; 4-~7->6-~5->3-membered ring, for the N-methyl cyclicimines; $(CH_3)_2NH \sim CH_3NH_2 > (CH_3)_3N \sim NH_3$, and $(CH_3)_3N \sim (C_2H_5)_3N \sim C_5H_5N$. These orders are different from the corresponding orders of ^{19}F, ^{11}B, and ^1H nmr chemical shifts. The enthalpy of formation of $BI_3 \cdot CH_3CN$ is -45.3 Kcal/mole on the basis of its measured enthalpy of hydrolysis.

Infrared frequency shifts, $\Delta\nu$(C-D), and ^1H nmr chemical shifts, $\Delta\delta(^1H)$, of $CHCl_3$- cyclicimine complexes do not correlate with enthalpies of formation determined by calorimetry or with a ^1H nmr technique.

Enthalpies of formation of crystalline $MX_4 \cdot 2L$ complexes (where M = Si, Ge, Sn; L = py or iq; X = F, Cl, or Br, except X = Cl only when M = Sn) have been redetermined with a more sensitive calorimeter and using improved techniques to exclude water impurity. Contrary to previous results, values do not vary greatly in each series of related adducts, except for the order $GeF_4 \cdot 2L > SiF_4 \cdot 2L$.

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A Thesis Submitted to the Faculty of
Graduate Studies and Research at
McGill University in Partial Fulfillment
of the Requirements for the
Degree of Doctor of Philosophy

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July, 1970

ACKNOWLEDGEMENTS

The author wishes to thank Dr. M. Onyszchuk for his assistance throughout this research.

The author is indebted to Dr. T.H. Chan for the procedure used in preparing N-methyl trimethyleneimine.

Dr. C. Matthews, Dr. D.F.R. Gilson and Mr. A.D. Adley are thanked for the ^{19}F nmr measurements. Dr. C. Matthews is also thanked for the ^{11}B nmr measurements.

The author recognizes that he found room 335 a most fascinating place.

To Jay Peak

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LIST OF ABBREVIATIONS

TMA	- Trimethylamine
MMA	- Monomethylamine
DMA	- Dimethylamine
TEA	- Triethylamine
DEA	- Diethylamine
MEA	- Monoethylamine
NB	- Nitrobenzene
py	- Pyridine
TMB	- Trimethylboron
TMP	- Trimethylphosphine

1. INTRODUCTION

During the last hundred years that the concept of acids and bases has evolved, a voluminous literature on their preparation, properties, structure and theory has accumulated (1-9). Since this material has been historically surveyed in several monographs, the present work will begin by reviewing briefly only recent developments in the following areas:

1.1 Electronic theories of acids and bases.

1.2 Steric effects and reorganization energies.

1.3 Measures of acid and base strength.

1.3.1 Thermochemical measurements.

1.3.2 Hydrogen bonding studies.

1.3.3 Ultraviolet spectroscopic measurements.

1.3.4 Nuclear magnetic resonance studies.

1.3.5 Infrared spectroscopy.

1.1 Electronic Theories of Acids and Bases

From the definition of acids and bases in terms of the presence of particular elements such as hydrogen or oxygen, resulted the Solvent Systems Theory (4), the Bronsted Theory (3), and finally the Lewis Theory of acid-base interaction (2,7). The last theory is the most general and relates acid and base properties to the acceptance by acids and the donation by bases of electron pairs to form covalent bonds, irrespective

of whether a transfer of protons or other ions is involved. This definition includes boron trichloride as a typical acid and trimethylamine (TMA) as a typical base as well as those acids and bases previously described by other theories. Sidgwick (10) proposed the definition of donors for bases and acceptors for acids to emphasize as characteristic the sharing of an electron pair.

Later Mulliken (11) suggested that the donor-acceptor linkage (A←B) was a resonance hybrid composed of a "no bond" structure (A,B) and an electron transfer structure (A^-B^+). The wave function for the ground state, ψ_N, was described by:

$$\psi_N = a\psi_0(A,B) + b\psi_1(A^-B^+) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

in which ψ_0 is the no bond wave function, or a description of the classical intermolecular ion-dipole, dipole-induced dipole, dipole-dipole and London forces involved; ψ_1 is the wave function corresponding to the complete transfer of charge from the donor to the acceptor molecule; "a" and "b" are mixing coefficients.

Although this equation was criticized for not adequately describing the donor-acceptor linkage in strong molecular addition compounds such as BF_3·pyridine (py) it leads to the following more accurate description (12);

$$\psi_N = a\psi(A^-B^+) + b\psi(A:B) + c\psi(A^+B^-) \quad \ldots\ldots\ldots\ldots (2)$$

where ψ_N is the ground state wave function,

$$\psi(A^-B^+) = \chi_A(1)\chi_A(2)$$

$$\psi(A^+B^-) = \chi_B(1)\chi_B(2)$$

$$\psi(A:B) = \tfrac{1}{2}\{\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)\}$$

χ_A and χ_B are wave functions for the valence orbitals of A and B respectively; "a", "b" and "c" are mixing coefficients. An analysis of this equation reveals that for a relatively strong bond the following are important (11):

(a) A low ionization potential for the base and a high electron affinity for the acid.

(b) A strong coulombic interaction and a weak exchange repulsion.

(c) The relative stabilization of the product species over the reactant species by the reaction medium.

Further progress in analyzing the parameters affecting donor-acceptor interaction was made by Pauling (13) when he used electronegativity theory to describe the dissociation energy of the bond A-B in terms of the well known equation:

$$D(A\text{-}B) = \tfrac{1}{2}\{D(A\text{-}A)+D(B\text{-}B)\} + 23(\chi_A-\chi_B)^2 \quad \ldots\ (3)$$

where D(A-B), D(A-A) and D(B-B) are the dissociation energies of the bonds A-B, A-A, and B-B, respectively, and χ_A and χ_B are the electronegativities of atoms A and B. This equation

suggests that the energy of the bond A-B can be divided into a covalent part, the first term, and an ionic part, the second term. Charge transfer is then associated with electronegativity in a natural way, bearing a close relationship to the concept of acid-base interaction given by Mulliken, by saying that A is more electronegative than B if a>c and A ≡ B if a = c in equation (2). Although Pauling defined electronegativity as an atomic parameter, this was later recognized as an orbital parameter by Mulliken (14,15) and defined by the function $\frac{1}{2}(I+A)$, where I and A are the ionization potential and electron affinity respectively of the species considered. Subsequently Iczkowski and Margrave (16) described electronegativity as the derivative of the energy of an orbital with respect to the charge transferred to it when the energy of an orbital is given by:

$$E = aq + bq^2 + cq^3 + dq^4 \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

where a,b,c, and d are the coefficients of the power series in the charge "q". Over the range of orbital energy associated with the formation of chemical bonds this relationship is given approximately by:

$$E = aq + bq^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where $E = Iv = a + b$ at $q = 1$

and $E = Iv + Ev = 2a + 4b$ at $q = 2$.

Therefore;

$$E = \frac{(3Iv - Ev)}{2} q + \frac{(Ev - Iv)}{2} q^2 \quad \ldots\ldots\ldots \quad (6)$$

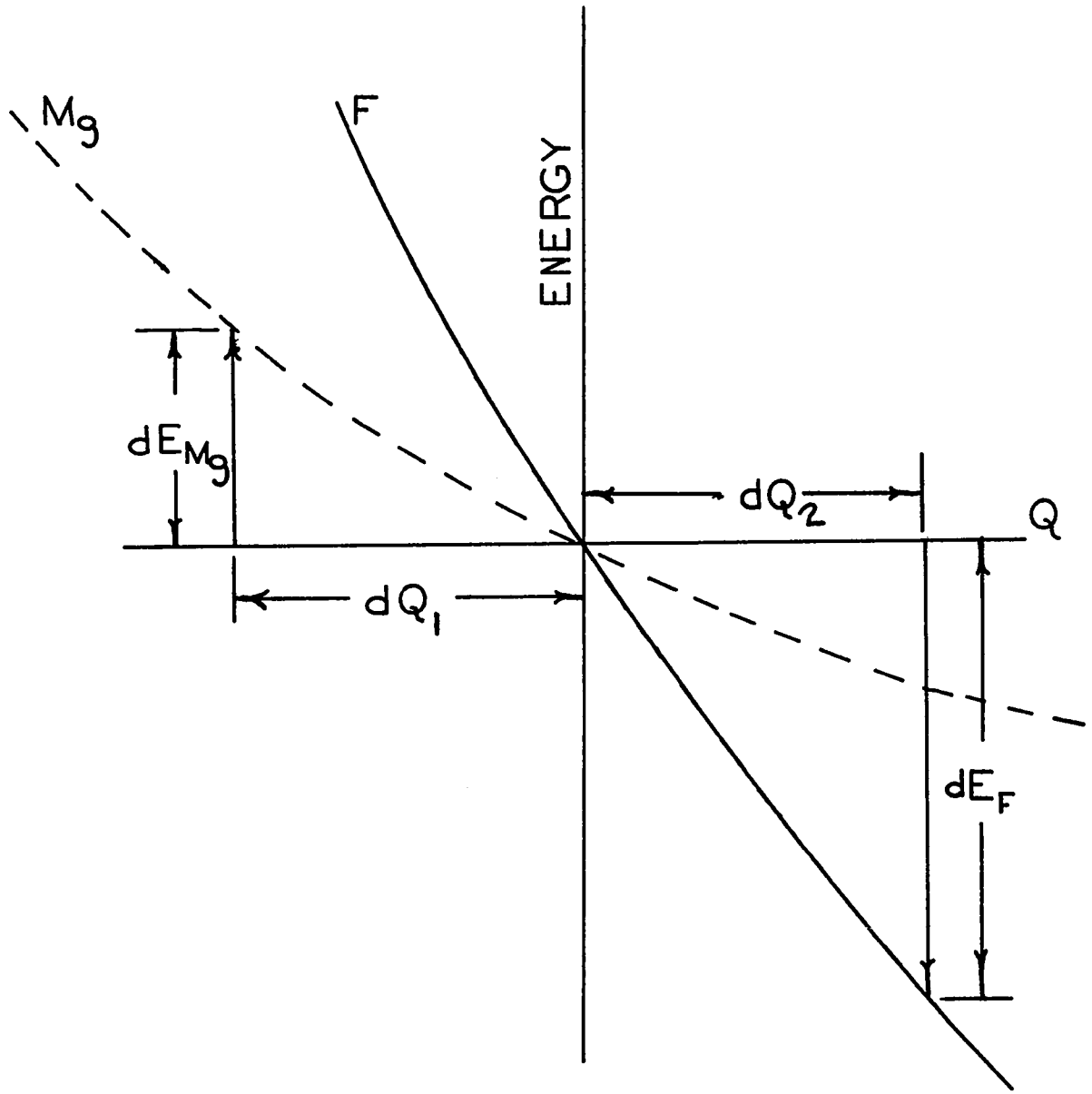
where Iv and Ev are the ionization potential and electron affinity respectively, of the orbital being considered. Hence, if the electronegativity is defined as the force acting at an orbital, i.e. $\frac{\delta E}{\delta q} = a + 2b(q)$, then equation (6) reduces to Mulliken's definition for the case of the neutral atom, i.e. $\chi = \frac{Iv + Ev}{2}$ for $q = 1$. Since equation (6) is meaningful only for the doubly occupied orbital, the idea of electron pairing originally suggested by Lewis is still valid.

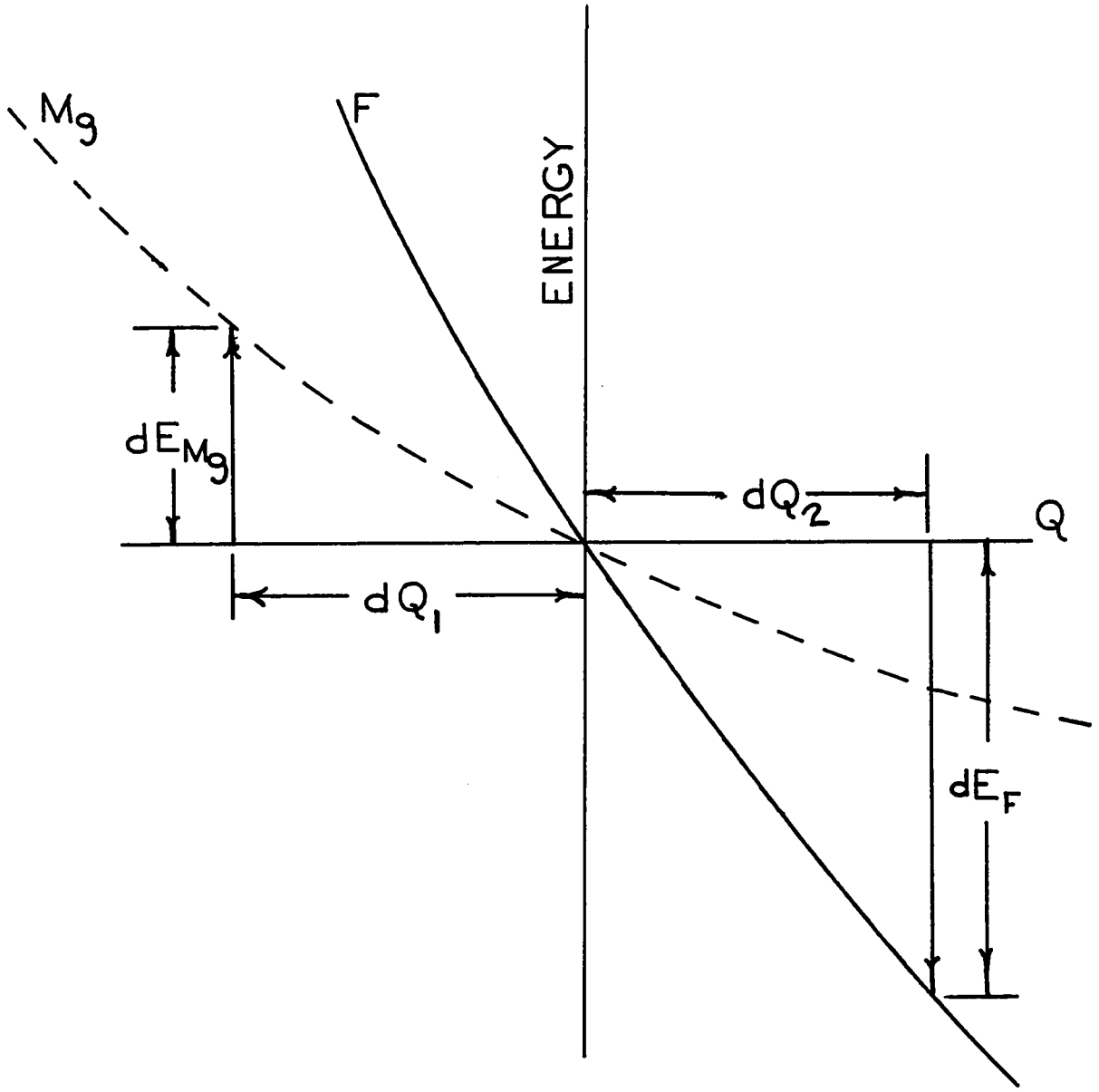
An alternative approach to electronegativity has been proposed by Sanderson (17) who described the energy process involved in the formation of MgF, as indicated in figure 1., where the curves represent the energies of the respective orbitals of magnesium and fluorine as a function of the charge in these orbitals given by equation (6).

A small transfer of charge, $dq_2 = dq_1$. from magnesium to fluorine results in a decrease in the total energy of the system, $dE_{(fluorine)} > dE_{(magnesium)}$. The direction of charge transfer is determined by the relative electronegativities of the two atoms; charge transfer occurring from the least electronegative to the most electronegative atom until the forces acting on a unit charge at each orbital are the same and the energy is a minimum. At equilibrium the electronegativities of the two orbitals are therefore the same.

Jorgenson (18) and Ferreira (19) have criticized Sanderson's Energy Equalization Principle on the basis

Figure 1 Behaviour of Mg toward F in molecule MgF.


Mg
F
ENERGY
dE_Mg
dQ_2
Q
dQ_1
dE_F


Mg
F
ENERGY
dE_Mg
dQ_2
Q
dQ_1
dE_F

that it is the total energy of the system which must be a minimum and not just the energies of the combining atoms. The principle applies only for the hypothetical case involving charge transfer between atoms which are separated by an infinite distance, where there is no overlapping of orbitals and no electrostatic interaction. Thus as charge is transferred one must take into account the simultaneous decrease in covalent energy due to decreased overlap, and the increase in electrostatic energy due to charge separation. Accordingly Sanderson's principle must be corrected for covalent and Madelung energies.

Having defined the important variables, ionic and covalent energies, associated with adduct formation, it is necessary to show how these might be related to bond strength (20). Consider the case of HCl in which the hydrogen atom uses a 1s orbital and the chlorine atom a combination of 3s and 3p orbitals to form the bond. The covalent energy is assumed proportional to the overlap integral $S(\alpha)$ where $S(\alpha)$ is a function of the s-character α. Hence

$$S(\alpha) = S(1) + (1-\alpha^2)^{\frac{1}{2}} S(o) \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

where $S(o)$ is the overlap integral using a pure p-orbital. The covalent energy is approximately given by

$$D(H\text{-}Cl) \quad \frac{S(\alpha)}{S(o)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where D(H-Cl) is the energy previously indicated as the covalent energy in Pauling's equation. The total covalent

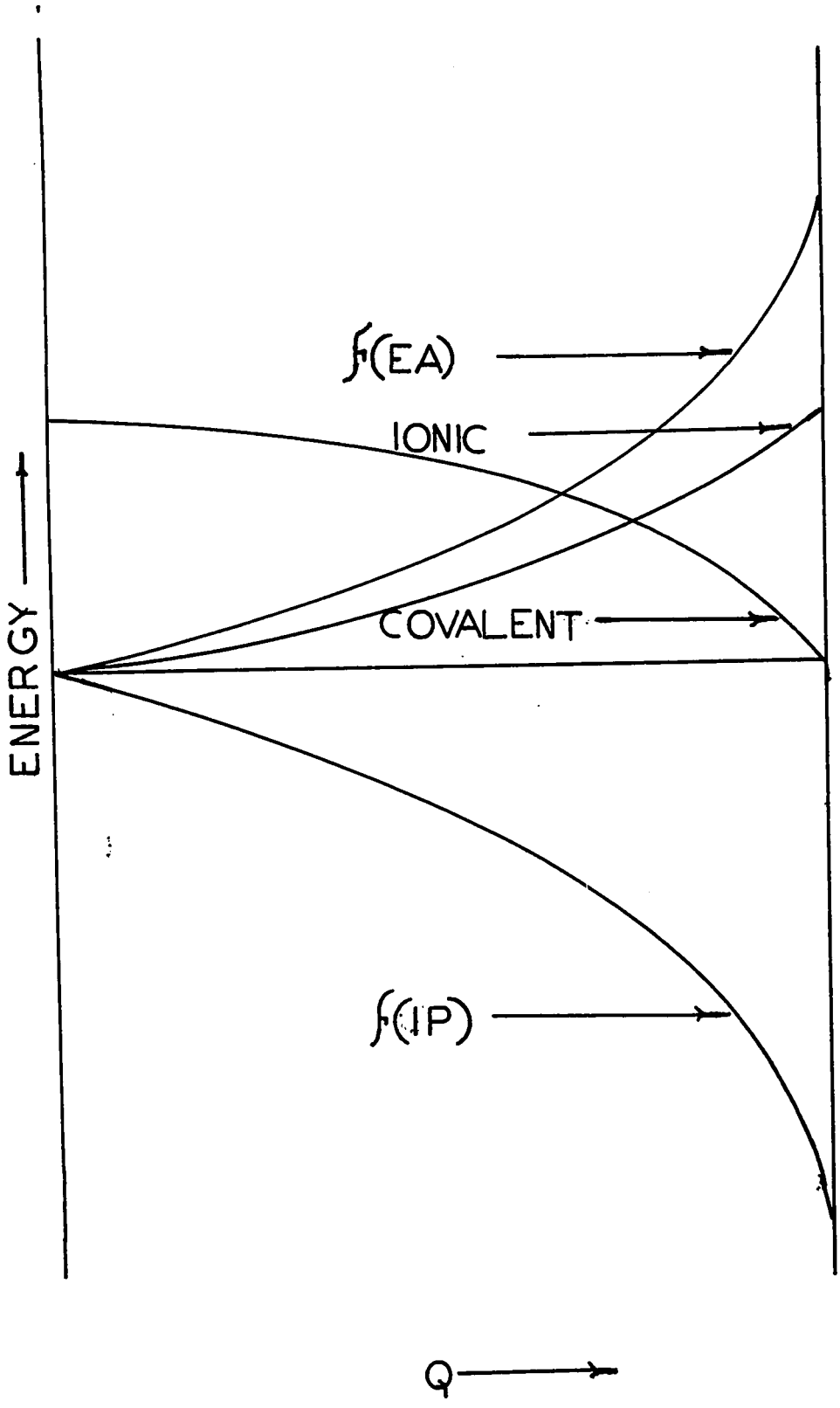
energy is also a function of the ionic character in the bond, q, where $q = a^2 - b^2$ and a^2 and b^2 are the coefficients of the first two terms in the wave equation (2). The ionic character is related to the bond order, $p_{H-Cl} = \sum_j n_j b_j$, where n_j is the number of electrons in the j^{th} orbital, and b_j is the coefficient of the j^{th} orbital. For the simple covalent bond in H-Cl, p_{H-Cl} is $(1 - q^2)^{\frac{1}{2}}$. Thus the total covalent energy is given by:

$$D(H\text{-}Cl)\ \frac{S(\alpha)}{S(0)}\ (1 - q^2)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

The ionic energy is the sum of a charge transfer energy and the electrostatic energy arising from the resultant charge separation. The latter is estimated by the usual Madelung potential. The charge transfer energy is calculated with equations of type 6 where the expressions for Ev, and Iv are expanded in terms of the hybridization parameter α and electronegativity χ. The total energy of the bond is then minimized with respect to the two variables q and α and the equation is solved. The contributions of the ionic and covalent energies to the total energy of the bond (27) are shown in figure 2.

In deriving the relative contributions of the ionic and covalent energy to the total bond energy several questionable approximations were made. The covalent energy D(H-Cl) was estimated by Pauling's crude equation (13); classical polarization forces (London, etc.) have been neglected. Moreover the Madelung function used to estimate electrostatic energies is

Figure 2 Plots showing change in three contributions to total binding energy (a) ionic or Madelung energy (b) charge transfer energy $\Sigma(f(EA) + f(IP))$ (c) covalent contribution from overlap.


f(EA)
IONIC
COVALENT
ENERGY
f(IP)
Q

only valid for ionic crystals. Hence this treatment, even for the case of the simple diatomic HCl, is at best qualitative. More complicated systems such as donor-acceptor bonds in molecular addition compounds have yet to be solved quantitatively. However, as a general aid in predicting bond strengths several qualitative principles have been proposed.

1.1.1 Principle of Energy Matching

Several authors (21) have proposed that the strongest bonds occur in a molecule X-A-Y when the energies of all orbitals are matched. If atom Y were replaced by a more electronegative atom, then A would rehybridize to use more s-character in its orbital towards this new atom for better energy matching and stronger bond formation, while at the same time A would use more p-character in its bond towards X for better energy matching with the orbital used by X and stronger bonding. According to this principle, overlap is greater and the bond formed stronger, for orbitals which have similar energies. Unfortunately this model emphasizes covalent bonding only.

1.1.2 Bent's Principle (22)

If a group X in molecule X-A-X is replaced by a more electronegative group Y, where $\chi_Y > \chi_A > \chi_X$, then the central atom A will rehybridize to use less s-character in its bond towards Y and more s-character in its bond towards the more electropositive atom X. As indicated in figure 3 the electron density in either bond lies closest to the atom using the lowest

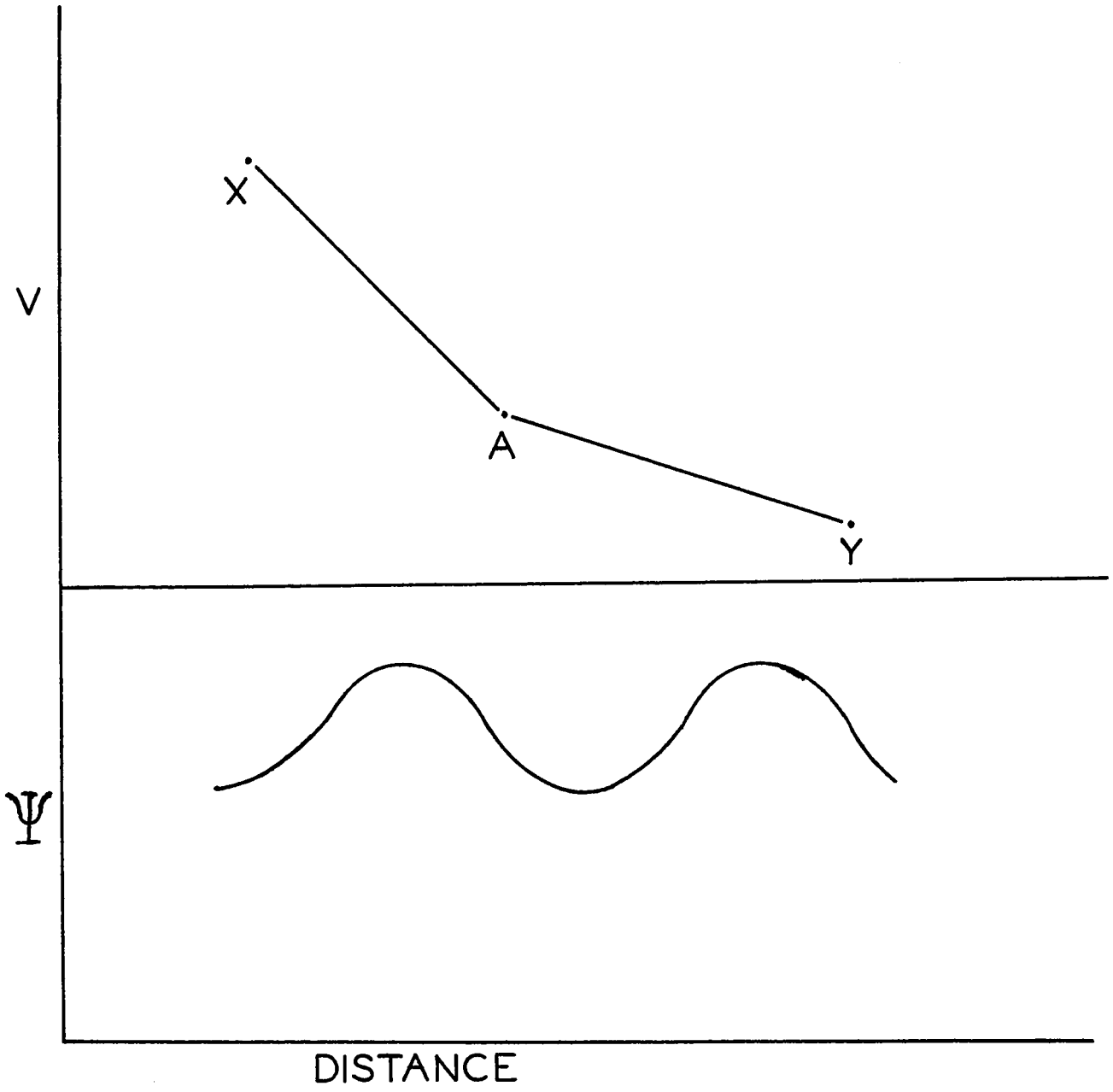
energy orbital, hence closer to A in the A-X bond and closer to Y in the A-Y bond. Bent suggests that A uses more s-character towards X because this low energy s-character should stabilize the adjacent charge density in this bond. Loss of s-character in the A-Y bond does not appreciably weaken this bond as most of the charge density lies closest to the Y atom. Thus, this perturbation of s-character decreases the energy of the A-X pair more than it increases the energy of the A-Y pair. The net effect is a decrease in the total energy of the molecule. This model emphasizes ionic interaction.

1.1.3 Principle of Hard and Soft Acids and Bases

Ahrland, Chatt and Davies (23) recognized that metals and metal ions could be classified into the general categories class (a) or class (b) depending upon the magnitudes of their interaction with non-polarizable or polarizable bases, respectively. The first row metal ions, or class (a) acids, are not easily distorted and interact most strongly with polar bases. The second and third row metal ions, or class (b) acids, have easily distorted charge clouds and they interact most effectively with distortable bases.

Pearson (24-26) has recently extended this classification to include a much wider range of acids and bases. Base strength is determined on the basis of the direction of equilibrium of the reaction;

Figure 3 One-dimensional model of the structure X-A-Y when χ_Y (the electronegativity of Y) > χ_A > χ_X.


X
A
Y
V
Ψ
DISTANCE

$$CH_3Hg(H_2O)^+ + BH^{+} \rightleftarrows CH_3Hg^+B + H_3O^+ \quad \ldots\ldots\ldots \quad (10)$$

which is dependent upon whether the base combines best with CH_3Hg^+ or H^+. He notes that bases in which the donor atom is N,O,F prefer to coordinate to the proton, whereas I,Br and Cl prefer to coordinate with CH_3Hg^+. He then identifies class (a) acids as those of small size, high positive charge and without unshared pairs of valence electrons. These properties Pearson associates with high electronegativity and low polarizability and considers that they reflect hardness. The class (b) Lewis acids have acceptor atoms of large size, low positive charge and unshared pairs of valence electrons, properties which reflect softness. Pearson proposes the principle that "hard acids prefer to bind with hard bases and soft acids prefer to bind with soft bases".

In view of the most obvious drawback of this principle, namely, its vagueness and qualitative basis, Pearson suggested that the Edwards equation, a four parameter equation which has been useful in correlating reaction rate and equilibrium data, be used to describe quantitatively the softness or hardness of an acid or base, i.e.

$$\log_{10}(K/K_0) = \alpha E_n + \beta H \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

where E_n is a redox factor defined as $E_n = E^0 + 2.60$ and E^0 is the standard oxidation potential for the process $2B^- \rightleftarrows B_2 + 2e^-$, H is a proton basicity factor defined by $H = 1.74pK_a$ where $H = 0$ and $E_n = 0$ for water at 25^oC.

β is large for Lewis acids with a high positive charge and small size, and small for Lewis acids of low charge and large size. H is large for bases of similar characteristics. α is large for Lewis acids of large size, low positive charge and containing unshared electrons in p or d orbitals in the valence shell, such as Ag^+, and small for Lewis acids of opposite characteristics. E_n is large for bases such as I^- which are easily oxidized and small for hard to oxidize bases such as F^-. Hence, the term βH is large for a hard-hard interaction and αE_n large for a soft-soft interaction, providing a physical basis for Pearson's principle.

In spite of the general qualitative value of Pearson's principle it has been criticized for several reasons:

(a) Although its physical basis is in rate data, no satisfactory correlation of this kind has been established (27). For example, for the reaction:

$$X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} XY \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

Soft acids, X, and bases, Y, give rise to large k_1, by definition, but it is also true that good attacking groups are generally good leaving groups, k_{-1} is also large, whence k_1/k_{-1} can be large, small and unrelated to k_1. Thus the equilibrium constant, k_1/k_{-1}, need not classify acids in the

same way as k_1 does.

(b) The rate data forming the basis of this general principle is for processes occurring in aqueous solution where the magnitude of acid-base interaction is complicated by solvation effects. Care must be exercised in applying such a principle to predict the magnitude of gas phase reactions. Hard-hard interactions in the gas phase may be soft-soft interactions in aqueous solution.

(c) Finally the subjective concept of polarizability discussed by Pearson has, itself, been criticized by Hale (27). It is interesting to note that consideration of permanent polarization of a charge cloud of an anion or cation by the field of an opposite ion gives rise to the constant α/r_e^4, where α is the polarizability of the polarizable ion and r_e is the equilibrium interionic distance. The maximum value of this term arises from the largest cation interacting with the smallest anion and vice-versa. Hence, class (b) character of a polarizing but not polarizable cation is increased by this term. Conversely, for a large polarizable cation the strong polarization by small anions increases class (a) behaviour.

Pearson has previously stated that polarizability measures softness and that permanent charge distortion is

responsible for class (b) behaviour. Unfortunately polarization energies of this kind work in two ways to generate class (b) behaviour due to anion polarizability, but class (a) behaviour due to cation polarizability. Thus if softness and polarizability are related, they are not necessarily related to class (b) behaviour. On the basis of polarization of this type there can be no preferential soft-soft or hard-hard interaction.

1.1.4 Double Scale Enthalpy Equation

More recently, Drago (28,29) formulated the following equation for the enthalpy, ΔH, of a donor-acceptor interaction:

$$-\Delta H = E_A E_B + C_A C_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

E_A and E_B are interpreted as the susceptibility of an acid and base to undergo electrostatic interaction; C_A and C_B are interpreted as the susceptibility of the acid and base to form a covalent bond. Acids such as $HCCl_3$ and C_6H_5OH with large E_A values interact most effectively with bases such as $(CH_2)_4SO$ and C_5H_5N having large E_B values. Since TMA and $(C_2H_5)_2S$ are bases with large C_B parameters, they interact strongly with I_2 and ICl, acids with large C_A terms. Drago has calculated E and C parameters for a variety of acids and bases and has used them successfully to estimate the enthalpy change in weak acid-base interactions.

Several points have been made, however, which tend to restrict the usefulness of the double-scale enthalpy equation.

(a) The E and C parameters obtained for the many acids and bases reported by Drago are all based on an initial set of parameters for the methylamines and I_2. He assumed that the covalent parameter is related to the polarizability and the electrostatic parameter to the dipole moment of the amine. The concept of polarizability in discussions of acid and base strenth was critisized by Hale (27) (see page 15), while the relationship between dipole moment and electrostatic character has never been verified. The dipole moment is now known to be a complex function of smaller moments (12);

$$\text{total dipole moment} = \mu_1 \begin{pmatrix}\text{bonding}\\ \text{electrons}\end{pmatrix} + \mu_2 \begin{pmatrix}\text{homopolar}\\ \text{moment}\end{pmatrix} + \mu_3(\text{hybridization}) + \mu_4 \begin{pmatrix}\text{atomic}\\ \text{dipole}\end{pmatrix} \quad \ldots\ldots\ldots \quad (14)$$

Thus, even Drago's initial assumptions are questionable.

(b) Drago has considered only those acids and bases for which heats of reaction are less than 10 Kcal/mole, a severe limitation indeed to a general discussion of acid and base chemistry.

(c) To calculate heats of reaction, or the E and C parameters for a particular acid or base, using the double-scale enthalpy equation one must have a large amount of enthalpy data and this is seldom available. Drago has limited his equation to weakly interacting species because thermochemical

information is more available for such systems.

(d) Klopman (30-32) in a theoretical derivation of the double-scale enthalpy equation, suggested that each E and C parameter is the summation of a number of other parameters. Hence actual values of the parameters for a particular acid probably change from complex to complex. Certainly Drago's suggestion that an acid or base display the same parameters towards all other acids or bases is difficult to accept in the light of the very complex nature of the donor-acceptor interaction.

To summarize this section; several principles regarding the strength of acid-base interaction have been examined. These principles have been moderately successful in predicting the way in which acids and bases will react but are limited to systems from which the theory has evolved. For example, Drago's theory has been successful for weakly interacting species in non-polar or slightly polar media, whereas Pearson's theory evolved from studies in aqueous solution. Pearson's theory is further limited as it is based upon kinetic rather than concrete thermodynamic data.

There is clearly a definite need for more thermodynamic data with regard to the interaction of strong acids and bases in a variety of solvents to test current theories and/or extend these ideas to develop more general theories of acid-base interaction.

1.2 Steric Effects and Reorganization Energies

Of similar importance to electronic effects in predictions of acidity and basicity are reorganization energies and steric strains; concepts usually invoked to explain deviations from expected orders of reactivity in closely related systems of compounds. These effects will be discussed in this section with particular emphasis on π-bonding, F-strain, I-strain and B-strain.

1.2.1 Reorganization Energies

The relative acceptor power of the boron trihalides towards pyridine (py) and acetonitrile is Br>Cl>F, contrary to the order expected on the basis of their electronegativities, i.e. F>Cl>Br. Cotton and Leto (33) suggested that strong partial π-bonding exists between boron and the halogen atom in the trigonal boron trihalide and that the energy due to this π-bonding is greatest for BF_3 and decreases with increasing halogen size. Since π-bonding is completely destroyed in the tetrahedral configuration of the complex, each boron halide has a constant reorganization energy independent of the base to which it coordinates.

This explanation of the relative acceptor powers of the boron trihalides has been criticized by several authors (34,35) because it does not explain such intrinsic molecular parameters as ^1H chemical shifts. Nor does it explain the linear correlation between the heat of formation and the shift in C = 0 stretching frequency observed for ethyl

acetate adducts of acids having different reorganization energies (34). In the latter case the reorganization energy should be reflected in the overall heat reaction; hence, the frequency shift should be larger than expected. Since a linear relationship exists between $\Delta\nu(C = O)$ and ΔH for ethyl acetate complexes with phenol, I_2, BF_3 and $SbCl_3$, Drago (34) concluded that π-bonding cannot be completely destroyed in the adducts. He further suggested, for the case of BF_3, that a competition exists between the π-electrons of the halogen and the donor electrons of the base for the vacant boron p-orbital. Drago also proposed that reorganization energy increases linearly with the availability of electrons from the donor molecule. Ibers and Shriver (35) interpreted X-ray data for the BCl_3 and BF_3 adducts of acetonitrile on the basis that BCl_3 is reorganized to a larger extent than BF_3. They suggested that it is the ease of distortability of the former acid which is responsible for its better acceptor properties. This ease of distortability was attributed to the strength of π-bonding in the BX_3 moiety. The most satisfactory description of the relative acceptor powers of the boron trihalides is probably a combination of both descriptions. The most important results derived from these studies is that reorganization energies exert a marked effect on the acidity of an acceptor and that they are at present variables of uncertain magnitudes.

1.2.2 I-strain, F-strain, B-strain

The gas phase heats of formation of trimethylboron

(TMB) with cyclicimines, $(CH_2)_nNH$ (n = 2 to 5), are in the order; 4->5->6->3-membered ring (36). To explain this order Brown introduced the concepts of F-strain and I-strain. The former, which is the steric strain between the bulky methyl groups on TMB and the α-methylene ring groups, should increase with increasing ring size. The latter, which is the internal strain introduced into the ring upon coordination should decrease with increasing ring size. Apparently the two strain effects are a minimum in the 4-atom ring because this base is the strongest donor.

Brown et al (37) explained the following order of the heats of formation of TMB with the methylamines; DMA>MMA>TMA>NH_3 by invoking the concept of B-strain. B-strain is the back strain between the bulky methyl groups in the methylamines which results from coordination. This strain should increase with increasing methyl substitution. At the same time increasing methyl substitution enhances the donor power of the nitrogen base. Brown suggests that these two opposing effects combine to produce the observed order.

Brown et al (37) confirmed the existence of B-strain in these methylamine complexes by measuring their pK_a values, where it is expected that F-strain effects between the proton and the amine are negligible. However, the use of pK_a values as a measure of base strength is questionable because of the uncertainty of solvation effects on base strength orders. Indeed, substitution of methyl groups on the donor nitrogen

atom seems to decrease the degree of solvation of the product species. Accordingly, the concept of B-strain has not yet been adequately substantiated. In fact, the order observed with TMB as acid can easily be rationalized on the basis of F-strain effect alone.

Other concepts outlined in this section have proven of great usefulness in summarizing a large body of chemical information and will be referred to in a later section. Some of the physical measurements usually related to acid and base strength such as nuclear magnetic resonance (nmr), ultraviolet (uv) and infrared (ir) shifts and heats of reaction in the gas phase, or in solution will now be described to provide a background for the present research. Particular attention will be paid to the literature involving cyclicimines, ethers, thioethers, methylamines, and Group IVa tetrahalide complexes.

1.3 Measures of Acid-Base Strength

1.3.1 Thermochemical Measurements

1.3.1.1 Gas Phase Heats of Reaction

The strength of a donor-acceptor bond in a complex A-B is most satisfactorily defined as the enthalpy change $\Delta H(g)$ or free energy change $\Delta F(g)$ accompanying the gas phase dissociation of the complex.

$$AB(g) \rightarrow A(g) + B(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Since the entropy change $\Delta S(g)$ is constant for this reaction, most authors prefer to use $\Delta H(g)$ in comparisons of donor-acceptor strength.

The majority of molecular addition compounds are solids and measurement of $\Delta H(g)$ requires that their heats of sublimation be known.

Several criteria must be met experimentally before measurement of $\Delta H(g)$ for a molecular addition compound is possible, namely:

(a) The adduct must be a stable substance which does not undergo chemical change under the conditions required for measurement of its dissociation constant.

(b) The complex must undergo reversible dissociation and exhibit a measurable dissociation pressure.

(c) Its heat of sublimation must be known or easily estimated.

Several molecular addition compounds involving cyclic donors satisfy these requirements. The heats of dissociation of the TMB complexes of the cyclicimines, $(CH_2)_nNH$ (n = 2 to 5), are in the order; 4->5->6->3-membered ring, indicating this to be the stability order of the complexes (36). Brown explained this order by introducing the concepts of F-strain and I-strain as previously discussed (page 20).

Searles et al (38) measured the heats of dissociation of the TMB adducts of the N-methyl cyclicimines, $(CH_2)_nNCH_3$ (n = 2 to 5). The observed order of decreasing $\Delta H(g)$; 3->4->5->6-membered ring, was attributed to the predominance of F-strain over I-strain and to an increase of F-strain with increasing ring size. I-strain for these complexes was assumed to be the same as I-strain in the TMB complexes of the cyclicimine series $(CH_2)_nNH$ (n = 2 to 5). The higher steric strain was associated with the N-methyl substituent. This appears reasonable as the $\Delta H(g)$ values for the TMB complexes of the cyclicimines of series $(CH_2)_nNCH_3$ (n = 2 to 5) are lower than their unmethylated analogues and the difference, $\Delta(\Delta H(g))$, increases with increasing ring size.

McLaughlin, Tamres and Searles (39) measured the gas phase heats of dissociation of several BF_3-ether adducts.

The order of stability obtained: tetrahydrofuran>tetrahydropyran> dimethyl ether>diethyl ether, agreed well with the order obtained in hydrogen bonding (40) and I_2 charge transfer studies (41). Tamres concluded that the same ring size effect must operate in strong as well as in weak interactions. It seems preferable not to invoke F-strain to explain the relative donor ability of the 5- and 6-membered ring cyclic ethers towards BF_3 since the same order of basicity was observed towards I_2 and $CHCl_3$ in which F-strain was shown not to apply. Tamres suggested that F-strain must be minor as steric requirements in complex formation of the ethers with the two reference acids I_2 and BF_3 are similar.

The requirements for gas phase heat of dissociation measurements are also satisfied by the TMB complexes of the methylamines, pyridine (py) and triethylamine (TEA) where the order of adduct stability is DMA>TMA>MMA>py>NH_3>TEA (8,37). This order has been rationalized by Brown et al on the basis of F-strain and/or B-strain (page 21).

Bauer and McCoy (42) have measured the heats of reaction of BH_3 with the methylamines for the process:

$$BH_3(g) + \text{methylamine (g)} \rightarrow \text{complex (s)} \quad \ldots (16)$$

When their data is combined with recently available sublimation energy values (43) the order of adduct stability for these complexes becomes; TMA>DMA>MMA>NH_3. This order is

that expected for the methylamines on the basis of the increasing inductive effect with increasing methyl substitution as suggested by decreasing ionization potentials, by heats of reaction with I_2 and by shifts in the O-H stretching frequency of methanol. The heats of reaction measured by Bauer and McCoy are questionable, however, because recent work (43) indicates that their products were condensation rather than coordination compounds.

1.3.1.2 Solution and Condensed Phase Heats of Reaction

Unfortunately, for many molecular addition compounds gas phase heats are difficult if not impossible to obtain. Usually adducts decompose or do not exhibit an appreciable vapour pressure at elevated temperatures. In these cases comparisons of acid and base strength are made by measuring heats of reaction in solution or in the condensed phase. Under these conditions the measure of base strength is often given as the enthalpy for the processes;

$$A(g) + B(\text{solution}) \xrightarrow{\Delta H_1} A{\cdot}B(\text{solution}) \quad \ldots\ldots \quad (17)$$

or

$$A(g) + B(\text{solution}) \xrightarrow{\Delta H_2} A{\cdot}B(s) \quad \ldots\ldots\ldots\ldots \quad (18a)$$

$$\text{or } B(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18b)$$

The reliability of the standards of acid or base strength established by the heats of reaction for processes (17) or (18) above can be tested by comparison with the gas

phase heats of formation in the following thermochemical cycle:

$$\begin{array}{ccc} A(g) + B(g) & \xrightarrow{\Delta H_a} & A\cdot B(g) \\ & \uparrow \Delta H_c \quad \uparrow \Delta H_d & \\ A(g) + B(solution) & \xrightarrow{\Delta H_b} & A\cdot B(solution) \end{array}$$

ΔH_b must be corrected by the arithmetical operation: $-\Delta H_c + \Delta H_d$ before direct comparison with ΔH_a is possible. If we vary B in equation (17) and establish a scale of basicity, this scale is a true measure of base strength only if ΔH_c and ΔH_d vary by equal amounts from one base to another.

The way in which ΔH_d varies has never been adequately determined and comparisons of base strength are usually made with the assumption that this parameter is constant in a closely related series of adducts. Values of ΔH_c change appreciably from base to base and their effect on the final enthalpy and hence the final order of base strength is significant. For example, the heats of formation of the $BF_3\cdot py$ (44) and $BF_3\cdot TMA$ (45) complexes for the reaction conditions given by equation (17) are -32.9 and -38.2 Kcal/mole, respectively, suggesting that TMA is stronger base. However, enthalpies for conditions in which bases are in the vapour phase are -42.7 and -42.0 Kcal/mole suggesting that

both bases have equal strength.

Some evidence for the constancy of ΔH_d can be derived from the order of base strength as established by enthalpies obtained for condensed phase systems (46-48) such as from equation (18b) where ΔH_d differs from ΔH_s (the heat of sublimation) by the heat of solution. ΔH_s is assumed constant because for a closely related series of molecular addition compounds lattice energies should be similar. Comparisons of acid or base strengths under the conditions of equation (18) have been numerous and the assumption of a constant ΔH_s has been suggested and refuted successfully on a number of occasions. The assumption of a constant ΔH_d is a better approximation, however, as variations in energies of solvation from complex to complex in solution are probably smaller than variations in crystal lattice energies (44). This proposal needs further testing by measurements of heats of formation of molecular adducts in different solvents.

Geurtin and Onyszchuk (49), measured the heats of dissociation of $SiF_4 \cdot 2(CH_2)_nO$ (n = 2 to 5) complexes for the reaction conditions corresponding to equation (18b). Heats of dissociation were in the order; 4->5->6->3-membered ring base, the same as that observed for the gas phase heats of formation of TMB-cyclicimine complexes (36). They suggested, as did Tamres et al (41), that it is the variation in hybridization of the oxygen lone pairs which is responsible for the observed order.

Heats of formation of crystalline $MX_4 \cdot 2L$ complexes (where M = Si, Ge, or Sn; L = pyridine or isoquinoline; X = F, Cl or Br, except X = Cl when M = Sn) have been measured by Miller and Onyszchuk (122) for process (18a). Towards isoquinoline (iq) heats of formation are in the orders (i) $SiF_4 > SiCl_4 > SiBr_4$, (ii) $GeF_4 > GeCl_4 > GeBr_4$, (iii) $GeF_4 > SiF_4$ (iv) $SnCl_4 > GeCl_4 > SiCl_4$, and (v) $GeBr_4 > SiBr_4$. Towards py on the other hand (i) $SiCl_4 > SiBr_4 >> SiF_4$, orders (ii) and (iii) the same as with iq as base, (iv) $SnCl_4 \sim SiCl_4 > GeCl_4$ (v) $GeBr_4 > SiBr_4$. The differences in the orders observed with py and iq are not readily understood, however, as pK_a values and stability constants of their Ag^+ complexes (86) suggest that their basicities are similar. Furthermore, molecular models indicate that there is negligible steric interaction in the MX_4 complexes of either base (88). The heat of formation of $SnCl_4 \cdot 2py$ of -60.7 Kcal/mole reported by these authors is not in good agreement with the value of -47.4 reported by Zenchelsky and Segatto (89).

Wannagat et al (119,134) have measured the heats of formation of $SiF_4 \cdot 2py$, $SiCl_4 \cdot 2py$ and $SiBr_4 \cdot 2py$ for process (18a) with the acid component in the condensed phase. These values -17.9, (-30.5, -27.7, -29.3), and (-26.8, -29.6) Kcal/mole respectively differ remarkably from those reported by Miller and Onyszchuk (122). Evidently the relative acceptor powers derived from the thermochemical work of Miller and Onyszchuk, $SiF_4 << SiCl_4 > SiBr_4$, needs further checking.

1.3.2 Hydrogen Bonding Studies

The H-bonding properties of the cyclicimines $(CH_2)_nNH$ (n = 2 to 5), cyclic ethers $(CH_2)_nO$ (n = 2 to 5), and methylamines have been extensively studied. This information is discussed under the separate headings; H-bonding with chloroform, H-bonding with phenol and methanol, and pK_a measurements.

1.3.2.1 Hydrogen Bonding with Chloroform

Berkeley and Hanna (50) have investigated the H-bonding of nitrogen bases with $CHCl_3$, and their results are probably applicable to oxygen bases as well. They suggested that the principle contributions to the H-bond energy were classical electrostatic energies and quantum mechanical repulsion energies. Electrostatic forces, however, are independent of the changes in the degree of hybridization between the sp hybridized nitrogen atom of CH_3CN and the sp^3 hybridized nitrogen atom of TMA (50). Apparently then the difference in H-bond energies must be due to differences in the repulsive energies. The simplest estimate of this quantity is given by Mulliken's formula S^2I (51) where S is the overlap integral for the H-bond and I is the ionization potential of the base. As there is no appreciable difference in the overlap integrals between the TMA and CH_3CN lone pairs with the hydrogen 1s orbital of $CHCl_3$ at distances as large as the H-bond distance, the repulsive energy varies as the ionization potential of the base, emphasizing the importance of this quantity in determining H-bond energies.

Hence, on this basis alone the order of donor power of the cyclicimines and cyclic ethers should be 5~6~4->3-membered ring. The ionization potential data for these bases is given in table 1.

The following evidence indicates that the ionization potential does indeed play a large role in determining base strength.

(i) The heats of mixing of $CHCl_3$ with cyclic ethers (40) are in the order 5~6~4->3-membered ring, the same order suggested from their ionization potentials. However, some criticism should be made of the technique used in deriving these values. No corrections were made for heats of dilution, and for the fact that at the unusual final composition (a 50:50 mixture of ether and $CHCl_3$) the 1:1 complex would be only partly formed and the heat released a function of the formation constant for each ether. The formation constants must therefore follow the observed heats of dilution for the quoted results to follow the base strengths of these cyclic ethers.

(ii) Berkeley and Hanna (53) have derived a relationship between the proton nuclear magnetic resonance shift, δ^1H, of the $CHCl_3$ proton for the 1:1 complex, and the H-bond length in amine-$CHCl_3$ complexes. If this relationship is true, the H-bond length should vary

Table 1

Ionization Potentials of Cyclic Bases

Base	Ionization Potential (e.v.) (52,139)
Ethyleneimine	9.94 ± 0.15
Trimethyleneimine	9.1 ± 0.15
Pyrrolidine	9.0 ± 0.15
Piperidine	9.15 ± 0.15
Ethylene oxide	10.65 ± 0.1
Trimethylene oxide	9.85 ± 0.1
Tetrahydrofuran	9.45 ± 0.1
Tetrahydropyran	9.45 ± 0.1

inversely as the chemical shift and directly as the ionization potential of the amine (repulsive forces vary in proportion to the ionization potential and therefore so should the H-bond length). Hence, chemical shifts should vary inversely as the ionization potentials of the bases. This is observed for the cyclicimine -$CHCl_3$ complexes where the δ^1H $CHCl_3$ chemical shifts are in the order 4->5->6->3-membered ring (100). As Berkeley and Hanna's results indicate that the δ^1H chemical shift of $CHCl_3$ is independent of the extent of hybridization of these cyclic bases, their explanation contradicts Tamres suggestion (41) that differences in hybridization are responsible for the observed order.

1.3.2.2 Hydrogen Bonding with Phenol and Methanol

Drago has suggested the linear relationship, $-\Delta H = 0.011\Delta\nu$ (OH) + 2.79, between the shift in the O-H stretching frequency, $\Delta\nu$ (OH), and the heat of formation of phenol complexes (54). This relationship was derived experimentally and later theoretically justified by Kimura and Fujishiro (55).

Correlations between heats of reaction and some easily measurable physical parameter such as shifts in infrared frequencies have met with success (54) and failure (56,57) on many occasions and their application is certainly not general. Lippert and Prigge (58) have measured the heats of reaction and O-H stretching frequency shifts of phenol-cyclic ether adducts, but their values do not agree with heats calculated using Drago's relationship (54) as shown in table 2.

Table 2

Base	Lippert and Prigge $\Delta\nu$ (OH)	Lippert and Prigge ΔH Kcal/mole	Drago ΔH Kcal/mole
Propylene oxide	220	3.75	4.15
Trimethylene oxide	290	4.97	5.44
Tetrahydrofuran	295	4.25	5.35
Tetrahydropuran	290	4.32	5.27

Agreement between measured and calculated heats varies from 0.5 to 1 Kcal/mole or 10-20%. The general order of basicity of these cyclic ethers is however, 4->6->5->3-membered ring as suggested by Lippert and Prigge or 4- $\hat{=}$ 5- $\hat{=}$ 6->3-membered ring from Drago's enthalpy equation.

Searles, Tamres and Block (59) have recommended that the methanol $\Delta\nu$ (OD) shift be used as a measure of basicity because orders derived from such measurements and from heats of mixing of $CHCl_3$ with several reference bases correlate well. They found that relative basicities of the cyclicimines and N-methylcyclicimines towards methanol are; 4-~5-~6->3-membered ring and 4- $\hat{=}$ 5->6->3-membered ring, respectively. However, $\Delta\nu$ (OD) shifts do not correlate with pK_a values (59) for these bases since a larger $\Delta\nu$ (OD) shift and a lower pK_a value for the N-methyl cyclicimine complexes is observed. This agrees with the suggestion that pK_a values are not useful criteria of base strength when substitution occurs at the donor atom.

Shifts in the ν(OD) frequency for methanol-methylamine complexes are in the order TMA>DMA>MMA>NH_3, suggesting this to be the order of base strength (60). This is the generally accepted order of base strength in the absence of steric effects and the order is attributed to the increasing inductive effect with increasing methyl substitution.

1.3.3 Ultraviolet Measurements

Ultraviolet spectroscopy has been used by several authors to measure the heat of formation of I_2 charge transfer complexes (61). This method was initiated by Benesi and Hildebrand (62), and received theoretical import from Mulliken's charge transfer theory (11) and the general considerations of acid-base theory (8).

Tamres et al (41) found that the enthalpies of formation of I_2-cyclic ether adducts are in the order; 4->5->6->3-membered ring, in agreement with previous reports on H-bonding studies (63) and nuclear magnetic resonance measurements (64). As 2-methyl-tetrahydrofuran is stronger donor than tetrahydrofuran towards the bulky acid I_2, it was concluded that the concepts of F-strain and I-strain proposed by Brown et al (36) to correlate basicity with ring size for the addition compounds of the cyclicimines with TMB do not seem to apply to the I_2·ether series. They suggested that, "the change in angular requirements in forming different sized rings must result in rehybridization of the orbitals, which in turn affects the electron distribution on the oxygen atom and hence the availability of the lone pair electrons to form a donor-acceptor bond". This proposal does not apply for the case of the H-bond except on the basis that repulsive energies are related to the extent of hybridization of the donor orbital which is in turn related to the ionization potential of the donor electrons.

Tamres and Searles, Jr. (65) reported that the heats of formation of the I_2-cyclic sulphide complexes follow the order;5->6->4->3-membered ring. This is in sharp contrast to the order found for the cyclic ethers, namely;4->5->6->3-membered ring. Evidently the ring size effect differs for hetero atoms even if they both belong to the same family of the Periodic Table.

1.3.4 Nuclear Magnetic Resonance Measurements

Several authors have correlated adduct stability with nmr chemical shifts or differences in nmr chemical shifts (66-69). These correlations are based upon the belief that the chemical shift is a measure of electron density at the nuclear site. The simple qualitative description of the formation of molecular addition compounds implies that the electron attracting power of the donor and acceptor atoms in an adduct will be different from that in the separated atoms and will depend in part upon the strength of the coordinate bond. This correlation of chemical shift with donor-acceptor bond strength provides the basis for the use of nmr in attempting to establish the relative stabilities of molecular addition compounds.

1.3.4.1 Proton Nuclear Magnetic Resonance Measurements

The relationship between proton nmr chemical shifts, δ^1H, and adduct stability has been proposed and criticized on several occasions (68,73). Pople (70) has pointed out that the total shift δ^1H is often a function of a number of non-local magnetic effects. For example the internal shift difference, $\delta CH_2-\delta CH_3$, of the diethyl sulphide adduct is in the order $BF_3>BH_3 = BMe_3$(68), and yet the order of acidity is $BH_3>BF_3>BMe_3$(71,72). These orders have been rationalized on the basis of multiple bonding. Apparently the ^1H chemical shift is not always a simple function of local electron density. Interestingly, the order of acceptor power of the

boron halides with TMA: $BBr_3>BCl_3>BF_3$, as established by ^1H nmr chemical shifts, has never been verified by calorimetric measurements (73).

1.3.4.2 Fluorine-19 Nuclear Magnetic Resonance Measurements

The use of ^{19}F nmr measurements as a measure of donor-acceptor power is based upon the suggestion by Saika and Slichter (74) that the ^{19}F chemical shift should be a measure of the electronegativity of the attached substituent. Support for this general correlation is provided by ^{19}F measurements on a series of halomethanes by Gutowsky (75), where successive replacement of the hydrogen atoms of methane by the more electronegative ^{19}F atoms causes a progressive displacement of the ^{19}F resonance to lower field. The effective electronegativity influencing the ^{19}F resonance in each compound should increase in the order $-CH_3<-CH_2F<-CHF_2<-CF_3$; which is consistent with the observed order of ^{19}F chemical shifts. On the other hand, substitution of chlorine rather than fluorine atoms causes the reverse displacement. This suggests increased double bonding to the fluorine atom and further points out that chemical shifts are complex parameters. Orders of donor-acceptor bond strength deduced from such measurements could be erroneous.

Heitsch (76) found that the ^{19}F resonance position shifted upfield with increasing methyl substitution in BF_3-methylamine adducts. The order of upfield shift; $TMA>DMA>MMA>NH_3$

is the basicity order previously observed for the methylamines towards several other acceptors (60,28) and suggests that it is also the order of their donor power towards BF_3. Unfortunately, thermodynamic data for the BF_3-methylamine complexes is not available for comparison.

Diehl and Noth (66,67) have measured the variation in the ^1H and ^{19}F chemical shifts of BF_3-alcohol mixtures and concluded that the order of stability was; $H_2O>CH_3OH>C_2H_5OH>n\text{-}C_3H_7OH$. The differences in chemical shifts of the free and complexed Lewis acids and bases are undoubtedly related to changes in the electronic structure of these molecules that occur on complex formation. They suggested that the magnitudes of these differences might be related to the strength of the donor-acceptor bond.

Mooney (77) has measured the ^{19}F chemical shifts of BF_3-ether complexes. The suggested order of donor-acceptor bond strength, namely: $Me_2O\cdot BF_3>Et_2O\cdot BF_3>Pr_2O\cdot BF_3$, is in good agreement with thermodynamic data for these complexes (78,79). It is interesting that a ^{19}F chemical shift of 158.6 p.p.m. is observed for both the $Me_2O\cdot BF_3$ (77) and $DMA\cdot BF_3$ (76) adducts. Although enthalpy data is not available for these two complexes, BF_3-amine complexes are usually more stable than BF_3- ether complexes (111). Thus, the fact that BF_3 complexes of Me_2O and DMA have similar shifts suggests again that the relationship between the magnitude of the ^{19}F chemical shift and the donor-acceptor bond strength is not general.

1.3.4.3 Boron-11 Nuclear Magnetic Resonance Measurements

Muetterties (80) suggested that ^{11}B chemical shifts can be explained on the same basis as ^{19}F shifts and therefore might be used as a measure of donor-acceptor interaction.

Heitsch (76) found the ^{11}B chemical shifts for BH_3-amine complexes to be in the order: NH_3>MMA>DMA>TMA. While there is no reliable thermochemical evidence to support this order, a similar order towards any other reference acid, the steric effects of which are minor, has not been observed.

It is noteworthy that the ^{11}B chemical shifts of the methylamine-TMB adducts are in the reverse order to that expected on the basis of thermodynamic data. Heitsch suggested that the observed order is the result of two strains; (i)F-strain, forcing the methyl groups on TMB to withdraw negative charge from the ^{11}B atom, and (ii) a second steric stress, which is dependent on the B-N bond length and should follow enthalpies of dissociation inversely. The resultant of these two stresses, he said, should produce the observed order of ^{11}B chemical shifts.

^{11}B chemical shifts are the same for all members of the BF_3-methylamine series. Heitsch attributed this to the great ability of the fluorine atom to remove charge from the boron atom, and thereby equalize the charge density about this atom for all members of the series. Whether this

explanation can be generalized to include all BF_3 adducts has yet to be proven, as very little work has been done in this area. Mooney (77) found, however, that the ^{11}B chemical shifts of BF_3-ketone complexes are similar, although in these cases changes in basicity and the consequent changes in electron density at the ^{11}B atom site, expected for weak ketone donors, may be small.

Mooney (82) found that the ^{11}B chemical shifts for the boron trihalide-py adducts are in the order Br>Cl>F. This order has been verified calorimetrically (83) as the order of acceptor power of these acids and lends some support to the use of ^{11}B shifts as a measure of acidity or basicity. Mooney (81) has attributed deviations of the ^{11}B chemical shifts from the expected order in boron trihalide-ethylacetate complexes to the presence of steric effects. However, such an explanation is not valid until the participation of steric effects in these complexes is understood quantitatively in terms of thermodynamic data.

1.3.5 Infrared Measurements

The infrared stretching vibration of the B-N bond in BF_3-amine adducts is in simplest terms related to the force constant or strength of the bond. This relationship requires that the B-N stretching vibration involve a major contribution from the B and N atoms and a minor contribution from other atoms in the complex. This is often true for vibrations involving one light atom, such as in the N-H bond. Several workers (84,85) have reported, however, that no correlation exists between adduct stability and the B-N stretching frequencies in BF_3-methylamine adducts. Normal coordinate (85) analyses suggest that the B-N and B-F stretching modes are strongly coupled to give two skeletal motions which are best described as out-of-phase and in-phase N-BF_3 modes. As a result of such mixing neither frequency can be considered to give a true indication of the strength of the B-N bond.

Bhiwandker (84) reported a linear correlation between the B-N stretching frequency and the number of methyl groups in the BF_3-methylamine adducts. He suggested that the decreasing frequency observed with increasing methyl substitution was due to the increasing effective mass of the nitrogen atom.

The use of infrared spectroscopy as a tool in the investigation of adduct stability in hydrogen bonded systems has already been discussed (page 33).

2. RESEARCH PROPOSAL

Most attempts to develop theories of acids and bases have evolved from reactions in aqueous solution, and even here correlations and classifications have been based on kinetic and equilibrium data rather than on thermodynamic parameters. In non-aqueous solvent systems Drago's concepts have been reasonably successful in explaining and predicting the magnitudes of weak interactions (e.g. H-bonding, charge transfer complexes) in non-polar and weakly polar solvents, where solvation effects are negligible. However, this theory is based on thermodynamic data obtained with a spectroscopic procedure and the relationship of these data to the magnitude of the donor-acceptor interaction is still questionable. There is an urgent need then to obtain accurate thermodynamic data using calorimetric procedures, especially with regard to strong interactions, and in a wider range of solvents to provide a better basis on which to test theoretical ideas.

More thermodynamic data is essential also to test the frequently suggested correlations between thermodynamic stability and some intrinsic molecular parameters such as infrared or ^{1}H, ^{19}F, and ^{11}B chemical shifts.

Complexes of BF_3 are of particular interest because of their wide range of stability and because the literature contains little information about the thermodynamics

of their formation. What few studies have been made involved condensed phases and comparisons based on limited series.

Complexes of BF_3 with cyclicimines, $(CH_2)_nNH$ (n = 2 to 6), and N-methyl cyclicimines $(CH_2)_nNCH_3$ (n = 2 to 6) were selected because they offer the possibility of measuring changes in stability as a function of the ring size of the cyclicimine, and of testing relationships between heats of formation with ^{19}F, ^{1}H and ^{11}B chemical shifts. These complexes are especially suitable for such studies because they are easily prepared, readily soluble, undissociated in suitable solvents, and of well-defined (1:1) stoichiometry. Unfortunately, they do not dissociate reversibly in the gas phase without decomposition so that it was necessary to obtain thermochemical data in solution rather than in the more desirable gas phase.

Complexes of $CHCl_3$ with cyclicimines, $(CH_2)_nNH$ (n = 2 to 6), were selected because they also offer the possibility of studying the effect of ring size on basicity. The strength of the H-bond in $CHCl_3$-amine adducts has been little investigated calorimetrically. Hence, it would prove of interest firstly to compare enthalpy values derived by a calorimetric method with values derived by a ^{1}H nmr technique to test the use of the latter technique as a measure of acid-base interaction. Secondly, it would be interesting to compare orders of basicity derived from the frequently used spectroscopic parameters, $\Delta\delta(^{1}H)$,

defined as $\delta(^1H)^{free}_{CHCl_3} - \delta(^1H)^{complexed}_{CHCl_3}$, and $\Delta\nu(C\text{-}D)$, defined as $\nu(C\text{-}D)^{free}_{CDCl_3} - \nu(C\text{-}D)^{complexed}_{CHCl_3}$, obtained from nmr and infrared procedures, respectively, with calorimetric measurements.

Complexes of BF_3 with methylamines, $(CH_3)_{3-n}NH_n$, and NH_3, were also selected because enthalpies of formation in the literature were not complete for the series and reported values were difficult to compare because of differences in experimental conditions of solvent and phase. The techniques previously employed were often crude and their accuracy questionable. The selected series also offered the opportunity to test correlations between spectroscopic parameters and heats of adduct formation in a systematic way.

A critical evaluation of previously reported condensed phase heats of formation of Si, Ge and Sn tetrahalide complexes of py and iq (122) prompted a reinvestigation of these complexes. The following anomalies were noted:

(1) Heats of formation of $SiCl_4 \cdot 2py$ and $SiBr_4 \cdot 2py$ were almost double that of $SiF_4 \cdot 2py$. Since $SiF_4 \cdot 2py$ appeared to be trans-octahedral whereas $SiCl_4 \cdot 2py$ $SiBr_4 \cdot 2py$ appeared to be cis on the basis of infrared spectra (93), the large difference in heats of formation was tentatively attributed to the greater crystal lattice energies of the complexes. This could not be tested experimentally because none of the complexes vaporizes without dissociation

and/or decomposition. It has now been confirmed by X-ray diffraction measurements (90) that all three complexes are trans-octahedral. Thus, the differences in their heats of formation appear to be unusually great.

(2) Heats of formation are about twice as great for py adducts as for iq adducts of silicon and germanium tetrachlorides and tetrabromides. This is surprising because py and iq should have similar basicities towards Group IV tetrahalides unless steric effects are important (86,88).

(3) The heat of formation of crystalline $SnCl_4 \cdot 2py$ (-52.9 Kcal/mole) from its components in the liquid state (122) was appreciably greater than its heat of formation (-39.5 Kcal/mole) from its components in benzene solution (89), a surprisingly large discrepancy even after the heats of solution of $SnCl_4$ and py in benzene are taken into account.

(4) The heats of formation of $SiF_4 \cdot 2py$, $SiCl_4 \cdot 2py$ and $SiBr_4 \cdot 2py$ are almost twice the values reported by Wannagat et al (119). The order of adduct stability suggested by these authors of $SiF_4 << SiCl_4 \sim SiBr_4$ is quite different from the order suggested by Miller and Onyszchuk (122) of $SiCl_4 > SiBr_4 > SiF_4$.

After some preliminary measurements suggested that traces of water in py produced high results, heats of formation

were measured in a systematic way using improved experimental techniques and a more sensitive calorimeter.

3. EXPERIMENTAL

3.1 Apparatus

A standard glass vacuum line (91) was used in the preparation of all complexes because of the air and moisture sensitive nature of the materials used. A mercury manometer equipped with a spiral null point gauge was used for all pressure measurements. Stopcocks were lubricated with Kel - F 90 stopcock grease, and o-rings replaced greased joints when prolonged exposure of materials to stopcock grease was anticipated. All adducts were handled in an evacuable nitrogen-filled dry box during preliminary investigations and subsequently if they were found to be sensitive to moisture.

3.2 Quantitative Synthesis

The cyclicimine-BF_3 complexes were prepared using the following standard procedure. A measured quantity of base (2mmoles) was condensed onto a cold finger at liquid nitrogen temperature. BF_3 was added in approximately 1 mmole excess and the mixture was then slowly warmed to the lowest temperature at which effective interaction of the acid and base occurred. A suitable low-temperature slush bath helped to dissipate rapidly the large reaction heat generated, and thereby prevented polymerization of the cyclic bases. The amount of BF_3 present in excess was measured and the stoichiometric ratio obtained.

No attempt was made to synthesize BF_3-methylamine adducts quantitatively as these have been previously verified to be 1:1 composition.

Adducts of py and iq with the tetrahalides of silicon, germanium and tin were also prepared by vacuum line synthesis. The 1:2 nature of these complexes has already been proven (92,93).

3.3 Materials

In table 3 the sources, methods of purification and purity of materials are listed.

3.4 Boron-11, Fluorine-19, Proton Nuclear Magnetic Resonance Spectra

Fluorine-19 and ^{11}B nmr spectra of BF_3-amine complexes were recorded on a HR-60 high resolution nuclear magnetic resonance spectrometer. Sidebands generated from the internal standard, $FCCl_3$ and $B(OCH_3)_3$, were used to calibrate ^{19}F and ^{11}B peak positions, respectively. The concentration and solvent dependence of the ^{19}F chemical shifts were checked in $CHCl_3$ and CH_3CN solution in the concentration range 0 - 14 mole percent.

^{1}H nmr chemical shifts of BF_3-amine complexes were recorded on a Varian A-60 high resolution nuclear magnetic resonance spectrometer, using $(CH_3)_4Si$ as an internal standard. Measurements were made on 0.02 to 0.08 mole fraction solutions of the adducts in $CDCl_3$.

Table 3

Source, Purification, Purity of Materials

Compound	Source	Method of Purification	Purity
TMA	Matheson	Dried by passing through P_2O_5, stored over sodium.	M, calc. 59.2 M, found 59.0
TEA	Aldrich	Distilled from CaH_2, redistilled from BaO^2 in vacuo.	
DMA	Matheson	Dried over sodium, redistilled -78°C.	M, calc. 45.0 M, found 45.9
Pyridine	Fisher	Distilled twice from CaH_2, pretreated with acid prior to use.	BP found 115° BP lit. 115-116 (95)
BF_3	Matheson	Distilled through trap at -152°C.	M, calc. 67.9 M, found 67.7
CH_3CN	Fisher certified	Distilled 3 times from fresh P_2O_5, redistilled	BP found 81.5° BP lit. 81.6-81.8 (96)
SiF_4	Matheson	Distilled through trap -78°C, redistilled from CS_2 slush bath.	M, calc. 104.9 M, found 104.6 ir spectrum
$SiBr_4$	Anderson	Distilled in a vacuum, after shaking with Hg.	BP found 153.5 BP lit. 153.0 (97) M, found 355.0 M, calc. 353.2

Table 3 (continued)

Source, Purification, Purity of Materials

Compound	Source	Method of Purification	Purity
$SiCl_4$	Fisher	Distilled from Cu, redistilled in vacuum.	M, calc. 172.8 M, found 169.9 VP found 7.6 mm/0° VP lit.(98) 7.7 mm/0°
GeF_4	Ozark - Mahoning	Vacuum distilled from pentane slush twice.	M, found 149.2 M, calc. 148.6 ir spectra
Ethyleneimine	Chemirad		M, calc. 43.1 M, found 43.1
2-methyl ethyleneimine	Chemirad		M, calc. 57.9 M, found 57.8
Pyrrolidine	Aldrich		ir (99), nmr (100,101)
Piperidine	Aldrich	Distilled from CaH_2, and redistilled from BaO in vacuo at 25°.	ir (99) nmr (100)
Hexamethyleneimine	Aldrich		ir (99) nmr (100)
N-methyl ethyleneimine	K & K		ir (102) nmr*
N-methyl pyrrolidine	K & K		ir (99) nmr*
N-methyl piperidine	K & K		ir (99) nmr*

Table 3 (continued)

Source, Purification, Purity of Materials

Compound	Source	Method of Purification	Purity
N-methyl hexamethyleneimine	Synthesized (103)	Distilled from sodium.	M, calc. 113.9 M, found 113.2
Trimethyleneimine	Synthesized (104,105)	5 distillations from Na and final distillation in vacuo.	M, calc. 57.1 M, found 57.9
NH_3	Matheson	Formed sodium solution.	M, calc. 17.1 M, found 17.3
MMA	Matheson	Dried over sodium, distilled -78°C.	M, calc. 31.4 M, found 31.0
$GeBr_4$	Chemicals Procurement Laboratories	Shook with Hg, distilled.	
$SnCl_4$	Fisher	Vacuum distilled at 20°, shook with mercury.	VP found 23.1 mm/25° VP lit. (98)23.0 mm/25 BP 124° BP found (123.5°)
Isoquinoline	Eastman	Distilled twice from CaH_2, predried with acid.	BP lit. 243° (106) BP found 241°-242°

Table 3 (continued)

Source, Purification, Purity of Materials

Compound	Source	Method of Purification	Purity
$CHCl_3$	Fisher	Passed through column of AL_2O_3 twice.	nmr and ir spectra
CCl_4	Fisher	Distilled twice from CaH_2.	ir and nmr spectra
Cyclohexane	Fisher	Distilled twice from CaH_2.	ir and nmr spectra
N-methyl trimethyleneimine	Synthesized	Prepared ethyl formate derivative of azetidine, reduced by lithium aluminum hydride in n-butyl ether, recovered from picrate by neutralization $NaOH/H_2O$, dried over NaOH, distilled and dried in vacuum over sodium.	nmr* MP picrate found 134-136 lit. (59) 135-136

* Assignments made by comparing spectra of unmethylated cyclicimine bases.

3.5 Infrared Spectra

Infrared spectra of all complexes were recorded on a Perkin-Elmer model 521 dual grating infrared spectrometer. Samples of adducts were run as liquid smears between KBr plates or as Nujol or Fluorolube mulls. Spectra of gases were obtained in a 10 cm gas cell fitted with KBr plates. Spectra of neat liquids were recorded when possible in 0.1 mm cells.

3.6 Hydrogen Bonding Measurements

3.6. 1 Infrared Measurements

The shift in the C-D stretching frequency, $\Delta\nu$ (C-D), defined as: $\Delta\nu$ (C-D)(free $CDCl_3$) - ν (C-D) (complexed $CDCl_3$), was determined for all cyclicimines. The magnitude of the shift was established from measurements of infrared spectra on a 521 dual grating infrared spectrometer equipped with 10X abscissa scale expansion. Measurements were made on five percent solutions of the amine in $CDCl_3$. Peaks were calibrated using the 521 frequency counter in conjunction with polystyrene film.

3.6.2 Proton Nuclear Magnetic Resonance Measurements

The shift in the ^1H resonance position, $\delta(^1H)$, defined as: $\Delta\delta(^1H) = \delta(^1H)$(free $CHCl_3$) - $\delta(^1H)$(complexed $CHCl_3$), was determined for all cyclicimines of general formula $(CH_2)_nNH$ (n = 2 to 6), at four concentrations of base, 0.03 to 0.2 molal in the cyclohexane-CCl_4 solvent mixture, and for each

base and each concentration at four different temperatures in the range -30° to +30°. The information derived from these measurements gives the ^1H infinite dilution shifts, formation constants, and heats of H-bonding for $CHCl_3$-cyclicimine complexes.

All measurements were made on a Varian A-60 ^1H nuclear magnetic resonance spectrometer equipped with a V-6040 variable temperature controller. Temperatures were measured by using the sample of methanol in CCl_4 provided by Varian; the distance between the methyl protons and hydroxyl proton had been calibrated for temperatures between -60° and +40° (94). Temperatures were found to vary by not more than 1° or 2° during all measurements at a given temperature. Samples were allowed to equilibrate for ten minutes for recordings below 10°. At higher temperatures equilibration took approximately four minutes. At these elevated temperatures, however, the amines reacted slowly with the CCl_4 solvent and this necessitated storing all samples in dry ice-acetone slush baths prior to measurements. The fact that similar results were obtained when cyclohexane was used as solvent instead of CCl_4 suggested that the slow decomposition in CCl_4 solution did not affect ^1H chemical shifts significantly.

The ^1H nmr shifts were measured with reference to the internal standard cyclohexane, which served as solvent and to correct for changes in bulk magnetic susceptibility

with changing base concentration. Spectra were calibrated by means of sidebands generated from the cyclohexane reference by means of audio oscillators and a Hewlett-Packard model 521C frequency counter. Three spectra were recorded for each concentration of base and the average result is accurate to ±0.1 hz.

3.7.1 Calorimeter

The glass calorimeter, figure 4, used to measure heats of reaction, is the same as one previously described (88). The stirrer, consisting of a flat spiral or chain adapted to fit the calorimeter B-24 ground glass socket by a quickfit ST10/2 ground sleeve stirrer gland sealed with mercury, was driven by a variable speed motor at about 120 revolutions per minute. Two B-10 joints provided for the entry of the thermister probe and calibration heater, and the ball and socket joint was used to flush the vessel during its assembly. The bath temperature was maintained at 25 ± 0.02° by a Tempunit regulator. This temperature was verified using a Fisher thermometer calibrated against an Erto model 57478 thermometer, a National Research Council Standard.

Temperature changes were measured with a Sargent thermister S-81620 and thermister bridge S-81601, which replaced the 12-junction thermocouple used previously (88). The output from the bridge was connected to a 1 mv recorder (Honeywell) calibrated in microvolts (μv).

Figure 4 Calorimeter reaction vessel.

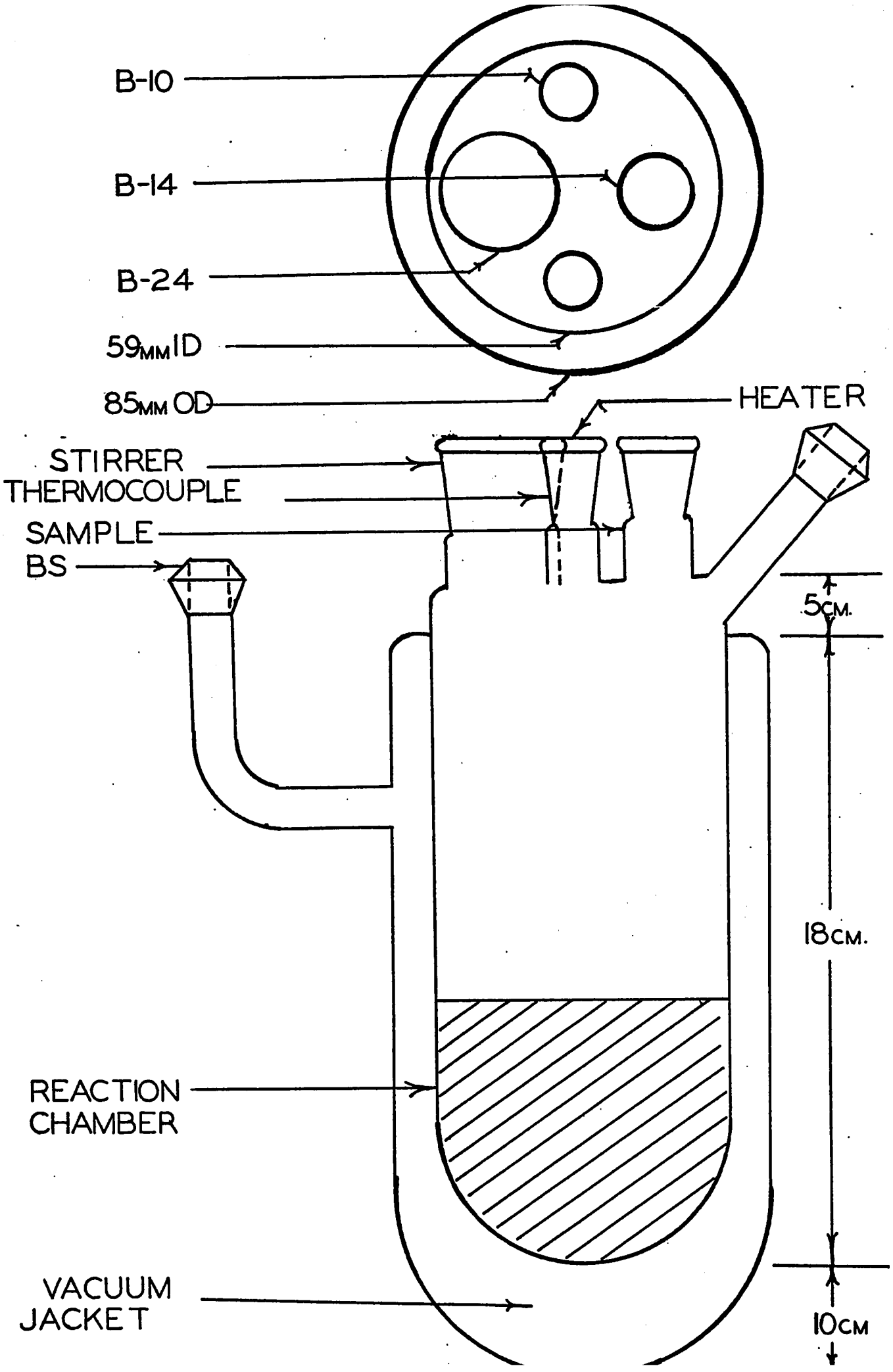
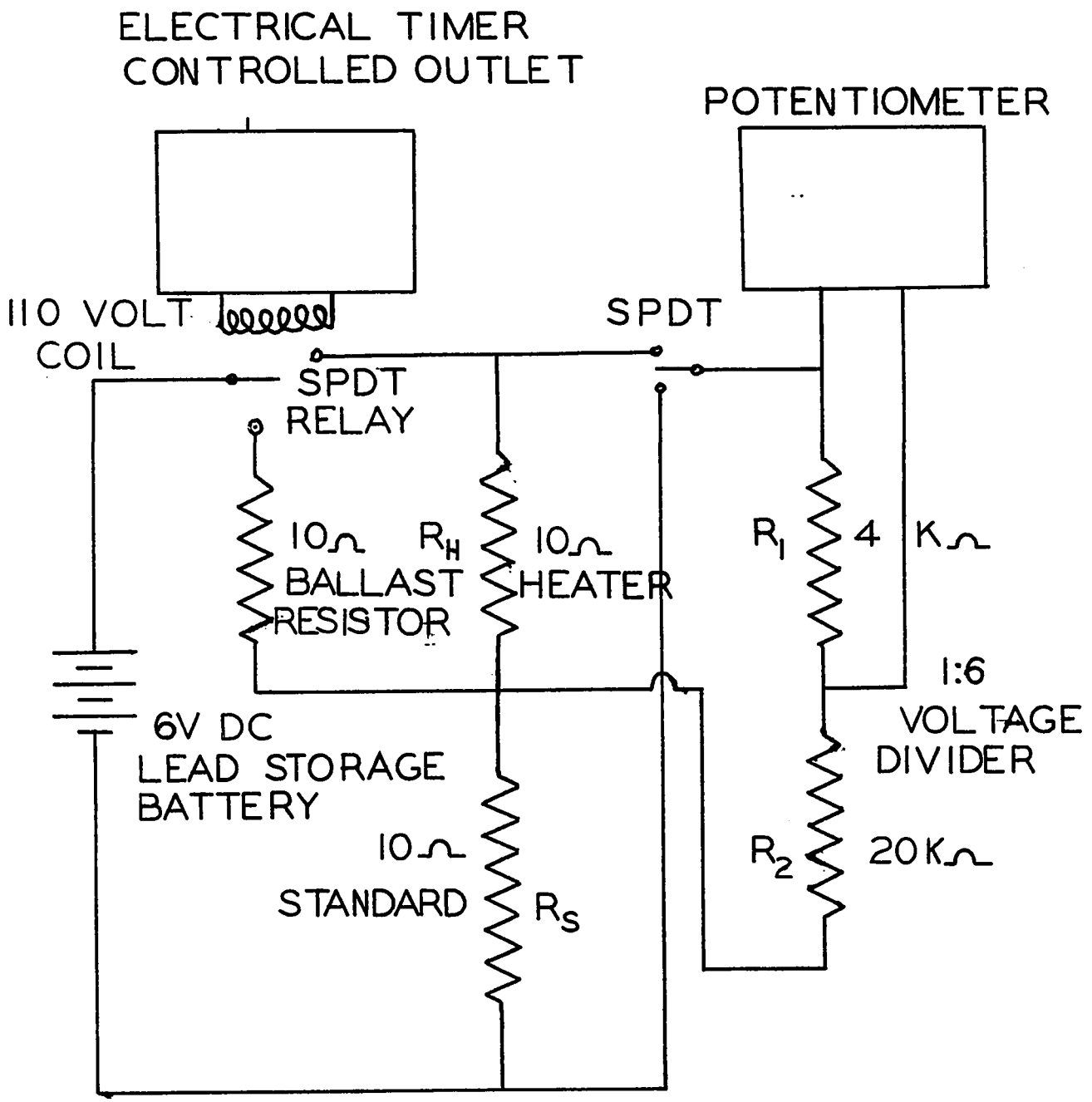

B-10
B-14
B-24
59MM ID
85MM OD
HEATER
STIRRER
THERMOCOUPLE
SAMPLE
BS
5CM.
18CM.
REACTION CHAMBER
VACUUM JACKET
10CM

Figure 5 Electrical calibration circuit.



TOLERANCE ON RESISTORS ±0·05%

The electrical calibration circuit is given in figure 5. Current through the 30 gauge constantan wire heater was determined by measuring the voltage drop across the standard resister. Voltage across the heater was measured by means of the 1:6 voltage divider and the Tinseley potentiometer. An electrical timer, connected to a single pole double throw relay was used to disconnect the ballast (used to stabilize the battery) and to connect the heater for the required time.

3.7.2 Sample Inlet Devices

Solids and liquids were sealed in fragile glass ampoules A and B, respectively, of figure 6, under a one atmosphere nitrogen pressure. The quantities of materials transferred were determined gravimetrically.

Gases were added with the device shown in A of figure 7. A sample of gas measured on a standard high vacuum apparatus equipped with a mercury manometer and spiral null point guage, was condensed into sample vial S and connected to the gas bubbler while the vial was maintained at liquid nitrogen temperature. The gas inlet valve E was completely evacuated and a 1 mmole sample of gas then bubbled into the calorimeter, at a rate controlled by slush baths. Any residual gas was then measured.

Heats of solution of liquids were determined with the sample inlet device shown in B of figure 7.

This device is essentially a 1 ml syringe which had been extended to allow complete immersion of its contents below the level of the calorimeter fluid. This facilitated rapid thermal equilibrium of the syringe contents with the calorimeter fluid. The quantity of material transferred was determined gravimetrically by difference or by gravimetrically calibrating the syringe for total transfer of its contents. The latter technique is the more rapid if a large number of determinations are to be made.

Heats of vaporization of liquids were measured with the device indicated in figure 8. A small quantity of material was vaporized from container A, maintained at 25°C into container B at liquid nitrogen temperature. The amount of material vaporized was determined by the gain in weight of vessel B.

3.7.3 Calorimeter Operation

The calorimeter was predried in an oven at 110° for 6 hours, flushed with nitrogen while it cooled to room temperature and finally assembled under a vigorous flow of nitrogen. Approximately 100 ml of dry calorimetric fluid, was then added from a syringe. The appropriate sample inlet device was attached and the system allowed to equilibrate at 25°C for about one hour. A small prerun of reactant was essential to remove trace amounts of water or other impurities still remaining in the calorimetric fluid.

Figure 6 A - solid inlet device.

B - liquid inlet device.

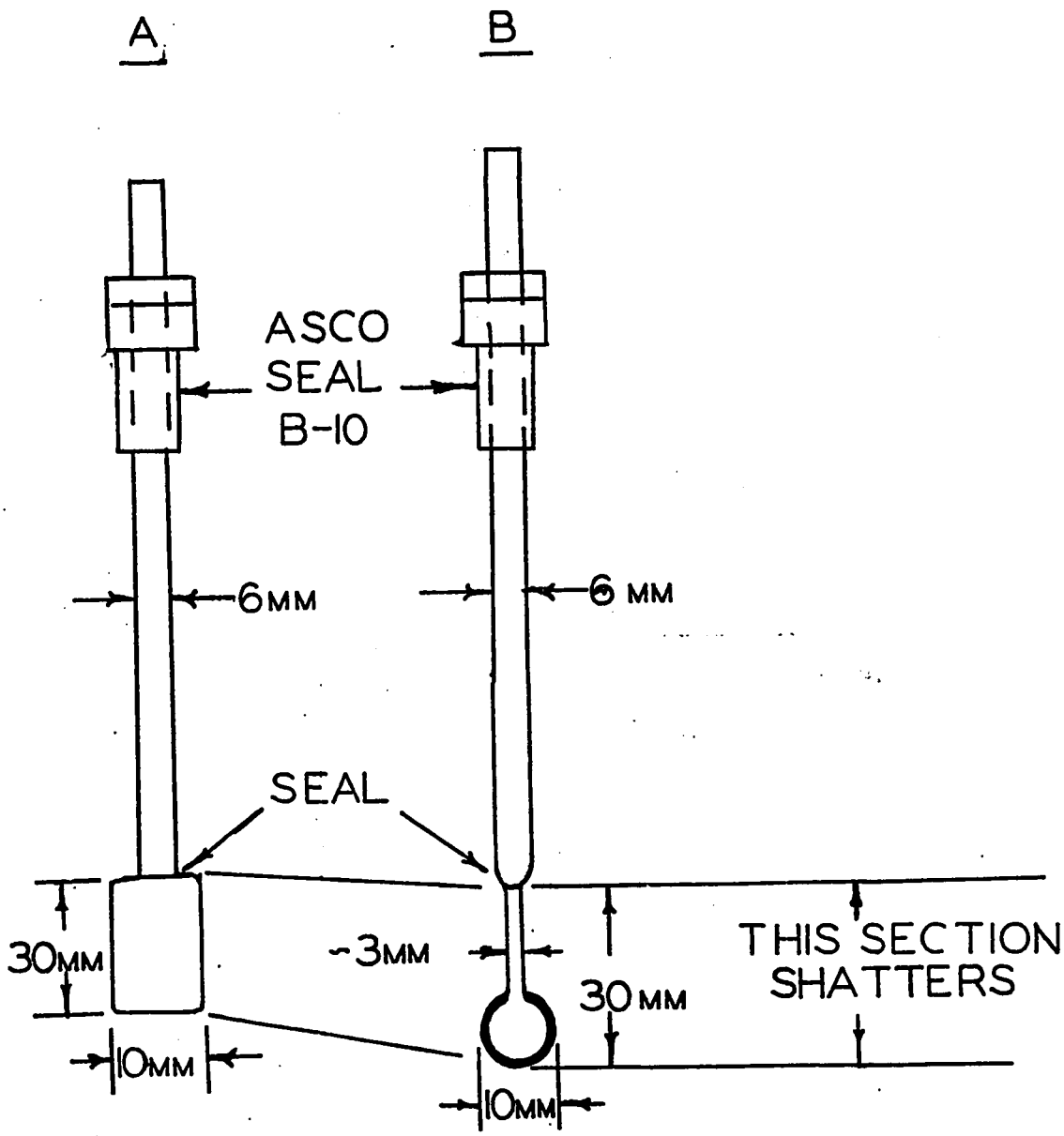
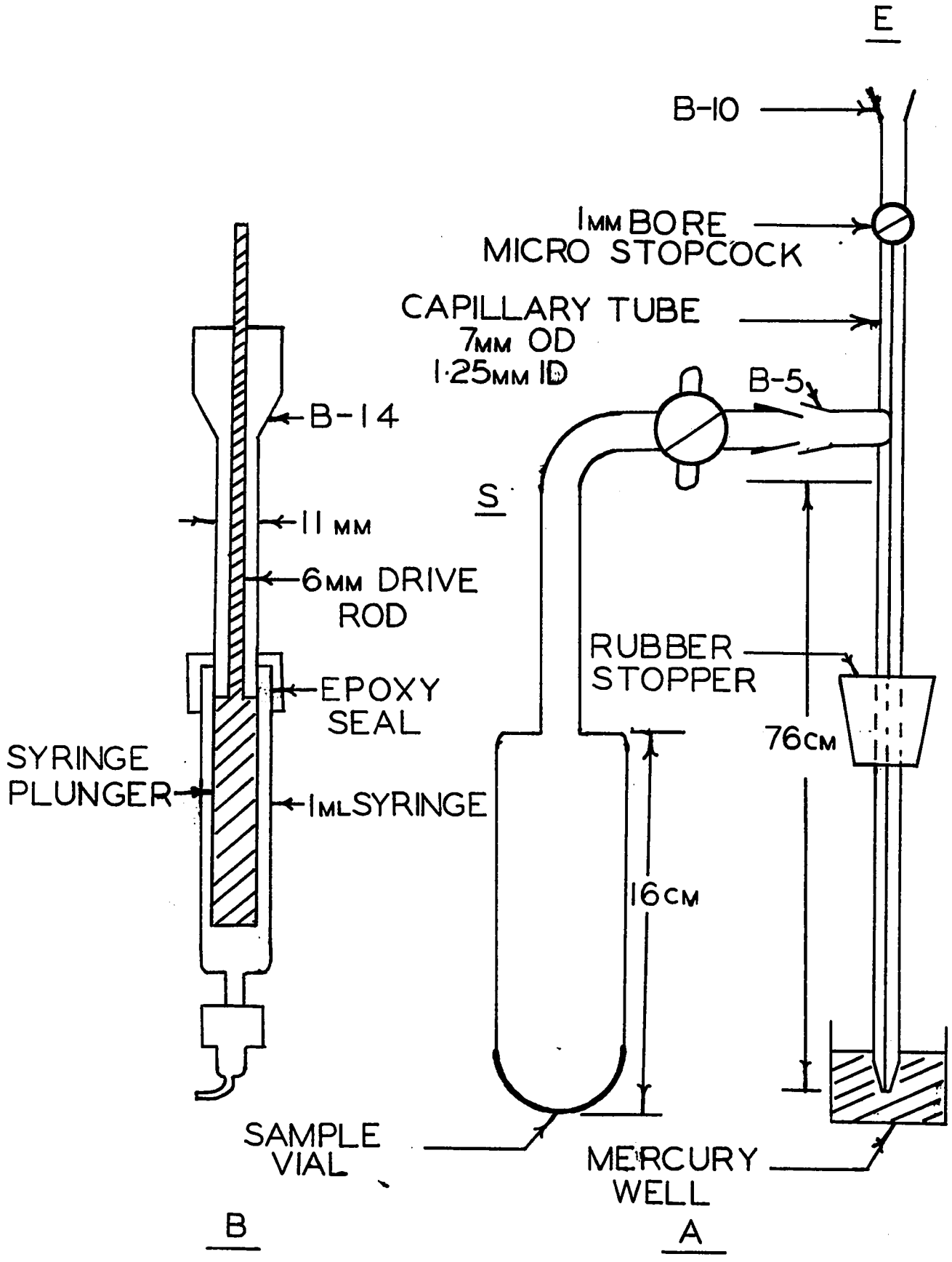

A
B
ASCO
SEAL
B-10
6MM
6 MM
SEAL
30MM
~3MM
30 MM
THIS SECTION
SHATTERS
10MM
10MM

Figure 7 Gas inlet and syringe injection systems.


E
B-10
1MM BORE
MICRO STOPCOCK
CAPILLARY TUBE
7MM OD
1·25MM ID
B-5
B-14
S
11 MM
6MM DRIVE
ROD
RUBBER
STOPPER
EPOXY
SEAL
76CM
SYRINGE
PLUNGER
1ML SYRINGE
16CM
SAMPLE
VIAL
MERCURY
WELL
B
A

When the temperature of the contents of the calorimeter approached 25° the jacket was evacuated. The cooling curve was then recorded for 3 minutes prior to, and 3 minutes after, mixing the reactants, for the purpose of extrapolation. A similar curve was recorded for a 120 second calibration heating cycle. The recorded cooling curves, an example of which is shown in figure 9, were extrapolated to obtaine $t_{\frac{1}{2}}$, i.e. the time half way between the initial temperature rise at t_o, and the maximum temperature, t_{max}. This extrapolation corrected for stirring lag and heat loss during the finite reaction and calibration time. The extrapolated total temperature change ΔT was rechecked on several occasions by using a graphical method devised by Boyd and Brown (45) and a Newtonian incremental method (108). Successive measurements usually agreed to within $\pm 3\mu v$.

For most reactions studied $t_{max}-t_o$ is almost zero, hence, there is little difficulty in obtaining an accurate extrapolation.

ΔT(reaction) and ΔT(calibration), obtained from the respective cooling curves, were used with the standard voltage (E_S) and heater voltage (E_H) to calculate the heat of reaction.

E_H = potentiometer reading x 6 = voltage across heater.

E_S = potentiometer reading x 6 = voltage across standard.

Figure 8 Apparatus for measurement of heats of vaporization.

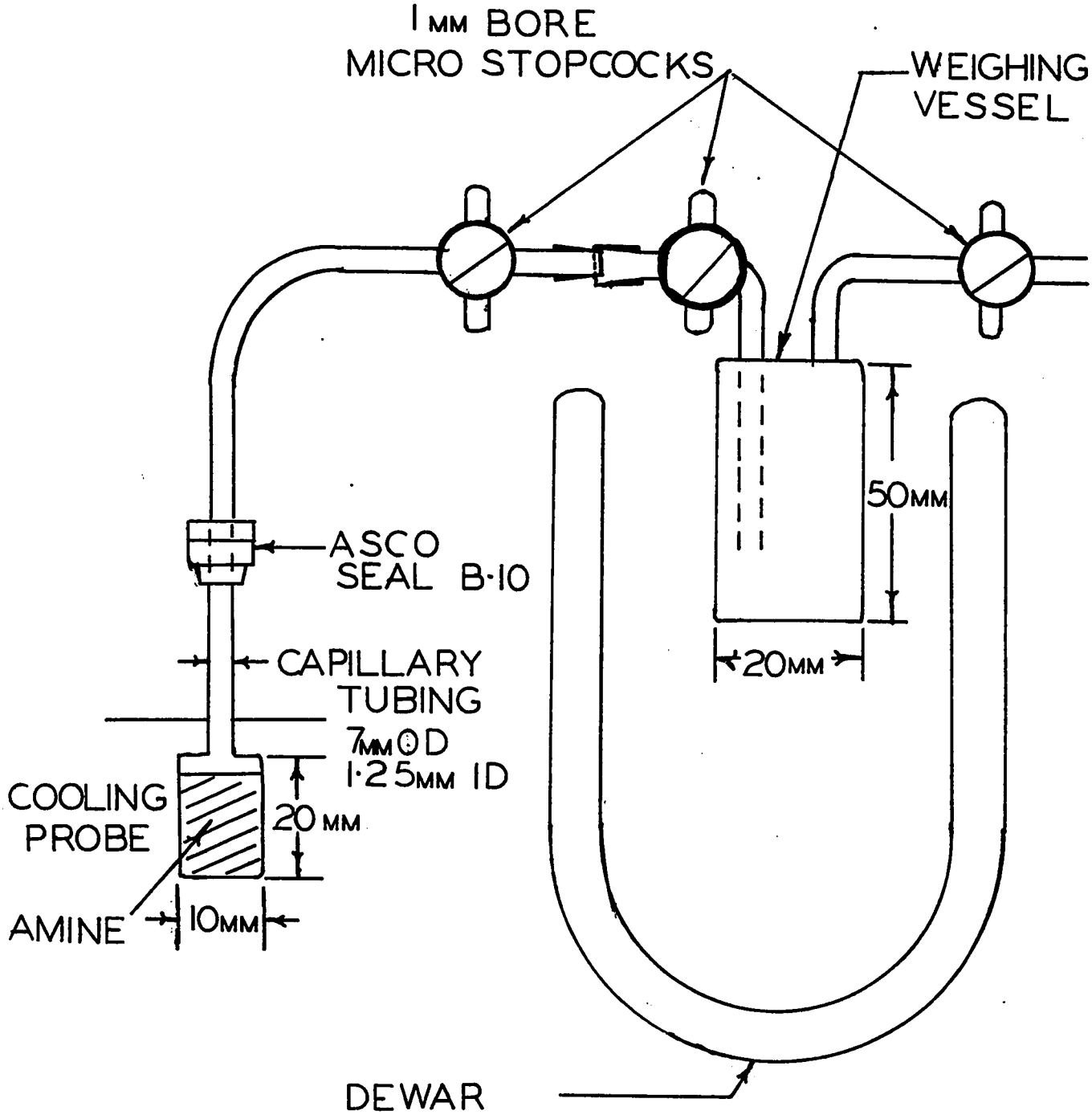
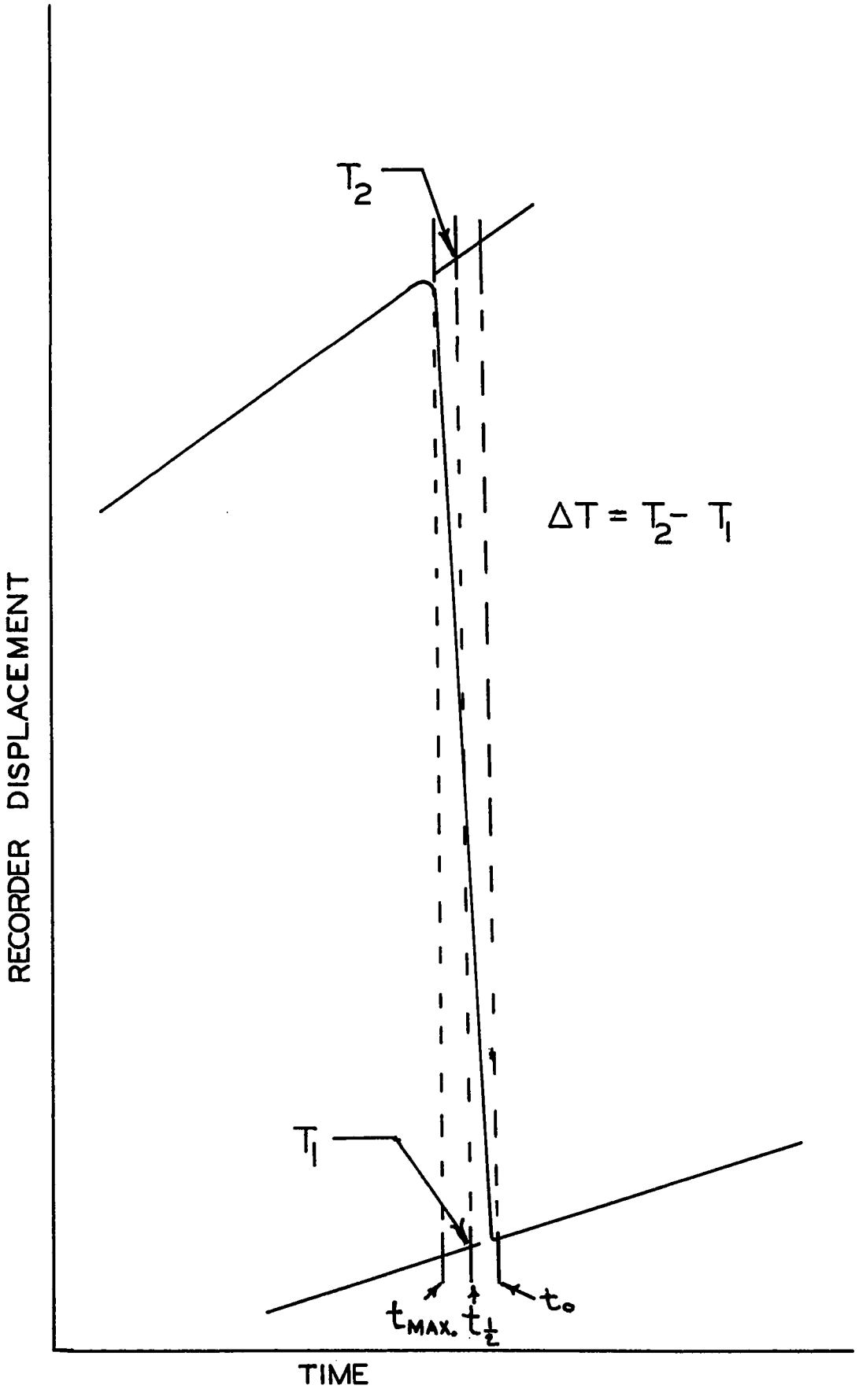

1 MM BORE
MICRO STOPCOCKS
WEIGHING
VESSEL
50MM
20MM
ASCO
SEAL B-10
CAPILLARY
TUBING
7MM O D
1·25MM I D
COOLING
PROBE
20 MM
AMINE
10MM
DEWAR

Figure 9 Typical cooling curve.


T_2
$\Delta T = T_2 - T_1$
RECORDER DISPLACEMENT
T_1
$t_{MAX.}$
$t_{\frac{1}{2}}$
t_o
TIME

These variables are related to the heat of reaction by the formula:

$$-\Delta H \text{ Kcal/mole} = \frac{E_H \times E_S \times (\text{calibration time} = 120 \text{ sec}) \times \Delta T(\text{reaction})}{4{\cdot}1840 \times \Delta T(\text{calibration}) \times \text{mmoles reactant}}$$

3.7.4 Estimate of Errors

A reasonable estimate of the errors involved in extrapolating either the calibration or reaction cooling curves is less than 5μv in 600μv. The latter figure corresponds to the recorder displacement for a 1 mmole addition of reactant or to a 120 second calibration heating cycle, the magnitudes of which are determined by the bridge sensitivity. The maximum total error in extrapolation techniques is less than $\frac{10}{600} \times 100$ or 1.5%.

Errors in sampling techniques are estimated to be 0.8% for the gas inlet device and 0.5% for the others. Errors in potentiometry are considered negligible. Hence, the expected total error in calorimetry is 2.0 to 2.3%. Experimentally it was found to be about 1%, much less than the estimated value.

3.7.5 Testing the Calorimeter

The calorimeter was tested by measuring the heats of solution of HCl in H_2O, HCl in 0.004M NaOH and the heat of reaction of BF_3 with py. These results are given in table 4.

Table 4

Heat of Solution (ΔH_1)

$HCl(g) + H_2O(l) \rightarrow HCl(H_2O)$

Trial Number	HCl Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_1$ (Kcal/mole)
1.	1.3027	.08791	263	17.7
2.	2.0149	.08888	410	18.1
3.	1.1611	.08888	232	17.8

Average value = 17.9 ± 0.2.

Literature value (109) = 17.88 Kcal/mole.

Heat of Neutralization (ΔH_2)

$HCl(g) + NaOH(\cdot 004 \text{ molar}) \rightarrow NaCl(H_2O) + H_2O(H_2O)$

Trial Number	HCl Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
1.	1.2744	.09221	436	31.5
2.	1.2390	.09241	421	31.4

Average value = 31.45 Kcal/mole.

The heat of neutralization for the reaction:

$HCl(H_2O) + NaOH(H_2O) \rightarrow NaCl(H_2O) + H_2O(H_2O)$ is given by

$\Delta H_2 - \Delta H_1 = 13.6$ Kcal/mole.

Literature value (110) = 13.44 Kcal/mole.

.....

Table 4 (Continued)

Heat of Reaction (ΔH_3)

$$BF_3(g) + py\,(\text{nitrobenzene solution}) \rightarrow BF_3 \cdot py\,(\text{nitrobenzene solution})$$

Trial Number	BF_3 Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_3$ (Kcal/mole)
1.	0.8048	.04779	549	32.6
2.	0.6681	.04899	455	33.4

Average value = 33.0 Kcal/mole.

Literature value (83) = 32.8 Kcal/mole.

Since the three results are in excellent agreement with literature values the calorimeter and the experimental procedures were used with confidence in measuring heats of reaction of BF_3 with amines, MX_4 acids with py and iq, the heat of hydrolysis of $BI_3 \cdot CH_3CN$, and the heats of solution of cyclicimines in $CHCl_3$ and cyclohexane.

4. RESULTS SECTION

4.1 Heats of Reaction of amines with BF_3

It was convenient to compare the heats of formation of different BF_3-amine adducts under the following reaction conditions,

$$BF_3(g) + \text{amine (g)} \xrightarrow{\Delta H_{12}} BF_3\text{-amine } (CH_3CN \text{ solution}) \quad \ldots (19)$$

because:

(a) Heats of sublimation of BF_3-amine complexes could not be obtained due to their low vapour pressures. Consequently comparison of reaction heats under ideal reaction conditions with all components in the gas phase was not possible.

(b) Since the products were solids and liquids, it was necessary to choose the standard state as infinite dilution in a suitable solvent. The only common solvent was CH_3CN which is not an ideal choice because of its high dielectric constant (133). Brown (111) was successful, however, in using nitrobenzene, a solvent with similar properties, for his studies of the heats of formation of $BF_3 \cdot py$ adducts.

(c) The standard state of the reactants was chosen as the gaseous state to avoid energy changes which accompany condensation.

4.1.1 Measurement of ΔH_{12}

ΔH_{12} was obtained by measuring the heats of the following reactions:

$$BF_3(g) + CH_3CN(l) \xrightarrow{\Delta H_1} BF_3 \cdot CH_3CN(CH_3CN \text{ solution}) \quad \ldots\ldots (20)$$

$$\text{Amine } (l) + BF_3 \cdot CH_3CN(CH_3CN \text{ solution}) \xrightarrow{\Delta H_2} BF_3\text{-amine}(CH_3CN \text{ solution}) \quad (21$$

$$\text{Amine } (l) \xrightarrow{\Delta H_3} \text{amine } (g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

Therefore, $\Delta H_{12} = \Delta H_2 - \Delta H_3 + \Delta H_1$

4.1.2 Measurement of ΔH_1

The heat of reaction of measured quantities of BF_3 with the calorimeter fluid consisting of 20 mmoles of $BF_3 \cdot CH_3CN$ in 1000 mmoles of CH_3CN was obtained first. The latter standard state was chosen because (i) the displacement reaction (22) involving gaseous amines was greatly accelerated with higher concentrations of adduct, (ii) a constant heat of reaction was observed for as many as five successive mmole additions of BF_3 to the same reaction mixture. This showed that one could add in reaction (21) a number of successive additions of base confident that the heat of reaction ΔH_1 would be constant. Thermochemical data for reaction (20) is indicated in table 5.

Table 5

Thermochemical Data for the Reaction

$$BF_3(g) + CH_3CN(l) \xrightarrow{\Delta H_1} BF_3 \cdot CH_3CN(CH_3CN \text{ solution})^a$$

Trial Number	BF_3 Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_1$ (Kcal/mole)
1.	1.5887	0.04447	612	17.1
2.	1.5618	0.04447	580	16.5
3.	1.3211	0.04225	528	16.9
4.	1.4259	0.04340	555	16.9
5.	1.9229	0.07007	475	17.3
6.	2.1296	0.06832	532	17.1
7.	1.5887	0.04447	606	17.0

Average value = 16.9 ± 0.08[b]

[a] CH_3CN solution consisted of 20 mmoles $BF_3 \cdot CH_3CN$ in 1000 mmoles CH_3CN

[b] standard deviation

4.1.3 Measurement of ΔH_2

Because it was possible to measure the heats of 4 to 5 successive additions of amines to a solution of 20 mmoles of $BF_3 \cdot CH_3CN$ in 1000 mmoles of CH_3CN without any detectable change in the observed heat of reaction, the following procedure was adopted to avoid systematic errors in the techniques employed.

A series of ampoules of the different amines to be studied were prepared and in each sequence of 3 or 4 measurements the heats of at least 2 different amines were obtained. This procedure was repeated until all the results reported in table 6 were obtained. Thus, the final heats were those derived by successive comparisons in a large number of experiments and hence represent the sum of all possible errors.

Table 6

Thermochemical Results for ΔH_2

Amine (1) + $BF_3 \cdot CH_3CN$ (CH_3CN solution) $\xrightarrow{\Delta H_2}$ BF_3-amine (CH_3CN solution)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
Ethyleneimine				
1.	2.6418	0.05521	1020	21.3
2.	2.0762	0.05538	825	22.0
3.	2.0132	0.05538	785	21.6
4.	3.0648	0.06032	1087	21.4
5.	3.0983	0.06970	938	21.1
Average value = 21.5 ± 0.1[a]				
Trimethyleneimine				
1.	1.7305	0.05704	855	28.2
2.	1.5780	0.05658	767	27.5
3.	1.0708	0.05629	535	28.1
Average value = 27.9 ± 0.3[a]				

.....

Table 6 (Continued)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
Pyrolidine				
1.	1.9545	0.05505	919	25.9
2.	1.5000	0.05538	691	25.5
3.	1.7091	0.05538	777	25.2
4.	1.2100	0.05966	518	25.5
5.	1.2935	0.05977	565	26.1
6.	1.3154	0.05988	568	25.9
Average value = 25.6 ± 0.3[a]				
Piperidine				
1.	1.3418	0.06039	511	23.0
2.	1.4098	0.06076	567	24.4
3.	1.1432	0.05852	457	23.4
4.	1.3471	0.05852	556	24.2
5.	1.3865	0.06082	538	23.6
6.	1.1685	0.05990	450	23.1
Average value = 23.6 ± 0.5[a]				

.....

Table 6 (Continued)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
Hexamethyleneimine				
1.	1.0801	0.06089	420	23.7
2.	1.1054	0.06076	415	22.8
3.	1.3532	0.06076	515	23.1
4.	1.3727	0.05977	555	24.2
5.	1.4610	0.05977	583	23.9
Average value = 23.5 ± 0.5[a]				
Pyridine				
1.	1.3430	0.03382	595	15.0
2.	1.1440	0.03382	485	14.3
3.	1.5212	0.03498	661	15.2
Average value = 14.8 ± 0.4[a]				
Triethylamine				
1.	0.5942	0.03419	325	18.7
2.	0.8590	0.03419	450	17.9
3.	0.7515	0.03370	380	17.0
4.	0.8319	0.03419	430	17.7
Average value = 17.8 ± 0.6[a]				

.....

Table 6 (Continued)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
Ammonia				
1.	1.0754	0.04777	617	27.4
2.	1.0506	0.04845	583	26.9
3.	1.1738	0.04904	635	26.5
4.	0.8099	0.03668	594	26.9
5.	0.8722	0.03766	630	27.2
6.	1.0421	0.03778	758	27.5
7.	1.4698	0.07067	557	26.8
8.	1.6340	0.07067	631	27.3
9.	1.5151	0.07033	601	27.9
Average value = 27.1 ± 0.4[a]				
Dimethylamine				
1.	0.7518	0.04456	568	33.7
2.	0.7717	0.04496	560	32.6
3.	0.8269	0.04400	615	32.7
4.	0.8269	0.04436	617	33.1
5.	0.9841	0.04432	734	33.1
6.	1.0460	0.05406	643	33.2
7.	0.9260	0.05436	547	32.1
8.	1.2347	0.05406	752	32.9
Average value = 33.0 ± 0.4[a]				.....

Table 6 (Continued)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
Monomethylamine				
1.	0.6910	0.03947	585	33.4
2.	0.8963	0.04056	750	33.9
3.	0.9586	0.04009	794	33.2
4.	0.7080	0.03978	582	32.7
5.	0.9104	0.03976	760	33.2
6.	1.0860	0.04866	745	33.4
7.	1.1823	0.04872	807	33.3
8.	0.9558	0.04803	661	33.2
Average value = 33.2 ± 0.3[a]				
Trimethylamine				
1.	1.0322	0.04641	593	26.7
2.	0.9897	0.04672	572	27.0
3.	1.0719	0.04672	592	25.8
4.	1.6992	0.07007	647	26.7
5.	1.4698	0.07007	569	27.1
6.	0.7887	0.04145	510	26.8
7.	0.9869	0.04175	615	26.0
8.	0.8835	0.04175	565	26.7
Average value = 26.5 ± 0.4[a]				

.....

Table 6 (Continued)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
N-Methyl Ethyleneimine				
1.	1.6354	0.05261	535	17.2
2.	1.5326	0.05630	482	17.7
3.	1.2310	0.05630	378	17.3
Average value = 17.4 ± 0.4				
N-Methyl Pyrrolidine				
1.	0.9124	0.06419	324	22.8
2.	1.6029	0.06558	570	23.3
3.	1.4824	0.06451	501	21.8
4.	1.0057	0.06419	339	21.6
5.	1.2218	0.05235	493	21.1
Average value = 22.1 ± 0.8[a]				
N-Methyl Piperidine				
1.	1.0050	0.06451	305	19.6
2.	1.1835	0.05378	433	19.7
3.	1.2700	0.05372	467	19.8
4.	1.4141	0.05372	508	19.3
5.	1.0502	0.05977	334	19.0
6.	1.1523	0.05977	400	20.7
7.	1.1135	0.05977	343	18.4
Average value = 19.4 ± 0.7[a]				.....

Table 6 (Continued)

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
N-Methyl Hexamethyleneimine				
1.	1.2174	0.05354	473	20.8
2.	1.3402	0.05372	518	20.8
3.	1.2103	0.05261	497	21.6
4.	1.0384	0.05171	417	20.8
Average value = 21.0 ± 0.4[a]				
N-Methyl Trimethyleneimine				
1.	0.8859	0.7913	285	25.5
2.	0.4521	0.7971	143	25.2
3.	1.2160	0.7971	375	24.6
Average value = 25.1 ± 0.3[a]				

[a]standard deviation

4.1.4 Measurement of ΔH_3

Heats of vaporization of liquid amines were measured with the apparatus shown in figure 8. This probe was tested by measuring the corresponding heats for py and TEA, the results of which are shown in tables 7 and 8.

Table 7

Heat of Vaporization of Pyridine (ΔH_3)

Trial Number	Pyridine Vaporized (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH_3 (Kcal/mole)
1.	1.484	0.05538	262	9.8
2.	1.465	0.05644	248	9.6
3.	1.297	0.05585	220	9.5

Average value = 9.6 ± 0.1[a]

Literature value (112) = 9.6

Table 8

Heat of Vaporization of Triethylamine (ΔH_3)

Trial Number	Triethylamine Vaporized (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH_3 (Kcal/mole)
1.	1.131	0.05307	165	7.7
2.	2.084	0.05337	310	7.9

Average value = 7.8 ± 0.1[a]

Literature value (113) = 7.8

[a]standard deviation

Since the results agree with literature values, the method was used with confidence for all other amines. These data are indicated in the following table.

Table 9

Thermochemical Data for ΔH_3

Amine (l) $\xrightarrow{\Delta H_3}$ amine (g)

Trial Number	Amine Vaporized (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH_3 (Kcal/mole)
Ethyleneimine				
1.	2.999	0.05545	480	8.9
2.	2.369	0.05637	357	8.5
3.	2.247	0.05583	355	8.8
4.	2.641	0.05230	433	8.6
Average value = 8.7 ± 0.1[a]				
Trimethyleneimine				
1.	3.126	0.05270	557	9.4
2.	2.130	0.05270	375	9.3
Average value = 9.4 ± 0.1[a]				

.....

Table 9 (Continued)

Trial Number	Amine Vaporized (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH_3 (Kcal/mole)
Pyrrolidine				
1.	1.810	0.05807	307	9.8
2.	1.436	0.05789	245	9.9
3.	1.695	0.05789	295	10.1
4.	1.650	0.05746	275	9.6
Average value = 9.8 ± 0.1[a]				
Piperidine				
1.	1.838	0.05507	350	10.5
2.	1.316	0.05556	245	10.3
3.	1.039	0.04233	255	10.4
4.	1.071	0.04233	268	10.6
Average value = 10.4 ± 0.1[a]				
Hexamethyleneimine				
1.	0.555	0.05556	114	11.4
2.	0.614	0.05556	129	11.6
3.	1.000	0.04483	249	11.2
Average value = 11.4 ± 0.2				
N-Methyl Ethyleneimine				
1.	5.778	0.05352	535	5.0
2.	3.837	0.05352	380	5.3
Average value = 5.2 ± 0.1[a]				

.....

Table 9 (Continued)

Trial Number	Amine Vaporized (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH_3 (Kcal/mole)
N-Methyl Pyrrolidine				
1.	2.108	0.05581	301	8.0
2.	1.545	0.05581	230	8.3
3.	2.088	0.04439	383	8.1
Average value = 8.1 ± 0.1				
N-Methyl Piperidine				
1.	1.899	0.05425	330	9.4
2.	2.030	0.05301	357	9.3
3.	1.031	0.05301	175	9.0
Average value = 9.3 ± 0.1				
N-Methyl Hexamethyleneimine				
1.	0.6635	0.05315	131	10.5
2.	0.7486	0.05315	149	10.6
3.	1.5926	0.04439	373	10.4
Average value = 10.5 ± 0.1[a]				
N-Methyl Trimethyleneimine				
1.	2.3619	0.07910	215	7.2
2.	2.4302	0.07910	224	7.3
3.	2.1491	0.09316	164	7.1
Average value = 7.2 ± 0.1[a]				

[a] standard deviation

The thermochemical results for measurements of ΔH_1, ΔH_2, ΔH_3 and for the calculated values of $+\Delta H_{12}$ are summarized in the following table.

Table 10

Summary of Thermochemical Results for BF_3-Amine Adducts

Amine	ΔH_3 [a]	$-\Delta H_1$ [a]	$-\Delta H_2$	$-\Delta H_{12}$
Ethyleneimine	8.7	16.9	21.5 ±0.1	47.1 ±0.2
Trimethyleneimine	9.4	16.9	27.9 ±0.3	54.2 ±0.4
Pyrrolidine	9.8	16.9	25.6 ±0.3	52.3 ±0.4
Piperidine	10.4	16.9	23.6 ±0.5	50.9 ±0.6
Hexamethyleneimine	11.5	16.9	23.5 ±0.5	51.9 ±0.6
N-methyl ethyleneimine	5.2	16.9	17.4 ±0.4	39.5 ±0.5
N-methyl trimethyleneimine	7.2	16.9	25.1 ±0.3	49.2 ±0.4
N-methyl pyrrolidine	8.2	16.9	21.8 ±0.8	46.9 ±0.9
N-methyl piperidine	9.3	16.9	19.4 ±0.7	45.6 ±0.8
N-methyl hexamethyleneimine	10.6	16.9	21.0 ±0.4	48.5 ±0.5
MMA	0	16.9	33.2 ±0.3	50.1 ±0.3
DMA	0	16.9	33.0 ±0.4	49.9 ±0.4
TMA	0	16.9	26.5 ±0.4	43.4 ±0.4
NH_3	0	16.9	27.1 ±0.4	44.0 ±0.4
TEA	7.8	16.9	17.8 ±0.6	42.5 ±0.7
py	9.6	16.9	14.8 ±0.4	41.3 ±0.5

[a] standard deviation = 0.1

4.1.5 Miscellaneous Thermochemical Measurements

Heats of reaction of BF_3 with amines reported in the literature cannot be compared directly with the results obtained in this study, nor can they be compared among themselves because they are derived under different reaction conditions.

Literature values were corrected to the conditions

$$BF_3(g) + \text{base}\ (g) \rightarrow c(\text{solution}) \quad \ldots\ldots\ldots \quad (23)$$

where c(solution) is the complex at infinite dilution in CH_3CN or nitrobenzene solution. These results are listed in tables 11, 12a and 12b. A complete summary of results described in this study is given in table 13.

Table 11

Miscellaneous Thermochemical Measurements

Reaction Conditions	Reported Result $-\Delta H$ (Kcal/mole)	Ref.	ΔH Solution of Complex (Kcal/mole) in CH_3CN	in piperidine	$-\Delta H^{(x)}$ Corrected (Kcal/mole)	$-\Delta H$ This Study (Kcal/mole
$BF_3(g) + CH_3CN(g) \rightarrow C(s)$	26.5	(114)	$2.7^{(a)}$	-	23.8	$25.0^{(y)}$
$BF_3(g) + \text{piperidine}(g) \rightarrow C(\text{piperidine solution})$	53.8	(115)	$1.9^{(b)}$	$0.8^{(c)}$	$52.7^{(z)}$	50.9
$BF_3(g) + NH_3(g) \rightarrow C(s)$	41.3	(116)	$2.0^{(d)}$	-	39.3	44.0

C = Complex

y - corrected for heat of vaporization of CH_3CN of +8.0 Kcal/mole (114)

x - $\Delta H(\text{corrected}) = \Delta H(\text{reported}) + \Delta H(\text{solution } CH_3CN)$

z - $\Delta H(\text{corrected}) = \Delta H(\text{reported}) - \Delta H(\text{solution } CH_3CN) + \Delta H(\text{solution piperidine})$

a to d - see table 14 sections a to d

Table 12(a)

Miscellaneous Thermochemical Measurements

Reaction Conditions	Reported Result $-\Delta H$ (Kcal/mole)	Ref.	$+\Delta H^{(g)}$ Vaporization Base (Kcal/mole)	$+\Delta H$ Solution Base in NB (Kcal/mole)	$-\Delta H^{v}$ (Kcal/mole)
BF_3(g) + py(NB) → C(NB)	32.9	(83)	9.6	0.2 (e)	42.3
BF_3(g) + TMA(NB) → C(NB)	38.2	(45)	5.0 (h)	0.5 (m)	42.7
	40.1	(117)	5.0	0.5 (m)	44.6
BF_3(g) + TEA(NB) → C(NB)	35.7	(45)	7.8	0.5 (f)	43.0
BF_3(g) + N-methyl pyrrolidine(NB) → C(NB)	37.3	(45)	8.2	0.5 (m)	45.0
BF_3(g) + N-methyl piperidine(NB) → C(NB)	36.1	(45)	9.3	0.5 (m)	44.9

C = complex, NB = nitrobenzene

e to f - see table 14 sections e to f

g - table 9

h - reference 126

m - estimated from heats of solution of TEA and py

v - ΔH^{v} = ΔH(reported) - ΔH(vaporization base) + ΔH(solution base in NB)

Table 12(b)

Miscellaneous Thermochemical Measurements

Reaction Conditions	$-\Delta H^V$ (Kcal/mole)	$+\Delta H$ Solution of Complex in NB (Kcal/mole)	$+\Delta H$ Solution of Complex in CH_3CN (Kcal/mole)	$-\Delta H^W$ (Kcal/mole)
$BF_3(g)$ + py(NB) → C(NB)	42.3	2.4 (g)	2.6 (j)	42.1
$BF_3(g)$ + TMA(NB) → C(NB)	42.7 44.6	3.7 (h)	2.0 (k)	41.0 42.9
$BF_3(g)$ + TEA(NB) → C(NB)	43.0	0.8 (i)	-0.5 (l)	43.3
$BF_3(g)$ + N-methyl pyrrolidine(NB) → C(NB)	45.0	-	-	-
$BF_3(g)$ + N-methyl piperidine(NB) → C(NB)	44.9	-	-	-

C = complex, NB = nitrobenzene

g to l - see table 14 sections g to l

w - $\Delta H^W = \Delta H^V - \Delta H$(solution nitrobenzene) + ΔH(solution CH_3CN)

i.e. corrected to conditions g + g → C(CH_3CN solution)

Table 13

Summary of Results - Heats of Reaction of BF_3 with Amines

Reaction Conditions	Reported Result $-\Delta H$ (Kcal/mole)	$-\Delta H^v$ (Table 12a) (Kcal/mole)	$-\Delta H^w$ (Table 12b) (Kcal/mole)	$-\Delta H^w$ (This Study) (Kcal/mole)
$BF_3(g) + CH_3CN(g) \rightarrow C(s)$	26.5	-	26.5	27.5
$BF_3(g) + TMA(NB) \rightarrow C(NB)$	38.2 40.1	42.7 44.6	41.0 42.9	43.4
$BF_3(g) + TEA(NB) \rightarrow C(NB)$	35.7	43.0	43.3	42.5
$BF_3(g) +$ piperidine$(g) \rightarrow C($piperidine$)$	33.8	-	51.1	50.9
$BF_3(g) +$ N-methyl pyrrolidine$(NB) \rightarrow C(NB)$	37.3	45.0	-	46.9
$BF_2 +$ N-methyl piperidine$(NB) \rightarrow C(NB)$	36.1	44.9	-	45.6
$BF_3(g) +$ py$(NB) \rightarrow C(NB)$	32.9	42.3	42.1	41.3
$BF_3(g) + NH_3(g) \rightarrow C(s)$	41.3	-	39.3	44.0

v - corrected to reaction conditions: Base$(g) + BF_3(g) \rightarrow C$(nitrobenzene)

w - corrected to reaction conditions: Base$(g) + BF_3(g) \rightarrow C(CH_3CN)$

Table 14

Heats of Solution of BF_3-Amine Complexes

Trial Number	Complex Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH Solution (Kcal/mole)
(a) $BF_3 \cdot CH_3CN$ in CH_3CN				
1.	6.765	0.03010	584	2.6
2.	7.316	0.03010	680	2.8
			Average	2.7 Kcal/mole
(b) BF_3·piperidine in CH_3CN				
1.	2.018	0.02719	56	0.8
(c) BF_3·piperidine in piperidine				
1.	2.841	0.02975	183	1.9
(d) $BF_3 \cdot NH_3$ in CH_3CN				
1.	2.842	0.02720	210	2.0
(e) Pyridine in nitrobenzene				
1.	10.292	0.04980	30	0.1
(f) Triethylamine in nitrobenzene				
1.	3.977	0.04980	38	0.5
(g) Pyridine·BF_3 in nitrobenzene				
1.	4.045	0.02825	340	2.4

....

Table 14 (continued)

Trial Number	Complex Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH Solution (Kcal/mole)
(h) Trimethylamine·BF_3 in nitrobenzene				
1.	1.500	0.02825	195	3.7
(i) Triethylamine·BF_3 in nitrobenzene				
1.	2.0180	0.02825	57	0.8
(j) Pyridine·BF_3 in CH_3CN				
1.	3.7738	0.02720	355	2.6
(k) Trimethylamine·BF_3 in CH_3CN				
1.	2.842	0.02720	210	2.0
(l) Triethylamine·BF_3 in CH_3CN				
1.	3.065	0.2975	48	-0.5

4.2 Fluorine-19, Boron-11, and Proton Nuclear Magnetic Resonances of BF_3-Amine Complexes

To test the frequent suggestion that spectroscopic measurements are related to adduct stability, the ^{19}F, ^{11}B and ^{1}H nmr chemical shifts of the BF_3-amine complexes were measured. The results are reported in tables 15 to 17.

Measurements of ^{19}F chemical shifts were made on solutions of the complexes in the concentration ranges 2-10 and 10-15 mole percent in CH_3CN and 4-8 mole percent in $CHCl_3$ to verify that the order of chemical shifts observed were not changed by concentration or bulk susceptibility effects.

^{11}B chemical shifts did not appear to vary significantly from complex to complex to warrant an investigation of the solvent dependence of these complexes.

The solvent dependence of the ^{1}H chemical shifts was also not investigated as these spectra were characterized by broad unresolved peaks.

Table 15

^{11}B and ^{19}F nmr of BF_3-Amine Adducts in CH_3CN Solution

Amine	^{19}F Chemical Shift (ppm)[a]	^{19}F Chemical Shift (ppm)[b]	^{11}B Chemical Shift (ppm)[c]
Ethyleneimine	154.7	154.8	19.04
α-methyl ethyleneimine	-	-	18.86
Trimethyleneimine	-	159.5	18.71
Pyrrolidine	155.8	155.9	18.81
Piperidine	157.4	157.4	18.27
Hexamethyleneimine	156.8	156.6	18.31
N-methyl ethyleneimine	159.7	-	-
N-methyl pyrrolidine	160.4	160.4	18.03
N-methyl piperidine	161.8	161.8	18.05
N-methyl hexamethyleneimine	159.8	159.8	17.80
NH_3	-	146.5[d]	19.2[d]
MMA	-	152.7[d]	17.8[d]
DMA	-	158.8[d]	18.6[d]
TMA	-	163.5[d]	17.5[d]
PY	-	148.9[d]	18.3[d]
	±0.2	±0.2	±0.2

....

Table 15 (continued)

^{11}B and ^{19}F nmr of BF_3-Amine Adducts in CH_3CN Solution

a - average of six measurements on solutions in concentration range 10-15 mole % (internal reference $CFCl_3$)

b - average of six measurements on solutions in concentration range 2-10 mole % (internal reference $CFCl_3$)

c - average of six measurements on solutions in concentration range 10-15 mole % (external reference $(CH_3O)_3B$)

d - from reference (76)

Table 16

^{19}F and ^{1}H nmr of BF_3-Amine Adducts in $CHCl_3$ Solution

Amine	^{19}F Chemical[(a)] Shift (ppm)	^{1}H Chemical[(b)] Shift (ppm)
Ethyleneimine	-	0.87
α-methyl ethyleneimine	154.4	0.90
Trimethyleneimine	160.1	0.44
Pyrrolidine	157.1	0.41
Piperidine	157.8	0.30
Hexamethyleneimine	156.9	0.20
N-methyl ethyleneimine	161.3	0.90
N-methyl pyrrolidine	162.2	0.99
N-methyl piperidine	163.3	0.71
N-methyl hexamethyleneimine	161.6	0.61

a - average of six measurements on solutions in the concentration range 4-8 mole % (internal reference $CFCl_3$)

b - ^{1}H chemical shift = ^{1}H shift(free amine) - ^{1}H shift(complexed amine)

average of two measurements on solutions in concentration range 2-6 mole %

Table 17

^{11}B - ^{19}F Coupling Constants

Amine	From ^{19}F(a) nmr Spectra	From ^{19}F(b) nmr Spectra	From ^{11}B(c) nmr Spectra
Ethyleneimine	-	12.1	11.4
α-methyl ethyleneimine	13.3	-	-
Trimethyleneimine	16.4	-	-
Pyrrolidine	16.0	16.2	16.6
Piperidine	16.8	16.7	-
Hexamethyleneimine	17.1	16.6	16.2
N-methyl ethyleneimine	-	-	-
N-methyl pyrrolidine	15.7	15.6	15.6
N-methyl piperidine	15.7	15.7	15.6
N-methyl hexamethyleneimine	16.5	16.3	16.1
NH_3	13.8(d)		
MMA	15.7(d)		
DMA	15.5(d)		
TMA	13.8(d)		
TEA	18.4(d)		

a - from data table 16 column a

b - from data table 15 column a

c - from data table 15 column c

d - results are those of Heitsch (76).

Data reported is the result of at least six measurements.

Standard deviation = ±0.1 hz

4.3. Hydrogen Bonding of Cyclicimines with $CHCl_3$

4.3.1 Calorimetric Measurements

Following the method of Campbell and Kartzmark (120) the heats of H-bonding between $CHCl_3$ and cyclicimines, $(CH_2)_nNH$ (n = 2 to 6), were determined by measuring the heats of solution of these bases in n-hexane and in $CHCl_3$. The first measurement corresponds to the heat of dilution of one mole of cyclicimine in an infinite volume of inert solvent and the second to the heat of dilution of the same base in an infinite volume of $CHCl_3$ together with the heat of formation of the (1:1) $CHCl_3$-amine complex. The difference between these two measurements should correspond to the heat of formation of the H-bond.

$$\text{Cyclohexane (l) + cyclicimine (l)} \xrightarrow{\Delta H_1} \text{cyclicimine}\left(\text{in 1000 mmoles cyclohexane}\right)$$

$$CHCl_3\text{(l) + cyclicimine (l)} \xrightarrow{\Delta H_2} \text{cyclicimine}\left(\text{in 1000 mmoles } CHCl_3\right)$$

The required heat of hydrogen bonding is:

$$\Delta H_3 = \Delta H_2 - \Delta H_1$$

Calorimetric measurements were made with the calorimeter previously used for measuring heats of reaction of amines with BF_3. The cyclicimines were transferred to the calorimetric fluid (100 ml of n-hexane or $CHCl_3$) with the syringe injector, figure 7b. The injector was calibrated by measuring the heats of solution of py and acetone in $CHCl_3$, with the results indicated in table 18.

Table 18

Heats of Solution

Trial Number	Base Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	-ΔH (Solution) (Kcal/mole)
(a) Pyridine in $CHCl_3$				
1.	12.17	0.05295	479	2.08
2.	12.17	0.03826	601	1.89

Average value = 1.98 ± 0.05

Literature value (120) = 1.95

(b) Acetone in $CHCl_3$				
1.	13.15	0.05336	529	2.16
2.	13.15	0.05345	514	2.09

Average value = 2.10 ± 0.01

Literature (121) value = 2.09

Since the results are in good agreement with literature values the method was used with confidence for all the cyclicimines. These data are given in tables 19 to 21.

Table 19

Thermochemical Data for Heats of Solution of Cyclicimines in $CHCl_3$ (ΔH_2)

Trial Number	Cyclicimine Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H_2$ (Kcal/mole)
α-Methyl Ethyleneimine				
1.	13.39	0.05502	518	2.13
2.	13.39	0.05630	488	2.05
Trimethyleneimine				
1.	14.36	0.05711	680	2.70
Pyrrolidine				
1.	11.59	0.05511	775	3.69
2.	11.59	0.05532	772	3.68
Piperidine				
1.	10.06	0.05322	540	2.86
2.	10.06	0.05609	487	2.72
Hexamethyleneimine				
1.	8.87	0.06125	335	2.31
2.	8.87	0.06125	358	2.47

Table 20

Thermochemical Data for Heats of Solution of Cyclicimines in Cyclohexane (ΔH_1)

Trial Number	Cyclicimine Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	ΔH_1 (Kcal/mole)
α-Methyl Ethyleneimine				
1.	13.39	0.05053	710	2.68
2.	13.39	0.05244	673	2.64
Trimethyleneimine				
1.	14.36	0.05749	466	1.87
Pyrrolidine				
1.	11.59	0.05068	382	1.67
2.	11.59	0.05192	374	1.68
Piperidine				
1.	10.06	0.05419	203	1.09
2.	10.06	0.05440	198	1.07
Hexamethyleneimine				
1.	8.87	0.05814	123	0.80
2.	8.87	0.05773	133	0.86

Table 21

Summary of Thermochemical Results for

Heats of H-Bonding Of Chloroform-Amine Adducts

Cyclicimine	$-\Delta H_2$ (a) (Kcal/mole)	$+\Delta H_1$ (b) (Kcal/mole)	$-\Delta H_3$ (c) (Kcal/mole)
α-methyl ethyleneimine	2.08	2.66	4.72
Trimethyleneimine	2.70	1.87	4.57
Pyrrolidine	3.67	1.67	5.36
Piperidine	2.80	1.08	3.88
Hexamethyleneimine	2.40	0.88	3.23

a - ΔH_2 for the interaction:

$$CHCl_3(l) + \text{cyclicimine}(l) \rightarrow \text{cyclicimine} - CHCl_3\ (CHCl_3\ \text{solution})$$

b - ΔH_1 for the interaction:

$$\text{Cyclohexane}(l) + \text{cyclicimine}(l) \rightarrow \text{cyclicimine}\ (\text{cyclohexane solution})$$

c - ΔH_3 for the interaction:

$$\text{Cyclicimine}\ (\text{cyclohexane solution}) \rightarrow \text{cyclicimine} - CHCl_3\ (CHCl_3\ \text{solution})$$

4.3.2 Spectroscopic Measurements

The shift in the infrared stretching frequency, $\Delta\nu(C\text{-}D) = \nu(C\text{-}D)(\text{free } CDCl_3) - \nu(C\text{-}D)(\text{complexed } CDCl_3)$ of cyclicimine-$CDCl_3$ complexes, table 22, the infinite dilution ^1H chemical shifts $\Delta\delta(^1H) = \delta(^1H)(\text{free } CHCl_3) - \delta(^1H)$ (complexed $CHCl_3$) of cyclicimine-$CHCl_3$ complexes, table 23, and the heats of H-bonding of the cyclicimine-$CHCl_3$ complexes, table 23, as established by an nmr technique were all measured in an attempt to establish the relative strengths of the H-bond between $CHCl_3$ and cyclicimines.

Table 22

ν(C-D) Frequency Shifts[a] of $CDCl_3$-Cyclicimine Complexes

Cyclicimine	$\Delta\nu$(C-D)[a] cm^{-1}
α-methyl ethyleneimine	42.4
Ethyleneimine	37.2
Trimethyleneimine	68.5
Pyrrolidine	70.5
Piperidine	69.7
Hexamethyleneimine	69.9
N-methyl ethyleneimine	48.0
N-methyl pyrrolidine	78.3
N-methyl piperidine	79.3
N-methyl hexamethyleneimine	80.5

a - $\Delta\nu$(C-D) = ν(C-D)(free $CDCl_3$) - ν(C-D)(complexed $CDCl_3$)

Shifts are reproducible to ±1 cm^{-1}.

Table 23

$\Delta\delta(^1H)$ Infinite Dilution Shifts of $CHCl_3$-Cyclicimine Complexes and their Heats of H-Bonding

Cyclicimine	$\Delta\delta(^1H)$ (a) (hz)	$-\Delta H$ (b) (Kcal/mole)
Ethyleneimine	95	1.95
Trimethyleneimine	186	2.02
Pyrrolidine	160	2.01
Piperidine	153	2.14
Hexamethyleneimine	140	2.30
N-methyl pyrrolidine	133	2.08

a - $\delta^1H = \delta(^1H)$ (free $CHCl_3$) - $\delta(^1H)$ (complexed $CHCl_3$)
Shifts are reproducible to ±5 hz and are the average of 2-3 measurements.

b - the average of 2 to 3 measurements, the average deviations of which were ±0.2 Kcal/mole

4.4 Heats of Formation of $MX_4 \cdot 2py$ and $MX_4 \cdot 2iq$ Complexes

The heats of reaction of MX_4acids with py and iq were obtained using the same calorimeter previously described for the measurement of heats of reaction of amines with BF_3.

The major error in previous measurements (122) for py is evident from our analysis of the results in table 24 in which heats for the reaction:

$$SiCl_4\ (l) + 2py\ (l) \rightarrow SiCl_4 \cdot 2py\ (c),$$

are reported for different purities of py and different methods of transferring it to the calorimeter. In each series of experiments successive amounts of $SiCl_4$ were added to the same py in which the precipitated complex was allowed to accumulate. The complex did not precipitate under reaction conditions "a" because it had hydrolyzed completely. These results show clearly that extreme care must be taken to exclude moisture, otherwise erroneously high results are obtained due to hydrolysis. Even when py was dried with CaH_2, redistilled, and transferred to the calorimeter, which had first been kept at 110° for 6 hours and then flushed with dry nitrogen while it cooled to 25°, as in trial no.1 of reaction conditions "c", an abnormally high heat was obtained. Only with second and third additions of $SiCl_4$ to the same calorimetric mixture were heats of

reaction reproducible. This demonstrates that the first measurement with a given batch of py must be discarded as the precipitated complex removes the last traces of water from the py and the calorimeter reaction chamber, and successive additions of tetrahalide should be made to the ultra-dry py and calorimeter. In the previous study (122), each experiment was made with a fresh batch of what must have been insufficiently dry py so that consistently high results were obtained.

It was more convenient and less costly to use a mixture of 40 ml of py and 60 ml of n-hexane as the calorimetric fluid. The results of the "d" series of measurements in table 24 confirmed that the heat of reaction was the same under these conditions as when pure py was used. Subsequently all measurements were made under "d" conditions. Each series started with a prerun consisting of the addition of a small amount of tetrahalide to precipitate a small amount of complex which removed the last traces of water from the calorimeter. The detailed results, given in table 25a, for the experimental conditions specified, were accumulated by the technique of successive comparison outlined on page 73, so that the final results represent the sum of all possible errors. In table 26 the average heats of formation are compared with the previous (122) values after corrections were made for the heats of condensation of the tetrahalides (4.1 Kcal/mole for SiF_4 (123);

5.2 for GeF_4 (124)), the heats of vaporization of the liquid tetrahalides (7.19 Kcal/mole for $SiCl_4$ (158); 10.0 for $SiBr_4$ (125); 8.6 for $GeCl_4$ (125); 11.4 for $GeBr_4$ (125); 9.5 for $SnCl_4$ (125)), and the heat of solution of py in n-hexane (0.2 Kcal/mole, this work).

The errors in the previous measurements for iq arose not only from the use of insufficiently dry solutions of iq in n-hexane, but also from the use of 1% solutions (by volume). Under such dilute conditions poor cooling curves are obtained and extrapolations using them to give ΔT are subject to large errors. Good cooling curves and reproducible results are obtained with 40% solutions.

Table 24

Heat of Reaction of $SiCl_4$ with Pyridine under Different Experimental Conditions

Trial Number	Reaction Conditions	$SiCl_4$ (mmole)	Reaction (ΔT, μv)	Calibration (cal/μv)	$-\Delta H$ (Kcal/mole)
1.	a	0.5664	980	0.05740	99.3
2.	a	0.5937	1220	0.04631	95.2
1.	b	0.6467	875	0.04249	57.5
2.	b	0.6217	490	0.04271	33.7
3.	b	0.6058	470	0.04271	33.1
1.	c	0.7772	910	0.03477	40.7
2.	c	0.7521	668	0.03477	30.9
3.	c	0.5841	455	0.03671	28.6
1.	c	Prerun results not recorded.			
2.	c	1.2027	520	0.07161	30.9
3.	c	0.9703	405	0.07161	29.9
4.	c	1.1788	480	0.07161	29.2
5.	c	1.0050	418	0.07161	29.8
1.	d	Prerun results not recorded.			
2.	d	0.9549	723	0.03887	29.4
3.	d	0.8417	642	0.03853	29.4
4.	d	0.7912	580	0.03853	28.2
5.	d	1.2024	878	0.04057	29.6
6.	d	0.6437	476	0.03966	29.3

....

Table 24 (Continued)

Trial Number	Reaction Conditions	$SiCl_4$ (mmole)	Reaction (ΔT,μv)	Calibration (cal/μv)	$-\Delta H$ (Kcal/mole)
7.	d	0.9042	680	0.03966	29.8
8.	d	2.0395	782	0.07586	29.1
9.	d	1.3182	511	0.07586	29.4

Average value for "d" conditions 29.4 ±0.3[e]

a - "Reagent Grade" py (said to contain a maximum of 0.1% H_2O) was used and transferred in the presence of moist air

b - py which had been refluxed for 2 hours over CaH_2 and then distilled was used and transferred in the presence of moist air

c - py which had been refluxed for 6 hours over CaH_2 and then distilled under nitrogen was used and transferred under dry nitrogen conditions

d - py as in "c", but 40 ml mixed with 60 ml n-hexane and the mixture transferred under dry nitrogen conditions

[e]standard deviation

Table 25a

Thermochemical Data for the Reaction

$$MX_4\begin{pmatrix} l \\ \text{or} \\ g \end{pmatrix} + 2\ py \xrightarrow{\begin{pmatrix} 40\ ml\ py \\ 60\ ml\ hexane \end{pmatrix}} MX_4 \cdot 2\ py(s)$$

Trial Number	Acid Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	-ΔH (Observed) (Kcal/mole)
$SiF_4(g)$				
1.	0.6641	0.04862	465	34.0
2.	0.7122	0.04856	490	33.4
3.	0.6471	0.04890	456	34.5
4.	0.6910	0.04840	500	35.0
5.	0.7419	0.04304	597	34.6
Average value 34.3 ±0.6[a]				
$SiCl_4(l)$ (see table 1 series "d")				
Average value 29.4 ±0.5[a]				
$SiBr_4(l)$				
1.	0.9575	0.04371	650	29.7
2.	0.7514	0.04303	518	29.7
3.	0.5885	0.04168	402	28.5
4.	0.8588	0.04183	542	26.4
5.	0.8307	0.03860	580	27.0
6.	0.4402	0.03854	311	27.2
7.	0.7523	0.03854	535	27.4
Average value 28.2 ±1.4[a]				....

Table 25a (Continued)

Trial Number	Acid Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	-ΔH (Observed) (Kcal/mole)
GeF_4(g)				
1.	0.7929	0.04819	728	44.2
2.	0.8000	0.04715	770	45.4
3.	0.6995	0.04970	660	46.9
4.	0.6910	0.05008	647	46.9
Average value 45.8 ±1.1[a]				
$GeCl_4$(l)				
1.	0.7478	0.04841	525	34.0
2.	0.7000	0.04841	472	32.6
3.	0.8326	0.04841	555	32.3
4.	1.6882	0.04294	1150	29.3
5.	1.5882	0.06993	680	29.9
6.	1.1458	0.06661	540	31.4
7.	1.3150	0.06661	595	30.1
Average value 31.7 ± 1.7[a]				
$GeBr_4$(l)				
1.	1.5916	0.05242	860	28.3
2.	1.6650	0.05242	910	28.6
3.	1.6080	0.06960	675	29.2
4.	1.3448	0.05891	620	27.2
5.	0.7482	0.05716	365	27.9
6.	1.7271	0.05197	959	28.9
Average value 28.3 ± 0.7[a]				

Table 25a (Continued)

Trial Number	Acid Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	-ΔH (Observed) (Kcal/mole)
$SnCl_4$(l)				
1.	1.1410	0.04633	968	39.3
2.	1.2760	0.04627	1060	38.4
3.	0.9978	0.04637	850	39.5
4.	1.2582	0.04967	975	38.5
5.	1.5860	0.06208	990	38.8
6.	1.2785	0.06177	802	38.7

Average value 38.8 ± 0.5[a]

[a]standard deviation

Table 25b

Thermochemical Data for the Reaction

$$MX_4\begin{pmatrix}l\\ \text{or}\\ g\end{pmatrix} + 2 \text{ isoquinoline} \xrightarrow[\text{60 ml hexane}]{\text{40 ml isoquinoline}} MX_4 \cdot 2 \text{ isoquinoline (s)} \qquad \Delta H$$

Trial Number	Acid Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	-ΔH (Observed) (Kcal/mole)
SiF_4(g)				
1.	0.5734	0.01952	935	31.8
2.	0.5210	0.01893	895	32.5
3.	0.3695	0.01956	600	31.8
Average value 32.0 ± 0.4[a]				
$SiCl_4$(l)				
1.	1.1118	0.06223	540	30.2
2.	1.7460	0.05803	910	30.2
3.	1.4539	0.05480	815	30.7
4.	1.3461	0.05490	763	31.1
5.	1.3123	0.05475	740	30.9
Average value 30.6 ± 0.5[a]				

....

Table 25b (Continued)

Trial Number	Acid Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	-ΔH (Observed) (Kcal/mole)
$SiBr_4$(l)				
1.	0.9563	0.04503	580	27.3
2.	0.7275	0.04646	407	26.0
3.	1.6430	0.04646	930	26.3
4.	0.8812	0.05615	395	25.2
5.	0.9575	0.05666	425	25.1
6.	0.8740	0.05892	375	25.3
Average value 25.9 ± 0.7[a]				
GeF_4(g)				
1.	0.5833	0.04368	555	41.6
2.	0.5748	0.04368	535	40.7
3.	0.4686	0.04440	420	39.8
Average value 40.7 ± 0.7[a]				
$GeCl_4$(l)				
1.	0.8808	0.06881	405	31.6
2.	0.8758	0.06881	400	31.4
3.	1.2027	0.04677	869	33.8
4.	1.2775	0.04677	850	31.1
Average value 31.9 ± 1.0[a]				

....

Table 25b (Continued)

Trial Number	Acid Added (mmoles)	Calibration (cal/μv)	Reaction Displacement	-ΔH (Observed) (Kcal/mole)
$GeBr_4$(l)				
1.	1.1875	0.05809	580	28.4
2.	0.8658	0.05809	415	27.8
3.	0.8942	0.05765	425	27.4
4.	1.3245	0.03649	1027	28.3
Average value 27.9 ± 0.4[a]				
$SnCl_4$(l)				
1.	1.2550	0.06233	736	36.5
2.	1.4118	0.06262	790	35.0
3.	0.9504	0.06262	550	36.2
Average value 35.9 ± 0.7[a]				

[a]standard deviation

Table 26

Summary of Reaction Heats of Silicon, Germanium and Tin Tetrahalides with Pyridine and Isoquinoline

Acid	$-\Delta H^a$ Observed (Kcal/mole)	$-\Delta H^b$ Gas Phase (Kcal/mole)	$-\Delta H$ ref. 122 Gas Phase (Kcal/mole)	$-\Delta H$ ref. 119,134 Gas Phase (Kcal/mole)
py complexes				
SiF_4	29.8 ± 0.6[e]	33.9 ± 0.6[e]	33.1 ± 0.8[e]	17.9
$SiCl_4$	29.0 ± 0.6	36.2 ± 0.6	58.9 ± 0.7	34.9
$SiBr_4$	27.8 ± 1.4	37.8 ± 1.4	56.1 ± 0.7	36.8
GeF_4	40.2 ± 1.1	45.4 ± 1.1	53.6 ± 1.1	
$GeCl_4$	31.3 ± 1.7	39.9 ± 1.7	50.0 ± 1.0	
$GeBr_4$	27.9 ± 0.7	39.3 ± 0.7	45.2 ± 0.4	
$SnCl_4$	38.4 ± 0.5	47.9 ± 0.5	62.4	
iq complexes				
SiF_4	27.9 ± 0.4	32.0 ± 0.4	31.9	
$SiCl_4$	30.6 ± 0.5	37.8 ± 0.5	24.6	
$SiBr_4$	25.9 ± 0.7	35.9 ± 0.7	22.8	
GeF_4	35.5 ± 0.7	40.7 ± 0.7	40.9	
$GeCl_4$	31.9 ± 1.0	40.5 ± 1.0	30.9	
$GeBr_4$	27.9 ± 0.4	39.3 ± 0.4	29.4	
$SnCl_4$	35.9 ± 0.7	45.4 ± 0.7	46.9	

....

Table 26 (Continued)

a - $MX_4\left(\begin{matrix}l\\ or\\ g\end{matrix}\right)$ + 2 amine $\left(\frac{40\text{ ml amine}}{60\text{ ml n-hexane}}\right)$ → $MX_4 \cdot 2$ amine (s)

b - equation a, corrected for heat of vaporization of acid

$MX_4(l) \rightarrow MX_4(g)$

c - $MX_4(g)$ + 2 amine $\left(\begin{matrix}\text{amine or}\\ 1\%\text{ amine}\\ \text{in n-hexane}\end{matrix}\right)$ → 2 amine (s)

d - $MX_4(g)$ + 2 amine (benzene) → 2 amine (s)

e - standard deviation

4.5 The Heat of Hydrolysis of $BI_3 \cdot CH_3CN$

$BI_3 \cdot CH_3CN$ was prepared following the method of Schmulbach (135) (mp 211-214°C Lit. (135) 198-200).

The heat of the reaction:

$$BI_3(g) + CH_3CN(g) \overset{\Delta H_f}{\rightarrow} BI_3 \cdot CH_3CN(s)$$

was determined from the relation (88):

$$\Delta H_f = A + B + C + D - E$$

where ΔH_f is the heat of formation of crystalline $BI_3 \cdot CH_3CN$ from its components in the gas phase.

A = heat of hydrolysis of BI_3.

That is, the heat for the reaction:

$$(n + 3)H_2O + BI_3 \rightarrow H_3BO_3(nH_2O) + 3HI(H_2O)$$

where

$$\Delta H(\text{hydrolysis}) = \Delta H_f^\circ(H_3BO_3)(nH_2O) + 3\Delta H_f^\circ(HI)(H_2O) - \Delta H_f^\circ(BI_3) - 3\Delta H_f^\circ(H_2O)$$

$$= (-256.5 \pm 0.03, \text{ ref. } 128) + (13.79 \pm 0.1, \text{ ref. } 129) - (10.8 \pm 0.8, \text{ ref. } 130) - 3(-68.315, \text{ ref. } 131)$$

$$= -82.2 \pm 1.4 \text{ Kcal/mole}$$

B = heat of vaporization of BI_3

= $\Delta H_f^\circ(g) - \Delta H_f^\circ(s)$

= 4.7 - (-10.8±0.8) ref. 132

= 15.5±0.8 Kcal/mole

C = heat of vaporization of CH_3CN

= 8.0±0.1 Kcal/mole ref. 114

D = heat of solution of CH_3CN

= 1.1 Kcal/mole ref. 114

E = measured heat of hydrolysis

The thermochemical data for the hydrolysis reaction is given in table 27.

Table 27

Heat of Hydrolysis of $BI_3 \cdot CH_3CN$

Trial Number	$BI_3 \cdot CH_3CN$ Added (mmoles)	Calibration (cal/μv)	Reaction Displacement (μv)	$-\Delta H$ Hydrolysis
1.	0.2698	0.05103	330	62.4
2.	0.5208	0.05068	624	60.7
3.	0.1928	0.05061	234	61.4

....

$E = 61.50 \pm 0.4$

Therefore, the heat of formation of $BI_3 \cdot CH_3CN(s)$ is:

$= -(82.2 \pm 15.5 + 8.0 + 1.1 - 61.5) \pm 2.4$

$= -45.3 \pm 2.4$ Kcal/mole.

5. DISCUSSION

5.1. Enthalpies of Reaction of BF_3 with Amines

5.1.1 Enthalpies of Reaction of BF_3 with Methylamines, py and TEA

A detailed analysis of the enthalpies involved in the reaction of the methylamines, py, and TEA with BF_3 is presented in the following thermochemical cycle.

$$\begin{array}{lllll}
\text{Amine(l)} + \text{BF}_3\cdot\text{CH}_3\text{CN}\,(\text{}_{\text{solution}}^{\text{CH}_3\text{CN}}) & \xrightarrow{\Delta H_2} & \text{BF}_3\text{-amine}\,(\text{}_{\text{solution}}^{\text{CH}_3\text{CN}}) & + & \text{CH}_3\text{CN(l)} \\
\downarrow\Delta H_3 \qquad \downarrow\Delta H_{13} & & \uparrow\Delta H_5 & & \uparrow\Delta H_6 \\
\text{Amine(g)} + \text{BF}_3\cdot\text{CH}_3\text{CN(g)} & \xrightarrow{\Delta H_4} & \text{BF}_3\text{-amine(g)} & + & \text{CH}_3\text{CN(g)} \\
\downarrow \qquad \downarrow\Delta H_7 & & \uparrow & & \uparrow \\
\text{Amine(g)} + \text{BF}_3\text{(g)} + \text{CH}_3\text{CN(g)} & \xrightarrow{\Delta H_8} & \text{BF}_3\text{-amine(g)} & + & \text{CH}_3\text{CN(g)} \\
\downarrow\Delta H_9 \qquad \downarrow\Delta H_{10} & & \uparrow & & \uparrow \\
\text{Amine*(g)} + \text{BF}_3\text{*(g)} + \text{CH}_3\text{CN(g)} & \xrightarrow{\Delta H_{11}} & \text{BF}_3\text{-amine(g)} & + & \text{CH}_3\text{CN(g)}
\end{array}$$

Ideally, gas phase enthalpies of formation, ΔH_8, should be used when comparing the relative basicities of amines with BF_3. This is not possible, however, as these complexes either decompose or do not dissociate reversibly at the temperature required to measure their enthalpies of sublimation. Since it is impossible at this stage to obtain ΔH_5, the enthalpy of sublimation plus the enthalpy of solution of the complex, enthalpies of

formation of complexes are compared for the following conditions:

$$\text{Amine(g)} + BF_3\text{(g)} \xrightarrow{\Delta H_8 + \Delta H_5} BF_3\text{-amine}\ (\text{}^{CH_3CN}_{\text{solution}}) \cdots\cdots \quad (24)$$

where the reactants are referred to gas phase conditions and a dilute solution of the complex in CH_3CN is formed. These enthalpies are obtained from the measured enthalpies derived for the following processes:

$$BF_3\text{(g)} + CH_3CN\text{(l)} \xrightarrow{-\Delta H_6 + \Delta H_{13} + \Delta H_7} BF_3 \cdot CH_3CN\ (\text{}^{CH_3CN}_{\text{solution}}) \quad (25)$$

$$\text{Amine(l)} \xrightarrow{\Delta H_3} \text{Amine(g)} \cdots\cdots \quad (26)$$

$$\text{Amine(l)} + BF_3 \cdot CH_3CN\ (\text{}^{CH_3CN}_{\text{solution}}) \xrightarrow{\Delta H_2} BF_3\text{-amine}\ (\text{}^{CH_3CN}_{\text{solution}}) \quad (27)$$

by the summation: 25 + 27 - 26. These data are listed in tables 28 and 31.

There is little information in the literature to test the assumption that ΔH_5 is constant for complexes similar to those studied. It has been suggested on a number of occasions (46,47,141),however, that the enthalpies of sublimation of a closely related series of molecular addition compounds are the same. ΔH_5 is related to the enthalpy of sublimation through the enthalpy of solution of the complexes. It is expected that changes in solvation energies, ΔH_5, from complex to complex in a closely related series will be smaller than changes in crystal lattice energies.

Finally, when enthalpies of reaction are used as measures of acidity or basicity, comparisons are usually made for a series of bases reacting with a given acid or vice versa. In these cases when ΔH_8 or $\Delta H_8 + \Delta H_5$ is used as the measure of donor or acceptor power a scale of basicity based upon the thermodynamic stability of the adducts is established. The strength of the donor-acceptor linkage is simply the energy, ΔH_8, required to dissociate the gaseous adduct into the separate gaseous species. It follows from the results summarized in table 28 that the thermodynamic stabilities of the adducts are in the order: MMA≃DMA>TMA≃NH_3 and TMA≃TEA≃py.

Table 28*

Base	ΔH_3	$-(-\Delta H_6+\Delta H_{13}+\Delta H_7)$	$-(\Delta H_2)$	$-(\Delta H_8+\Delta H_5)$
MMA	0	16.9 ± 0.1	33.2 ± 0.3	50.1 ± 0.3
DMA	0	16.9 ± 0.1	33.0 ± 0.4	49.9 ± 0.4
TMA	0	16.9 ± 0.1	26.5 ± 0.4	43.4 ± 0.4
NH_3	0	16.9 ± 0.1	27.1 ± 0.4	44.0 ± 0.4
TEA	7.8 ± 0.1	16.9 ± 0.1	17.8 ± 0.6	42.5 ± 0.7
py	9.6 ± 0.1	16.9 ± 0.1	14.8 ± 0.4	41.3 ± 0.5

*All enthalpies are in Kcal/mole.

The sum $\Delta H_8 + \Delta H_5$ or ΔH_8, however, differs from the actual strength of the B-N linkage in these BF_3-amine adducts by the sum of the reorganization energies ΔH_9 and ΔH_{10} of the amine and BF_3, respectively. The first of these energies decreases in the order NH_3>MMA>DMA>TMA, as suggested from the reverse

order of adduct stability of the phenol (28), methanol (60), and I_2 (28) complexes and is assumed to vary with the coordinating acid. Drago et al (34) and Ibers and Shriver (35) have both recently suggested that the reorganization energy of BF_3, ΔH_{10}, varies with the attached base (see pages 19 to 21). If the strength of the B-N link, ΔH_{11}, were used to establish a scale of basicity, the results would refer to the process: amine*(g) + BF_3^*(g) → BF_3-amine(g), where comparisons would be for the basicity of a reorganized state of the base in the gas phase, amine*(g), with respect to a reorganized state of the acid in the gas phase, BF_3^*(g). Since the extent of reoganization of BF_3 differs with the coordinated base, the scale of basicity established from B-N bond energy considerations would refer to a series of hypothetical reorganized acids such as BF_3^{*1}(g), BF_3^{*2}(g) etc. Such an indefinite scale would not be useful; therefore, ΔH_8 or the sum $\Delta H_8 + \Delta H_5$, rather than ΔH_{11} was chosen as a more reasonable measure of basicity.

A proper assessment of the factors contributing to base strength requires an interpretation of an equation of the type:

$$\Delta H_8 = \Delta H_{11} - \Delta H_9 - \Delta H_{10}$$

$$= \Delta H_{\text{B-N bond}}^{\text{energy}} - \Delta H_{\text{amine}}^{(\text{reorganization}} - \Delta H_{BF_3}^{(\text{reorganization}} \quad (28)$$

Little information is available about the actual strength of the B-N bond in BF_3-amine adducts, since the strength of this bond can be related to the overall enthalpy of reaction only if the reorganization energies of the amine and of BF_3 are known. Since accurate values for these energies are not available, it is proposed to establish the relative strengths of B-N bonds by comparing enthalpies for BF_3-amine complexes obtained in this work with gas phase enthalpies of formation of corresponding TMB adducts. In order to clarify the comparison shown in table 29, the factors affecting the measured enthalpies will be discussed.

Table 29

Base	$-(\Delta H_8+\Delta H_5)$ BF_3 (Kcal/mole)	$-(\Delta H_8)$ TMB ref. 36 (Kcal/mole)
NH_3	44.0 ± 0.4	13.7 ± 0.1
MMA	50.1 ± 0.4	17.6 ± 0.1
DMA	49.9 ± 0.4	19.3 ± 0.1
TMA	43.4 ± 0.4	17.6 ± 0.1
TEA	42.5 ± 0.7	10.0 -
py	41.3 ± 0.5	17.0 ± 0.1

5.1.1.1 Factors Affecting the Measured Enthalpy of Reaction

The donor sequence: NH_3<MMA<DMA>TMA, towards TMB has been interpreted in terms of a balance between steric interference of the alkyl groups on the nitrogen atom

(F-strain) and inductive effects (136). Inductive effects alone would produce a monatomic increase in base strength in the sequence (28): TMA>DMA>MMA>NH_3. This is the basicity order towards I_2 (28) and methanol (60) where steric effects should be minimal. On the other hand, the presence of a steric effect should produce the opposite order of base strength (136). With boron alkyls and amines containing large substituents, steric interaction of groups on the acid and base become important (F-strain) and other sequences are observed. For example, with tri-t-butyl-borane as the reference acid, base strengths of the ethylamines, as measured by displacement reactions, diminish in the order: NH_3>MEA>DEA>TEA (136).

Drago (28) has calculated the relative magnitudes of steric and electronic energies in I_2 and TMB methylamine complexes. He found that the order of adduct stability: TMA>DMA>MMA>NH_3, towards I_2 was explainable in terms of electronic energies only (i.e. the change in inductive effect of the base through the series). When steric interactions occur in the acid - base pair, calculated enthalpies of adduct formation should be larger than measured. Indeed, the calculated enthalpy of interaction for the TMB - TMA adduct is -25.8 Kcal/mole, compared to a measured value of -17.6. The discrepancy is attributed to an F-type steric strain. The magnitude of this strain energy was predicted

to be 7.8 Kcal/mole by Brown (160) from combustion data on a hydrocarbon which is structurally analogous to the adduct, in excellent agreement with Drago's calculated strain energy of 8.2 Kcal/mole. A difference of 1.5 Kcal/mole between the calculated and observed enthalpies of formation of TMB - DMA was also attributed to steric strain. Whereas the calculated enthalpies of formation of TMB-methylamine adducts, based upon the electronic energies of the B-N bond formed, are in the same order as with I_2 as acceptor, the observed values are in the order: NH_3< MMA<DMA>TMA. This deviation from the calculated order was attributed to steric strain, and it emphasizes the importance of steric effects in producing changes in stability orders of methylamine complexes from the inductively controlled order towards I_2. It is the differences in sequences of adduct stability of the methylamines with TMB and BF_3 which forms the basis for the discussion to follow.

Since the methyl groups on TMB are comparable in size to an iodine atom, one might expect that steric effects would be greater in TMB complexes than in BF_3 complexes. To a first approximation the order of adduct stability should lie closer to the inductively controlled order: TMA>DMA>MMA>NH_3 for BF_3-methylamine complexes than for TMB-methylamine complexes. Yet towards BF_3 the order of adduct stability is: MMA $\cong$ DMA>TMA $\cong$ NH_3. Therefore, the

fact that the enthalpies of reaction of BF_3 with NH_3 and TMA are almost the same, whereas they are substantially different in the case of TMB, strongly suggests that BF_3 has greater steric requirements for F-strain than TMB in these adducts.

To examine this suggestion critically, consider the difference between the enthalpies of formation of TMA adducts of BF_3 and BCl_3. If it is assumed that BF_3 is strongly hindered in its TMA adduct then surely BCl_3 would be even more sterically hindered and the enthalpy of formation of BCl_3·TMA should be lower than that of BF_3·TMA were it not for the fact that BCl_3 is a stronger electron pair acceptor than BF_3. Hence, the difference between their enthalpies of formation of 8.7 Kcal/mole (45) might include differences in steric energy in addition to differences due to the stronger acceptor power of BCl_3. A similar difference of 7.8 Kcal/mole was observed between the enthalpies of formation of their py adducts (83), and 7.3 Kcal/mole between the enthalpies of formation of their CH_3CN adducts (114), where steric effects should be smaller or even negligible. It would seem reasonable, therefore to assume that the marked difference between the enthalpies of formation of BF_3·TMA and BF_3·DMA cannot be attributed to a steric energy of the type invoked for TMB-methylamine complexes.

Moreover, if methyl and ethyl groups have similar inductive effects(45), one would expect similar

enthalpies of formation for the TEA and TMA adducts of either BF_3 or TMB. Although this is observed when BF_3 is the acceptor, it is certainly not the case for TMB. Thus, if F-strain were operating in BF_3-methylamine adducts, one would have anticipated an even lower enthalpy of formation for BF_3·TEA than for the TMB - TEA adduct, contrary to experimental results.

Complexes of BF_3 with tertiary cyclicimines have enthalpies of formation which are about 5 Kcal/mole less than those of the corresponding secondary cyclicimine derivatives. A similar difference 6 Kcal/mole is evident when the enthalpies of formation of BF_3·TMA and BF_3·DMA are compared and this seems to be typical of the difference between the enthalpies of formation of secondary and tertiary amine adducts with BF_3. It is remarkable that the orders of adduct stability of BF_3-cyclicimine complexes; 4->5->6->3-membered ring, and BF_3-tertiary cyclicimine complexes; 4->5-~6->3-membered ring (table 31, page 137) are so similar and yet previous arguments suggested that a strong steric effect is operating in tertiary amine complexes. Evidently, this cannot be an F-strain effect: firstly because the order of adduct stability of TMB-tertiary cyclicimine complexes, where strong F-strain probably operates, is 3->4->5->6-membered ring; secondly because the magnitude of the strain effect in BF_3-tertiary amine adducts is equal to or larger than in TMB-tertiary

amine adducts, as deduced from differences in orders of stability of the methylamine adducts of the two acceptors.

To decide whether or not a similar steric effect is present in primary or secondary BF_3-amine adducts, enthalpies of formation of BF_3-methylamine adducts have been calculated using Drago's double scale enthalpy equation (28), $-\Delta H = E_A E_B + C_A C_B$, and the values are compared with experimental results in table 30.

Table 30

Calculated and Experimental Heats of Formation of Adducts of BF_3 and TMB with Methylamines

Amine	Amine Parameters (28)		$-\Delta H(g)^a$ BF_3(Calc.)[b]	$-(\Delta H_8+\Delta H_5)$ BF_3	$-\Delta H(g)^c$ TMB(Calc.)	$-\Delta H_8$ TMB
	C_B	E_B	(Kcal/mole)	(Kcal/mole)	(Kcal/mole)	(Kcal/mole)
NH_3	1.34	3.42	22.1	44.0	13.75	13.75
MMA	1.19	6.14	26.0	50.1	17.64	17.64
DMA	0.94	8.68	27.8	49.9	20.72	19.26
TMA	0.59	11.61	30.0	43.4	25.82	17.62

[a] BF_3 parameters (140); $C_A = 1.98$, $E_A = 11.6$

[b] $\Delta H_{(calculated)} - (\Delta H_8+\Delta H_5) = \Delta H_{(solution)}$ (complex(g)→complex(CH_3CN)

[c] TMB parameters (28); $C_A = 1.76$, $E_A = 5.77$

Because of the fixed nature of the parameters associated with each acid and base, enthalpies calculated with these parameters should be independent of changes in steric effects and reorganization energies and, therefore differences in enthalpies within a series should be related only to the different energies of the B-N bonds in these adducts.

From table 30 it is evident that (i) the predicted increase in the enthalpy of reaction between $BF_3 \cdot NH_3$ and $BF_3 \cdot MMA$ of 4 Kcal/mole is close to the 6 Kcal/mole experimental value, (ii) the predicted increase of 1.8 Kcal/mole between the enthalpies of formation of $BF_3 \cdot MMA$ and $BF_3 \cdot DMA$ is not observed, and (iii) the predicted difference between the enthalpies of formation of $BF_3 \cdot DMA$ and $BF_3 \cdot TMA$ is 2.2 Kcal/mole and experimentally it is -6.5 Kcal/mole. These comparisons suggest that steric strain is probably absent in the $BF_3 \cdot NH_3$ and $BF_3 \cdot MMA$ adducts, a 1.8 Kcal/mole steric strain might be present in the $BF_3 \cdot DMA$ adduct, and an 8.7 Kcal/mole steric strain occurs in the $BF_3 \cdot TMA$ adduct. It is interesting that an analysis of the predicted and observed values of enthalpies of formation of TMB-methylamine adducts suggests that steric strains of 1.5 and 8.2 Kcal/mole are present in TMB·DMA and TMB·TMA adducts (table 30), respectively. These values are remarkably similar to steric strains predicted for $BF_3 \cdot DMA$ and $BF_3 \cdot TMA$.

To summarize the preceeding discussion briefly, it was first assumed that F-strain should be larger in TMB-methylamine adducts than in BF_3-methylamine adducts because methyl groups are much larger than fluorine atoms, but on this basis it was not possible to account for the large differences between the enthalpies of formation of primary, secondary and tertiary BF_3-amine adducts; nor could these large differences be accounted for on the basis of calculated electronic energies using Drago's method (table 30).

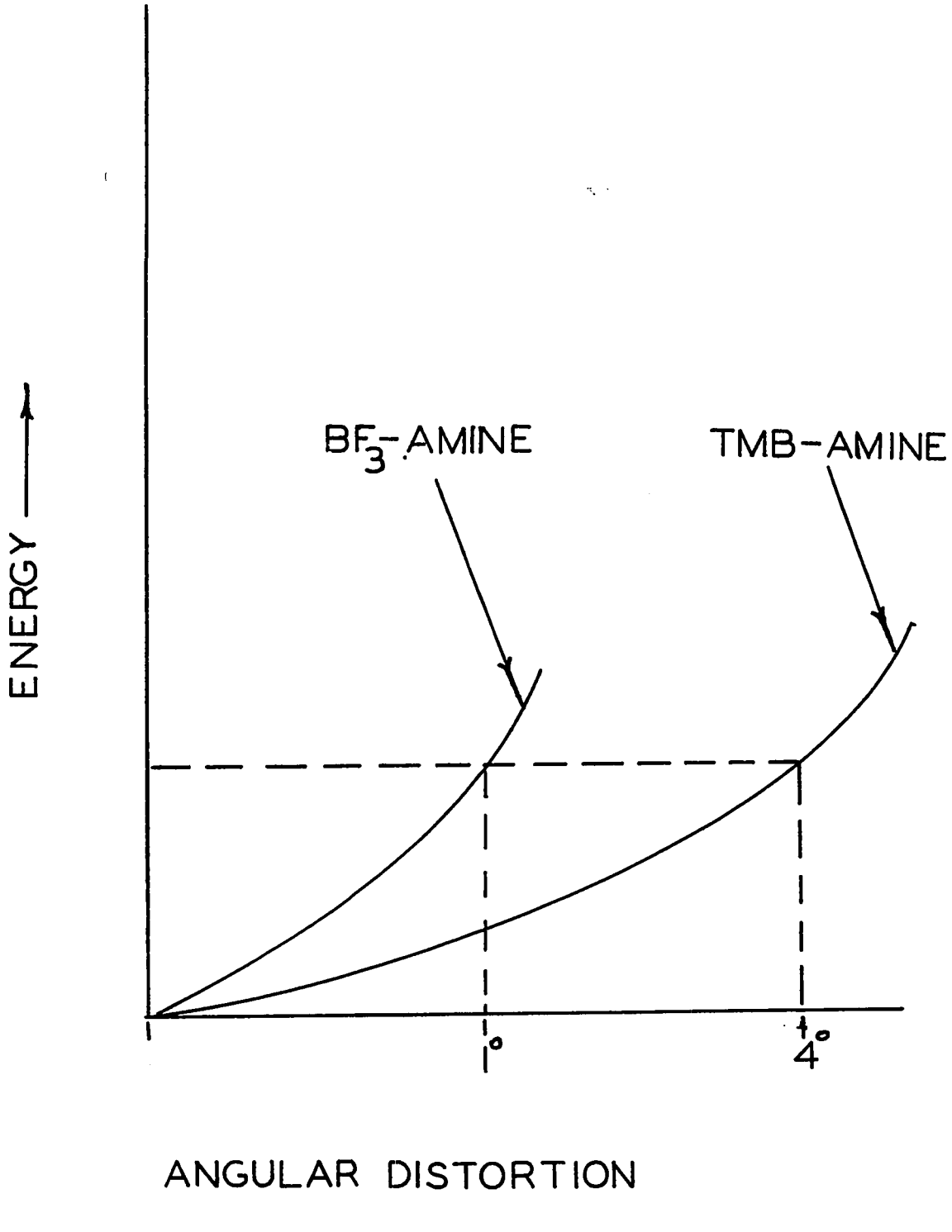
In order to explore the nature of the steric effect that appears to operate in BF_3·DMA and BF_3·TMA, an attempt will now be made to explain the differences in basicity order towards BF_3 and TMB on the basis of equation 28. If the reorganization energy of methylamines towards TMB and BF_3 are assumed to be similar, the large differences in enthalpies of formation can be attributed to: (i) increased reorganization energies of BF_3 while B-N bond energies remain constant, (ii) decreased B-N bond strengths while reorganization energies of BF_3 are constant, or to both (i) and (ii). As BF_3 reorganizes to a greater extent, its acceptor power should increase (35) and so should the B-N bond energy. The lower than expected enthalpies of formation of the BF_3-tertiary amine adducts, however, implies that the B-N bond energy remains approximately constant with increased reorganization of BF_3, as evident from equation 28.

This behaviour can be tentatively explained in the following way. When BF_3 coordinates with sterically unhindered bases, it might reorganize to an extent which would allow the maximum B-N bond strength for the minimum reorganization energy. With sterically hindered bases, however, a compromise must be struck between the BF_3 reorganization energy, steric effects and a maximum B-N bond energy. Steric effects might force BF_3 to reorganize more than is required for a given B-N bond energy to reduce this strain. It is this additional reorganization energy which is probably responsible for the lower enthalpy formation of BF_3·TMA compared to BF_3·DMA.

The way in which the reorganization energies of BF_3 and TMB might vary in their amine adducts is depicted in figure 10.

Although BF_3 might not be distorted by F-strain to as large an extent as is TMB, BF_3 might require more energy per degree of distortion because of its larger reorganization energy. Perhaps the same energy might be required to distort BF_3 1° as is necessary to distort TMB 4°. Hence, for a particular base, if BF_3 is distorted 1° and TMB only 3°, the latter acid would be energetically less strained. This might be the case for the TMA adducts of both acids. When the enthalpies of formation of their TEA and TMA adducts are compared, however, BF_3·TEA has the same enthalpy of formation as BF_3·TMA whereas the TMB·TEA

Figure 10 Suggested variation of reorganization energy with angular change of BF_3 and TMB in their amine adducts.


ENERGY
BF3-AMINE
TMB-AMINE
1°
4°
ANGULAR DISTORTION

adduct is unstable. It is tempting to use the proposal in figure 10 to suggest that because of its smaller size BF_3 experiences approximately the same strain in its TEA and TMA adducts. On the other hand because of its large size TMB might experience a larger angular distortion in its TEA adduct than in its TMA adduct.

Variations in the reoganization energy of BF_3 in its methylamine adducts are suggested by X-ray data (138). The F-B-F angle changes gradually from 107 to 111° from $BF_3 \cdot NH_3$ to $BF_3 \cdot TMA$, presumably because BF_3 is more reorganized in the latter complex. The similarity in the enthalpies of formation of these complexes suggests that the B-N bond strength does not increase with increased reorganization of BF_3, as expected from the previous discussion. The X-ray data used in making this comparison is questionable, however, because the uncertainties quoted (±2°) may render the regular variation of the F-B-F angle insignificant. There is an urgent need for accurate X-ray data.

The previous discussion is an example of the role that reorganization energies might play in contributing to the overall enthalpy of reaction. The enthalpies measured in this research can be divided into the general categories primary, secondary, and tertiary amine according to the anticipated amount of reorganization of BF_3. To relate the measured enthalpy of reaction directly to the strength of the B-N bond is not as straight forward as once expected because of the uncertainty in reorganization energy of BF_3.

It seems reasonable to suggest on the basis of a comparison of the enthalpies of formation of TMB and BF_3-methylamine adducts, that a lower than expected enthalpy of formation for a BF_3 complex is due to both an increased reorganization and a decreased B-N bond energy, both of which contribute to a lower enthalpy of formation.

5.1.2 Enthalpies of Formation of BF_3-cyclicimine Complexes

The enthalpies of reaction of BF_3 with cyclicimines, $(CH_2)_nNH$ (n = 2 to 6), and several N-methylcyclicimines, $(CH_2)_nNCH_3$ (n = 2 to 6) were corrected to the conditions employed in the comparison of enthalpies of formation of methylamine complexes, equation 1. These data are summarized in table 31 using the nomenclature of the general thermochemical cycle (page 122).

Table 31

Amine	ΔH_3[a]	$-(-\Delta H_6+\Delta H_{13}+\Delta H_7)$[a]	$-(\Delta H_2)$	$-(\Delta H_8+\Delta H_5)$
$(CH_2)_2NH$	8.7	16.9	21.5 ± 0.1	47.1 ± 0.2
$(CH_2)_3NH$	9.4	16.9	27.9 ± 0.3	54.8 ± 0.4
$(CH_2)_4NH$	9.8	16.9	25.6 ± 0.3	52.3 ± 0.4
$(CH_2)_5NH$	10.4	16.9	23.6 ± 0.3	50.9 ± 0.4
$(CH_2)_6NH$	11.5	16.9	23.5 ± 0.3	51.9 ± 0.4
$(CH_2)_2NCH_3$	5.2	16.9	17.4 ± 0.4	39.5 ± 0.5
$(CH_2)_3NCH_3$	7.2	16.9	25.1 ± 0.3	49.2 ± 0.4
$(CH_2)_4NCH_3$	8.2	16.9	21.8 ± 0.8	46.9 ± 0.9
$(CH_2)_5NCH_3$	9.3	16.9	19.4 ± 0.7	45.6 ± 0.8
$(CH_2)_6NCH_3$	10.6	16.9	21.0 ± 0.4	48.5 ± 0.5

[a] standard deviation ±0.1 Kcal/mole

5.1.2.1 Enthalpies of Formation of $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) Adducts

The enthalpies of formation of $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) adducts are in the range -47.7 to -54.8 Kcal/mole. This interval may be considered typical for BF_3 secondary amine complexes as it also includes the enthalpy of formation of $BF_3 \cdot$DMA of -49.9 Kcal/mole (table 28).

The enthalpies of formation of BF_3-cyclicimine adducts are in the order 4->5-~7->6->3-membered ring. Before any attempt is made to explain this order, the relative contributions of the reorganization energies of $BF_3 (\Delta H_{10})$, the reorganization energies of the cyclicimines (ΔH_9), and the enthalpy of formation of the B-N bonds (ΔH_{11}) to the overall enthalpies of reaction must be determined. This is not possible at this stage and the small changes in enthalpies of reaction through the series of complexes does not leave much room for speculation.

However, it is interesting to note (table 32), that this same order of adduct stability was observed with the cyclic ethers and cyclicimines towards a large variety of acceptors. Because of the different properties of the acceptor orbitals of such acids as $CHCl_3$, TMB and I_2, it is inviting to suggest that the reorganization energy of the base (ΔH_9) predominates in the overall enthalpies of formation (ΔH_8) of these cyclic donor complexes. This contrasts with the explanation of the trend observed for BF_3-methylamine

complexes (table 28) where it was suggested that the reorganization energy of BF_3 predominated.

The concept of reorganization energy as applied to cyclic donors was first dicussed by Brown (36) to explain the order of adduct stability 4->5->6->3-membered ring of cyclicimine·TMB complexes. He proposed that two effects were operating. On the one hand, the interaction of the bulky methyl groups of TMB with the α-methylene protons of the ring should increase with increasing ring size and produce an order of adduct stability 3->4->5->6-membered ring. On the other hand, the internal strain in the ring (i.e. the reorganization energy of the ring) should decrease with increasing ring size as is evident from the general chemical reactivity of these compounds (136). The combining effects have been tentatively suggested to produce the observed order.

Although this explanation was instrumental in emphasizing the importance of reorganization energy as a factor influencing orders of basicity, it does not seem applicable to cases such as the I_2-cyclic ether and $CHCl_3$-cyclic ether complexes (table 32) where steric effects should be minimal. It was from such studies that Tamres (41) suggested that the variation in the degree of hybridization of the lone pair in these cyclic bases is responsible for the basicity order observed.

Table 32

	pK_a (142)	$\Delta\nu$(OD)[e] CH_3OD (40)	ΔH_8^a BF_3 (143)	ΔH_f^a I_2 (41)	ΔH_f^a $CHCl_3$ (40)	ΔH_f^a SiF_4 (159)	$\Delta\nu$(OH)[e] Phenol (58)	ΔH_f^a Phenol (58)
Hexamethylene oxide	-2.02	122	-	-	-	-	-	-
Tetrahydropyran	-2.79	115	15.4	4.9	600	10.9	290	4.32
Tetrahydrofuran	-2.08	117	16.8	5.3	750	11.7	295	4.25
Trimethylene oxide	-	120	-	6.4	760	13.6	299	4.97
Propylene oxide	-	99	-	3.8	461	-	-	-
Ethylene oxide	-	-	-	-	-	10.7	220	3.75

	K_{ass}^b Phenol (58)	ΔH_8^a TMB (36)	$\Delta\delta_0^c$ $CHCl_3$ (100)	$\nu_a-\nu_{fl}^d$ (144)	pK_a (59)	$\Delta\nu$(OD)[e] CH_3OD (59)
Ethyleneimine	110.1	17.6	-2.24	3	8.04	221
Trimethyleneimine	200.5	22.5	-3.05	21	11.29	259
Pyrrolidine	195.0	20.4	-2.68	17	11.27	262
Piperidine	167.4	19.7	-2.58	12	11.22	259
Hexamethyleneimine	147.4	-	-2.56	8	-	-
DMA	-	19.2	-2.51	-	-	-

[a] Kcal/mole

[b] litres/mole

[c] $\Delta\delta_0$ = δ(free $CHCl_3$) - δ(complexed $CHCl_3$)

[d] $\nu_a-\nu_{fl}$ = ν_a(association TEA) - ν_{fl}(self association)
= a measure of association due to donor ability of lone pair

[e] cm^{-1}

Lippert and Prigge (144) presented a more thorough discussion of the properties of the lone pair in these cyclic ethers. For $(CH_2)_2O$, they claimed that the nonbonded orbitals on the oxygen atom did not hybridize but remained as pure s and p orbitals. The overlap potential of these non-hybridized orbitals should be less than those of the approximately sp^3 hybridized orbitals of the larger rings and hence $(CH_2)_2O$ should be a weaker base.

Geurtin (49) critized Lippert and Prigge's suggestion, however, on the basis that the pure s and p nonbonded orbitals on the oxygen atom of $(CH_2)_2O$ would likely hybridize to two equivalent sp-hybrids perpendicular to the plane of the ring; and, if Lippert and Prigge's suggestion that maximum overlap results from a hybrid orbital of s-character of about 0.5 is correct, $(CH_2)_2O$ would be the strongest base in the series. As this was not observed experimentally, Geurtin proposed that the order of adduct stability of his $SiF_4 \cdot 2$ ether complexes of 4->5->6->3-membered ring is explainable on the basis that overlap is greatest between the sp^3d^2 hybrid of silicon and the lone pair of the 4-membered ring base, making this adduct the most stable.

This type of explanation of the relative basicities of cyclic donors does not seem general, however, firstly because the relative magnitudes of overlap integrals of

cyclic bases should change with different acceptors and yet the same order of base strength 4-~5-~6-~7->3-membered ring is generally observed (table 32). The relative orders of basicity of the 4-,5-,6-, and 7-membered ring bases may change slightly with the coordinated acid but differences are usually very small. These bases are almost always stronger donors than the 3-membered ring base, however.

Secondly, the strength of the donor-acceptor linkage has been estimated simply in terms of the overlap integral. From our earlier discussion (page 30) the overlap integral should be a good measure of the covalent contribution to the bond energy but it neglects the charge transfer and electrostatic energies that are also important in adduct formation.

Finally, discussions such as those of Geurtin and of Lippert and Prigge attempt to explain extrinsic parameters such as heats of adduct formation in terms of an intrinsic parameter such as the strength of the adduct linkage, although the relationship between the two may be only an empirical one. It has already been mentioned in connection with the enthalpies of formation of BF_3-methylamine adducts that a good correspondence between the strength of the B-N linkage and the overall enthalpy of reaction is obtained only when the reorganization energies of the donor and acceptor are negligible or when one of them dominates.

In the case of these cyclic donors it seems reasonable to attempt an explanation of the overall enthalpy of reaction in terms of the factors which affect the reorganization energy of the base, as most data (table 32) suggests that it is this factor which dominates enthalpies of formation.

5.1.2.1.1 Factors affecting Reorganization Energies of Cyclicimines

Values of coupling constant $J(^{13}C\text{-}H)$ have been related to the amount of s-character in the C-H bond (101). In the case of cyclic donors, $J(^{13}C\text{-}H)$ values suggest that the s-character in such bonds decreases with increasing ring size. Maximum s-character is associated with the three atom ring, followed by a marked decrease to the four atom ring and then slowly decreasing with increasing ring size. The calculated s-character (101) corresponds to an sp^2 state for the carbon orbital towards hydrogen in the 3-membered ring, while for the remaining ring it is best described by an sp^3 state. This interpretation of s-character is supported by C-H bond angle data (22), $^{13}C\text{-}H$ bond length data (22) by $\nu C\text{-}H$ (144) and $\nu C{=}O$ stretching frequencies (146).

The s-character is higher in the $^{13}C\text{-}H$ bonds of cyclic ethers than of cyclopropanes as deduced from $J^{13}C\text{-}H$ coupling constants (101). Isovalent hybridization arguments suggest therefore that the carbon orbital towards nitrogen in

the cyclicimine bases must use less s-character. This conclusion follows from Bent's principle (22) where substitution of a more electronegative nitrogen atom for a ring carbon atom causes the neighbouring carbon atoms to withdraw s-character from the C-N bonds and to transfer this s-character to the C-H bonds. The nitrogen atom in its external orbitals to hydrogen and the lone pair must therefore use at least as much s-character as carbon does to its attached hydrogen atoms, otherwise the lower energy nitrogen orbitals used in bonding with the ring carbons would cause a larger orbital energy mismatch and a weaker bond (21). Furthermore, lone pair orbitals tend to "seek" s-character. The variation of s-character in the nitrogen lone pair as predicted by this approach should be sp^2 for ethyleneimine and approximately sp^3 for the higher membered ring bases (147-149). These changes in s-character are reflected in the decreasing ionization potential of these bases with increasing ring size (table 1).

A second effect might operate to influence the relative reorganization energies of these bases. Consider the possibility that as the base reorganizes to the approximately sp^3 state of the coordinated condition, s -character is transferred from the lone pair to the C-N ring bonds and the N-H bond. The fact that the change in infrared stretching frequency of the N-H bond increases with increasing ring size (table 2) suggests that most of the s-character is transferred to the C-N ring bonds in the smaller ring adducts. This increased s-character should widen the C-N-C bond angle,

weakening the C-N bond in the smaller ring through decreased overlap and greater C-N orbital energy mismatch. In the larger rings the change in s-character as well as the consequences of such changes should be less severe.

The two effects discussed above probably combine to produce an order of base reorganization energy 3->4-~5-~6-~7-membered ring. If the base reorganization energy, ΔH_9, of the cyclicimines dominates the overall enthalpy of reaction in their BF_3-cyclicimine adducts, enthalpies should be in an order inverse to these energies, i.e. 4-~5-~6-~7->3-membered ring, as is observed.

5.1.2.2 Enthalpies of Formation of $BF_3 \cdot (CH_2)_nNCH_3$ (n = 2 to 6) Adducts

The enthalpies of formation of $BF_3 \cdot (CH_2)_nNCH_3$ (n = 2 to 6) adducts are in the order, 4-~7->>5-~6->3-membered ring. This order may not be significantly different from the order of enthalpies of formation of the unmethylated cyclicimine-BF_3 complexes; 4->5-~7->6->3-membered ring. Because of the magnitudes of the uncertainties involved in the enthalpies of formation of $BF_3 \cdot (CH_2)_nNCH_3$ (n = 2 to 6) adducts it is difficult to make a distinction between the relative magnitudes of enthalpies of formation of the 4-,5-,6-, and 7-membered ring BF_3 adducts. Certainly, it is obvious that for both series, within the assumption that, ΔH_5, is constant, the 3-membered ring has an enthalpy of formation which is lower than that of the 4-,5-,6-, and 7-membered

ring bases.

In fact an approximate difference of about 5 Kcal/mole between the enthalpies of formation of analogous pairs of complexes in the two series is observed. It is remarkable that the difference between the enthalpies of formation of secondary and tertiary amines is maintained through the entire sequence of adducts (see page 131), in sharp contrast with TMB as acceptor (38). The enthalpies of formation of TMB·$(CH_2)_nNCH_3$ (n = 2 to 6) adducts decrease with increasing ring size as expected from a strong F-strain interaction between the bulky methyl groups on TMB, the α-methylene ring protons and the ring methyl group.

The $\Delta\nu$(OD) shifts of the CH_3OD-N-methyl cyclicimine adducts are in the order 4-≈5-≈6->3-membered ring base (59), similar to that observed for the analagous BF_3 adducts.

5.2 Spectroscopic Measurements on BF_3-cyclicimine Complexes

5.2.1 Fluorine-19 Nuclear Magnetic Resonance Results

The ^{19}F resonance absorptions of BF_3-amine complexes appeared as strong quartets. The splitting pattern observed is due to the coupling of the more abundant ^{11}B isotope with the $\frac{1}{2}$ spin of the ^{19}F atoms. All four peaks are not of equal intensity because of overlap of spectra of molecules containing the ^{11}B and ^{10}B isotopes (107). The observed ratio of peak intensities is about 1:1.2:1.2:1.

Fluorine-19 chemical shifts of $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) complexes are in the order 4->6->5->7->3-membered ring (tables 15 and 16), suggesting this to be the order of their adduct stability. This order differs from the thermodynamic order of stability of these complexes, 4->5-≅7->6->3-membered ring (table 10) and from the order of adduct stability of these cyclic donors towards other acceptors (table 32).

Saika and Slichter (74) proposed that the ^{19}F chemical shift is related to the paramagnetic screening constant of the ^{19}F atom, which in turn should be related to the Π-bond character in the B-F bond. The decrease in Π-bond character on complex formation should increase the paramagnetic screening constant of the ^{19}F atom and thereby produce the observed upfield chemical shift. As BF_3 reorganizes to different extents in a series of

related molecular addition compounds (34,35) one might observe a dependence between the amount of reorganization, or Π-bond character destroyed, and the ^{19}F chemical shifts. Hence, rather than reflecting the thermodynamic stabilities of the BF_3-cyclicimine adducts, ^{19}F chemical shifts are probably a measure of the extent of reorganization of BF_3 in these adducts.

This latter energy, ΔH_{10}, would be reflected in the overall enthalpy of formation of these adducts, $\Delta H_8 + \Delta H_5$, provided it varies in the same way as does the reorganization energy, ΔH_9, of the cyclicimine bases, since it was concluded in the previous section that the latter energy dominates the overall enthalpy of formation. This does not appear to be entirely the case as ^{19}F-chemical shifts are in the order 4->6->5->7->3-membered ring, while the overall enthalpies of formation of cyclicimine-BF_3 adducts are in the order 4->5-≙7->6->3-membered ring (table 31).

This lack of correlation of ^{19}F chemical shifts and enthalpies of formation of BF_3-amine adducts is also evident in methylamine-BF_3 complexes (76), where ^{19}F chemical shifts are in the order: TMA>DMA>MMA>NH_3, while enthalpies of formation are in the order: DMA≙TMA>MMA≙NH_3 (table 28). The marked deviation from the inductively controlled order of enthalpies of formation of these BF_3-methylamine adducts:

TMA>DMA>MMA>NH_3, (page 126) was previously attributed to the "additional" reorganization energy of BF_3, and this latter energy is reflected in the lower enthalpies of formation of these adducts. It is also evident in the increased ^{19}F chemical shifts of these adducts with increasing methyl substitution.

The secondary cyclicimine-BF_3 complexes have enthalpies of formation and ^{19}F chemical shifts similar to DMA·BF_3 and the tertiary cyclicimine-BF_3 adducts have ^{19}F chemical shifts and enthalpies of formation which are similar to BF_3·TMA. This supports the idea that steric effects force BF_3 to reorganize and exhibit a ^{19}F shift out of proportion to the observed enthalpy of adduct formation (page 134).

On the other hand, Mooney (77) has proposed a direct relationship between the enthalpies of formation and ^{19}F chemical shifts of BF_3 complexes of ethers and ketones. It is not clear, however, why an intrinsic parameter of BF_3, such as its ^{19}F chemical shift, should be simply related to the overall enthalpy of formation, which is a complex function of the reorganization energy of the base, the reorganization energy of BF_3 and the energy of formation of the donor-acceptor bond. Previously (page 147) it was suggested that the ^{19}F chemical shift is related to the reorganization energy of BF_3 which is only one of the energies involved in the enthalpy of

adduct formation. Furthermore, a ^{19}F chemical shift of 158.6 ppm is observed for both the $BF_3 \cdot Me_2O$ (78) and $BF_3 \cdot DMA$ (76) adducts. Although enthalpy data is not available for these two complexes, BF_3-amine complexes are usually more stable than BF_3-ether complexes (111). Thus, the fact that BF_3 complexes of Me_2O and DMA have similar ^{19}F shifts suggests again that the relationship between ^{19}F chemical shifts and enthalpies of adduct formation is not general.

The ^{19}F chemical shifts of the tertiary cyclicimine complexes are in the order 6->5->7->3-membered ring (tables 15 and 16). Although the ^{19}F chemical shift of the 4-membered ring-BF_3 complex was not measured, the observed order of ^{19}F chemical shifts still differs from the order of thermodynamic stability of these complexes of 4-~7-~5-~6->3-membered ring base. This is another example of the lack of correlation between ^{19}F chemical shifts and heats of adduct formation.

5.2.2 Proton Nuclear Magnetic Resonance Measurements

Proton nmr spectra of BF_3-cyclicimine adducts are characterized by broad unresolved peaks. It is well known that the nitrogen nucleus in BF_3 coordination compounds generally exhibits an appreciable quadrupole moment. The short spin lattice relaxation time of this nucleus is responsible for the broad absorption lines observed (70).

By contrast, the spectra of the cyclicimines are well-defined. The resonances of the α protons are shifted downfield upon coordination, and it is this shift which is reported in table 16.

The magnitude of these chemical shifts decreases in the order 3->4->5->6->7-membered ring for the $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) complexes, which is significantly different from the order of their enthalpies of adduct formation: 4->6-~7-> 5->3-membered ring. That there should be any correlation of chemical shifts and enthalpies of adduct formation has never been proved. Miller and Onyszchuk (73) found that the methyl proton chemical shifts of $TMA \cdot BX_3$ complexes (X = F, Cl, Br) increased in the order Br>Cl>F. This order has never been verified thermochemically. However, there is a rough linear correlation between ^1H chemical shifts and enthalpies of formation of $BX_3 \cdot CH_3CN$ adducts (73).

Wilson and Worrall (141) measured the enthalpies of formation and ^1H chemical shifts of 4-Et-py-ALX_3 complexes (X = Cl, Br, I) and found that ^1H chemical shifts occurred to low field in the order Cl→Br→I, while gas phase enthalpies are in the order Cl = Br I. They indicated that the ^1H chemical shifts of these complexes are complicated by ring current effects, paramagnetic shielding and possibly weak hydrogen-halogen interactions and are therefore not directly related to the thermochemical stability of these complexes.

Disagreement between nmr and thermochemical measurements is further evident from a comparison of the order of downfield ^{1}H chemical shifts: TMA>DMA>MMA>NH_3 of BF_3-methylamine complexes (table 15) with the order of their thermochemical stabilities: DMA≅MMA>TMA≅NH_3 (table 28). Finally, Coyle and Stone (68), from ^{1}H nmr measurements on a large series of molecular addition compounds found that the relationship of ^{1}H chemical shifts to enthalpies of adduct formation was certainly not general.

The ^{1}H chemical shifts of the cyclicimine bases can be best explained using the same type of argument previously used to explain ^{19}F chemical shifts in $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) complexes. That is, the ^{1}H chemical shift is an intrinsic parameter of the base rather than the acid and should therefore be related to the extent of reorganization of the base. The factors affecting the reorganization energies of these cyclic bases have been previously discussed (page 143) and it is noteworthy that ^{1}H chemical shifts decrease in the order of decreasing reorganization energy of these bases: 3->4-∿5-∿6-∿7-membered ring. Furthermore, it was suggested in the discussion of enthalpies of formation of BF_3-cyclicimine bases that reorganization energies of these bases dominate the overall enthalpy of formation of their adducts (equation 28). Therefore enthalpies of formation should follow an order opposite to the reorganization energies of these bases or 4-∿5-∿6-∿7->3-membered ring, as is observed.

Perhaps, by comparing ^{19}F chemical shifts and ^{1}H chemical shifts of $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) complexes, one can derive information on the extent of reorganization of both the acid and base in these complexes. This comparison suggests that BF_3 is reorganized least, the energy required to reorganize the base greatest, and the B-N bond energy is least in $BF_3 \cdot (CH_2)_2 NH$. Also, for the 4-,5-,6-, and 7-membered ring $BF_3 \cdot (CH_2)_n NH$ (n = 2 to 6) complexes, the enthalpy of reaction is greatest when BF_3 is reorganized most, the base reorganization energy is least and the B-N bond energy greatest.

The ^{1}H chemical shifts of the BF_3-tertiary cyclicimine complexes occur upfield by comparison with the unsubstituted complexes. This is probably due to the withdrawal by methyl groups of s-character from the nitrogen orbitals of the ring C-N bond. The ring carbon atoms compensate for this withdrawal by transferring s-character from their C-H bonds to their C-N bonds. It is this withdrawal of s-character from the C-H bonds which probably accounts for further shielding of the H-atoms and the upfield resonance position.

The ^{1}H chemical shift differences between the α-methylene protons of the free and complexed tertiary cyclicimine-BF_3 complexes are greater than those for the corresponding unmethylated analogues. Previously a relationship

between the extent of reorganization of the base and the ^1_H chemical shift was suggested. From this relationship it appears that methyl substitution produces greater reorganization energies for the larger ring bases. In the unsubstituted cyclicimines changes in s-character in the nitrogen lone pair orbital are compensated by the N-H and ring C-N bonds. In the larger rings it appears that s-character changes are largely compensated by the N-H bond. This is also reflected by the infrared shift (127) $\Delta\nu$ = ν(free cyclicimine) - ν(complexed cyclicimine), table 33, where $\Delta\nu$ is largest for the largest rings.

Table 33

Base	ν^a Complex	ν^a Donor	$\Delta\nu^a$
Ethyleneimine	3325	3328	3
Trimethyleneimine	3285	3346	61
Pyrrolidine	3270	3361	91
Piperidine	3241	3353	112
Hexamethyleneimine	3250	3368	118

[a] cm^{-1}

It is not clear why s-character shoud redistribute in this manner; however, since the small ring is highly strained, one would expect that changes in donor orbital characteristics would be largely compensated by the nitrogen N-H orbital.

If s-character is redistributed in the N-methyl cyclicimine bases as it is in the unmethylated cyclicimine bases, it is tempting to suggest that the methyl group cannot compensate for changes in s-character about the donor nitrogen atom because this would increase F-strain between the donor and acceptor moieties. Such strain could occur because increasing s-character in all C-N bonds about the nitrogen atom should increase their valence angle and crowd the fluorine atoms on BF_3. Therefore, the changes in s-character might be largely compensated by the ring, producing the larger ^1H chemical shifts in these complexes.

Finally, the order of ^1H chemical shifts (table 16) for the N-methyl cyclicimine-BF_3 complexes is 3->5->6->7-membered ring base, just as it is in the unmethylated cyclicimine-BF_3 complexes. This order is significantly different from the thermodynamic stability of these complexes (table 31).

5.2.3 Boron-11 Chemical Shifts

The ^{11}B chemical shifts of the BF_3 complexes of cyclicimines, N-methyl cyclicimines and methylamines are all very similar (table 15). The values range between 17.5 ppm for $BF_3 \cdot TMA$ to 19.2 for $BF_3 \cdot NH_3$. There is obviously no simple relationship between these values and the enthalpies of adduct formation. The expectation that the strongest base should transfer the greatest amount of charge and thereby produce the greatest reduction in ^{11}B paramagnetic shift is not realized (69,70).

Heitsch (76) has suggested that the highly electronegative ^{19}F atoms withdraw "excess charge" from the ^{11}B atoms in these complexes and therefore produce an insensitivity of the ^{11}B resonance to different bases. If this is true, ^{11}B resonances should not be related to the stabilities of BF_3 complexes.

On the other hand, Heitsch (76) also found that the order of ^{11}B chemical shifts in BH_3-methylamine complexes was: NH_3>MMA>DMA>TMA. This order has not been verified thermochemically and is not observed for other acids whose steric effects are minor.

Mooney (77,82) has used ^{11}B chemical shifts of boron trihalide complexes as a measure of donor-acceptor strength. The order of ^{11}B chemical shifts, $\Delta\delta$, between the free and complexed boron trihalide complexes of py correlated well with the order of their thermochemical stability (83): $BF_3<BCl_3<BBr_3$. There is some uncertainty, however, as to the actual significance of the criterion $\Delta\delta$ used by Mooney. Matthews (107) has calculated the contributions of the diamagnetic and paramagnetic shifts to the overall ^{11}B chemical shift in BX_3-alkyl substituted pyridines. His calculations indicate that the term $\Delta\delta$ (complexed - free acid) is more influenced by the change in paramagnetic susceptibility than on the amount of charge transferred from the donor to the boron atom. Further, ^{11}B chemical shifts in these complexes do not correlate

with pK_a values. Hence, it would be purely chance if the two competing contributions should correlate well with adduct stability. Further, $\Delta\delta$ for the BBr_3-benzophenone complex is 50.4 whereas that of BCl_3-py is only +39.6, which implies that the former complex is the more stable. Although the enthalpy of formation of BBr_3-benzophenone is not known it is probably less in absolute value than the 39.5 Kcal/mole enthalpy of formation of BCl_3-py. Evidently the criterion of base strength, $\Delta\delta$, requires further thermochemical investigation.

5.2.4 ^{11}B-^{19}F Coupling Constants

The ^{11}B-^{19}F coupling constants of the BF_3-amine complexes (table 17) all lie in the small interval 10 - 20 Hz. Heitsch (76) concluded from his measurements on a variety of BF_3 complexes that coupling constants which lie in this range are typical of tetrahedral BF_3 complexes.

^{11}B-^{19}F coupling constants of the 4-,5-,6- and 7-membered ring cyclicimine complexes, the 5-,6- and 7-membered ring N-methyl cyclicimine complexes, MMA, and DMA are all the same, although their enthalpies of formation differ greatly (table 31). On the other hand, coupling constants and enthalpies of formation both suggest an order of adduct stability: MMA≙DMA>NH_3≙TMA. Hence, it is not possible to deduce, even from this study of a

closely related series of adducts, any general relationship between adduct stability and ^{11}B-^{19}F coupling constants.

One interpretation of the coupling constant is as a measure of the degree of hybridization of the ^{11}B atom (167) or the degree of hybridization of the BF_3 moiety if the Fermi contact term dominates the coupling constant. If these assumptions are valid, the ^{11}B-^{19}F coupling constant should relate directly to the magnitude of the ^{19}F chemical shift (page 147) according to our earlier interpretation of these chemical shifts. Apparently this is not the case as the ^{19}F chemical shift is largest and the ^{11}B-^{19}F coupling constant least in the BF_3·TMA complex.

Evidently any attempt to equate small changes in ^{11}B-^{19}F coupling constants to subtle changes in basicity of amine donors is not possible until a better theoretical interpretation of bonding in these complexes is available.

5.3 Hydrogen Bonding Studies of Cyclicimines

5.3.1 Calorimetric Measurements

The difference between the enthalpies of mixing of the cyclicimines $(CH_2)_nNH$ (n = 2 to 6) in cyclohexane (ΔH_2) and in $CHCl_3$ (ΔH_1) is the enthalpy of H-bonding (ΔH_3). The first of these enthalpies is the enthalpy of dilution of the cyclicimines in an inert solvent and should represent the enthalpy associated with breaking intramolecular H-bonds of the base. The second enthalpy is associated with the energy required to break intramolecular H-bonds plus the enthalpy of formation of the 1:1 cyclicimine-$CHCl_3$ complex in $CHCl_3$ solution (120). The difference in these values is the enthalpy associated with forming the hydrogen bond provided that (a) the cyclicimine molecule is solvated to the same extent in cyclohexane as in $CHCl_3$, or (b) the differences in the degrees of solvation are the same energetically for the closely related series of bases studied. It is thought that (b) will be small.

Enthalpies of H-bonding of cyclicimines with $CHCl_3$ (table 21) are in the order 5->4-=3->6->7-membered ring, suggesting this to be the order of their basicity towards $CHCl_3$. This order has not been previously observed for other cyclic bases.

To gain further insight into the nature of the heat changes involved in the reaction, consider the following

thermochemical cycle:

$$\begin{array}{ccc} \text{Cyclicimine(g)} & + \text{CHCl}_3\text{(g)} \xrightarrow{\Delta H_a} & \text{cyclicimine} - \text{CHCl}_3\text{(g)} \\ \uparrow \Delta H_c & \uparrow \Delta H_d & \uparrow \Delta H_e \\ \text{Cyclicimine}^{(\text{cyclohexane solution})} & + \text{CHCl}_3\text{(l)} \xrightarrow{\Delta H_b} & \text{cyclicimine} - \text{CHCl}_3\ ^{(\text{CHCl}_3\ \text{solution})} \end{array}$$

Ideally, measurements of ΔH_a are required for comparisons of adduct stability as gas phase enthalpies are free of all interactions due to aggregation.

To correct the measured enthalpies, ΔH_b, to gas phase conditions values are required for ΔH_c, ΔH_d, and ΔH_e, not all of which are easily obtained. As ΔH_e cannot be experimentally measured, it is necessary to assume that either ΔH_c varies in proportion to ΔH_e or that ΔH_e is constant for a closely related series of adducts. Accordingly ΔH_a need only be corrected by ΔH_c before direct comparison with gas phase conditions is realized. Since it is difficult to see why ΔH_c should vary in exactly the same fashion as ΔH_e, the latter is assumed constant for the complexes studied (page 122).

The corrected enthalpies of formation are in the order 7-∿6-∿5->4->3-membered ring, parallelling the order of their ionization potentials (table 1). This order has also been previously observed towards TMB, CH_3OD, $CHCl_3$ and H^+, and it is also the order observed for the cyclic ethers towards BF_3, I_2, $CHCl_3$, and H^+ (table 32).

Drago (140) has recently found that the gas phase enthalpy of formation of DMA·$CHCl_3$ compares favorably with results for condensed phase enthalpies of H-bonding derived by calorimetric (156), nmr (50,157) and infrared techniques (145). It was interesting, therefore, to compare the calorimetric data derived in this section with enthalpies of formation obtained by an nmr technique.

5.3.2 Nuclear Magnetic Resonance Measurements

Enthalpies of H-bonding between cyclicimines and $CHCl_3$ were derived using an nmr technique. The values (table 23) are all similar and suggest little variation in basicity among the cyclicimines towards $CHCl_3$. They are also about half those reported in the literature for $CHCl_3$-amine complexes as obtained by infrared (145) and other nmr techniques (50).

In previous nmr measurements enthalpies of reaction were obtained by measuring the ^1H chemical shifts of $CHCl_3$ in different concentrations of a binary $CHCl_3$-amine mixture. Unlike the cyclicimines, the bases contained no free hydrogen on the nitrogen atom and offered no possibility for intermolecular H-bonding. In the present work the concentration of cyclicimine was varied from 0.03 to 0.2 mole fraction in the solvent mixture CCl_4-cyclohexane. Since the $CHCl_3$ concentration was constant, no correction was required

for its self association. By using cyclohexane as the internal standard, it was not necessary to correct for changes in bulk magnetic susceptibility with changing base concentration (70). Enthalpies of reaction obtained with neat cyclohexane and with the CCl_4 cyclohexane solvent mixture were similar; they are also in the same range as those reported by Woo (118) for ether-$CHCl_3$ complexes using the same technique.

Finally, to establish the effect of possible intermolecular H-bonding between cyclicimine molecules, one need only calculate the amount associated using the data of Bystrov and Lezina (100). They believe that the cyclicimines form trimers; the equilibrium constant for self association to form the trimer in the case of trimethyleneimine being 5.0×10^{-3}

(i.e.) $n(M) \rightleftharpoons (nM)$

since $K_n = 5.0 \times 10^{-3}$

therefore $\frac{(nM)}{(M)^n} = 5.0 \times 10^{-3}$

however, $(M) + 3(nM) = (B) = 0.1$

where (B) = total base concentration.

Therefore $(nM) = \frac{(0.1) - (M)}{3}$

$$(0.1) - (M) = 3 \times 5 \times 10^{-3}(M)^3$$

Since the upper limit to (M) = (0.1)

then $(M) \leq (0.1)$

and $(0.1) - (M) = 3 \times 5 \times 10^{-3}(0.1)^3 = 0$

or $(M) = (0.1)$

and $(nM) \sim 0$

Thus the association of cyclicimines should not affect the magnitude of heats of reaction.

It is difficult to explain why enthalpies of formation derived in this research are only half those previously obtained by other methods. The differences in the reported enthalpies are probably associated more with the methods employed than with the H-bond energies themselves.

Berkeley and Hanna (53) calculated the principal contributions to the shift of the $CHCl_3$ proton in $CHCl_3$-amine complexes, namely: (i) the Buckingham electric field effect (162), ΔE, and (ii) the neighbouring anisotropy effect (163,164), Δn, and found that the values were insensitive to all parameters except the H-bond length (161). Apparently these two effects are an adequate explanation of the shift occurring upon H-bond formation, and if neighboring anisotropy effects are negligible or approximately constant for a series of electron donors,

chemical shifts should be a fair estimate of the relative H-bond length, and accordingly the H-bond strength.

The ^{1}H chemical shifts of the cyclicimine-$CHCl_3$ adducts are in the order: 4->5-≙6->7->3-membered ring, suggesting this to be the order of basicity. This, order is the same as that reported by Bystrov and Lezina who used the dilution shift technique (100). It was suggested by Berkeley and Hanna (50) that the H-bond energies are determined mainly by repulsive forces. These forces are given by the formula S^2I, where S is the overlap integral and I is the ionization potential of the base. At distances as large as the H-bond distance S is constant and the H-bond energies should vary inversely as the repulsive forces, i.e. the ionization potential of the base. The order of ionization potentials is: 3->4-∿5-∿6->7-membered ring (table 1), suggesting that H-bond energies should be in the order4-∿5-∿6-∿7->3-membered ring, as is observed approximately. Few other attempts to estimate theoretically the factors influencing hydrogen bond energies have been made because of the difficulties in evaluating the many-center integrals involved.

Bystrov and Lezina (100) compared the chemical shifts of cyclicimine-$CHCl_3$ complexes with the enthalpies of formation of corresponding TMB adducts. The significance of such empirical relationships is not clear, however, and in most cases it appears that the donor properties of the

lone pair override all other factors in producing the linear correlation. In the light of our earlier analysis of enthalpies of formation in terms of reorganization energies and the complicated nature of H-bonding, it would be fortuitous if two such properties should vary linearly for the entire series of cyclicimines and, for that matter, towards two such different acceptor molecules as $CHCl_3$ and TMB.

The chemical shifts reported in this work do not correlate with the enthalpies of formation based on reactants in the gas phase nor with enthalpies of formation based on reactants in solution. This lack of correlation suggests that either some factors are affecting the shift position which Berkeley and Hanna have not anticipated, or the interpretation of calorimetric enthalpies in this research is not valid.

5.3.3 Infrared Measurements

Shifts in the C-D stretching frequency, $\Delta\nu$(C-D), of $CDCl_3$ in hydrogen bonded systems have frequently been proposed as measures of basicity (58-60).

In this work, the frequency shifts of $CHCl_3$-cyclicimine adducts are in the order: 4-≙5-≙6-≙7->3-membered ring, for the unsubstituted cyclicimines, and 5-≙6-≙7->3-membered ring for the methyl substituted cyclicimines

(table 22). Also, $\Delta\nu$(C-D) is larger in the N-methyl cyclicimine-$CHCl_3$ than in cyclicimine-$CHCl_3$ complexes. These basicity orders are very similar to orders observed with CH_3OD (59) as acceptor molecule and to the order of ionization potential of the bases (table 1).

Abel et al (165) observed a linear relationship between the ^1H chemical shift, δ_0, and frequency shift $\Delta\nu$(C-D) for several animosilanes. Such a relationship is not observed in this study for $CHCl_3$-cyclicimine complexes. Our conclusion is supported by similar measurements made by Zuckerman et al (166) on several bis (diethylamino) dialkyl derivatives of elements of group IV.

Nor is a linear relationship observed between the calorimetric enthalpies of formation and the $\Delta\nu$(C-D) frequency shifts. However, all measurements suggest that the 3-membered ring base is the weakest donor. The infrared technique does not appear to be sufficiently sensitive to differentiate between the donor abilities of the 4-,5-,6- and 7-membered ring bases, in contrast with the nmr technique which suggests that this order is 4->5->6->7-membered ring. It is interesting that infrared shifts imply that methyl substitution enhances basicity whereas the reverse is predicted from nmr measurements. Hence, even for a closely related series of bases, and for different measurements on the same systems, correlations break down. To clarify this situation it would be necessary to first measure

the gas phase enthalpies of H-bonding of these complexes and then compare the thermodynamic order of stability with orders of basicity suggested by the spectroscopic techniques employed in this work.

5.4 Enthalpy of Formation of $BI_3 \cdot CH_3CN$

The enthalpy of formation of $BI_3 \cdot CH_3CN$ for the process; g + g → s, is -45.3 Kcal/mole. This value is larger than that observed for the enthalpies of formation of other boron trihalide adducts (88) and, if crystal lattice energies are similar for all adducts, it suggests that BI_3 is the strongest acceptor of the boron trihalides. Thus, the relative acceptor powers of the boron trihalides towards CH_3CN is $BI_3 > BBr_3 > BCl_3 > BF_3$. This order of acceptor power has been previously explained on the basis of two opposing effects (33). Electronegativities decrease in the order: F>Cl>Br>I, and adduct stability should follow the same order. Reorganization energies on the other hand decrease in the order: F>Cl>Br, and adduct stability should follow the opposite order. These two effects combine to produce the observed order of acceptor power: Br>Cl>F, as deduced from calorimetric measurements (83) and suggest that it is the reorganization energy of the acid which dominates the overall enthalpies of formation of these adducts. The enthalpy of formation of $BI_3 \cdot CH_3CN$ is larger than the enthalpy of formation of the other boron trihalide-CH_3CN complexes suggesting that BI_3 has the lowest reorganization energy of the boron trihalides.

5.5 Enthalpies of Reaction of Silicon, Germanium and Tin Tetrahalides with py and IQ

The enthalpies of formation of crystalline $MX_4 \cdot 2py$ adducts measured in this work (table 26) are from 5 to 22 Kcal/mole lower than those previously reported (122), except in the case of $SiF_4 \cdot 2py$ for which the two values are in good agreement. After our value for $SiF_4 \cdot 2py$ is corrected for the enthalpy of vaporization of py (113) of 9.6 Kcal/mole, the resulting value (i.e. for g + g → c) of -53.1 ± 0.5 Kcal/mole agrees well with Ayletts (150) value of -52.0 Kcal/mole for the dissociation of the complex into its gaseous components. Beattie and Leigh (151) reported an enthalpy of formation of -11.2 Kcal/mole for crystalline $SiCl_4 \cdot 2py$ from its gaseous components compared with our value of -55.4 ± 0.4 Kcal/mole. However, their calculations based on vapour pressure-temperature data were erroneous. The enthalpy of dissociation for the process

$$SiCl_4(g) + 2py(g) \rightarrow SiCl_4 \cdot 2py(s)$$

is given by the equation

$$\Delta H_d = 3R \frac{\Delta \ln P_T}{\Delta (1/T)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

or

$$= 3 \times 1.98 \times 2.303 \frac{\Delta \log P_T}{\Delta (1/T)} \quad \ldots\ldots\ldots \quad (29b)$$

If two values of $\log P_T$ of 0.93 and 0.42 at the inverse temperatures of 30×10^{-4} and 27×10^{-4},

respectively (as estimated from the vapour pressure-temperature graph given by Beattie and Leigh (151)) are substituted into this equation, the enthalpy of dissociation is approximately -65 Kcal/mole. Even this value is questionable because dissociation of the complex did not appear to be reversible, nor did the temperature range for complete dissociation of the adduct correspond to that reported for the vapour pressure-temperature graph from which Beattie and Leigh derived their enthalpy of dissociation.

Wannagat et al (119,134) have measured the enthalpy of formation of $SiF_4 \cdot 2py$, $SiCl_4 \cdot 2py$ and $SiBr_4 \cdot 2py$ complexes for the conditions;

$$MX_4(\text{benzene}) + 2py(\text{benzene}) \rightarrow MX_4 \cdot 2py(s)$$

These values, with the tetrahalide corrected to gas phase conditions,are reported in table 26. The enthalpies of formation of $SiBr_4 \cdot 2py$ and $SiCl_4 \cdot 2py$ of -36.8 ± 0.3 and -34.9 ± 0.3 Kcal/mole respectively, are in good agreement with our values of -37.8 ± 1.4 and -36.2 ± 0.6 Kcal/mole respectively. This confirms that the results of Miller and Onyszchuk (122) were too high. The enthalpy of formation of $SiF_4 \cdot 2py$ of -17.9 ± 0.3 Kcal/mole reported by Wannagat et al is approximately half the value of -33.9 ± 0.6 Kcal/mole obtained in this work. This is difficult to understand as our value agrees with Aylett's value obtained from dissociation pressure

measurements (150) and with the previous values obtained by Miller and Onyszchuk (122). The enthalpy of formation of $SiF_4 \cdot 2NH_3$ for the reaction conditions; g + g → s, is -54.6 Kcal/mole, close to our value of -53.1 ± 0.5 Kcal/mole for the formation of $SiF_4 \cdot 2py$ for the same conditions and much larger than the value of Wannagat et al of -37.1 Kcal/mole. Furthermore, the enthalpy of formation of the 1:1 complex, $SiF_4 \cdot TMA$, for these same conditions is -27.4 Kcal/mole, about half the value reported for $SiF_4 \cdot 2py$ and $SiF_4 \cdot 2NH_3$ as expected for a 1:1 complex. Finally, the fact that the enthalpies of formation of $SiF_4 \cdot 2py$ and $SiF_4 \cdot 2iq$ are similar, tends to confirm the reliability of the -53.1 ± 0.5 Kcal/mole value for $SiF_4 \cdot 2py$.

The disparity between the present and previous results for $MX_4 \cdot 2$ iq complexes varies from 10 to 13 Kcal/mole with the values in this work greater than the previous ones, except in $SiF_4 \cdot 2iq$, $GeF_4 \cdot 2iq$ and $SnCl_4 \cdot 2iq$ for which the agreement is good. The new results are more reliable because they were obtained with: (i) a more sensitive calorimeter, (ii) experimental techniques which ensured the removal of the last traces of water, and (iii) the recording of good cooling curves (see page 57).

The new results reveal, in contrast to the previous report (122) that the enthalpy of formation of $SiCl_4 \cdot 2py$ and $SiBr_4 \cdot 2py$ are not appreciably greater than

that of $SiF_4 \cdot 2py$. In fact, within each series of $MX_4 \cdot 2py$ and $MX_4 \cdot 2iq$ complexes the enthalpies of formation vary neither greatly nor in any systematic manner.

Contrary to the previous results, the enthalpies of formation of corresponding pairs of py and iq adducts are similar. Values are not directly comparable between the two sets of data, however, as it is expected that enthalpies for the process corresponding to ΔH_2 (enthalpy cycle, page 173) for the two bases iq and py should differ. The similarity of their basicities in aqueous solution is evident from their similar pK_a values (86) of 5.17 and 5.14 respectively, and their stability constants in ethanol, 4.68 and 4.95, respectively, are also similar. Molecular models indicate that steric effects are neglible in the py and iq adducts of all acids studied (88), consequently the similar basicities of these bases to the MX_4 acids studied is expected.

Although the old and new values for the enthalpy of formation of $SnCl_4 \cdot 2iq$ are in good agreement, the new value for $SnCl_4 \cdot 2py$ is 14 Kcal/mole less than the previous one. The new value of -38.4 ± 0.4 Kcal/mole agrees remarkably well with that of -39.5 ± 0.8 Kcal/mole obtained by Zenchelsky and Segatto (89) for the reaction conditions;

$$SnCl_4(\text{benzene}) + 2py(\text{benzene}) \rightarrow SnCl_4 \cdot 2py(s).$$

It is doubtful that the slightly different reaction conditions

employed in this study;

$$SnCl_4(l) + 2py(hexane) \rightarrow SnCl_4 \cdot 2py(s)$$

would produce any marked difference in the observed enthalpies of formation. It certainly would not account for the 14 Kcal/mole higher enthalpy of reaction obtained by previous authors (122).

Any attempt to establish relative acceptor powers of a series of tetrahalides on the basis of differences in condensed phase enthalpies of formation, ΔH_1, must take into account differences in enthalpies of desolvation, ΔH_2, of L and of condensation (or crystal lattice energies), ΔH_4, as evident from the following enthalpy cycle in which ΔH_3 is the gas phase enthalpy of formation:

$$\begin{array}{ccc} MX_4(g) + 2L(solution) & \xrightarrow{\Delta H_1} & MX_4 \cdot 2L(c) \\ & \downarrow \Delta H_2 \qquad \uparrow \Delta H_4 & \\ MX_4(g) + 2L(g) & \xrightarrow{\Delta H_3} & MX_4 \cdot 2L(g) \end{array}$$

$$\Delta H_1 = 2\Delta H_2 + \Delta H_3 + \Delta H_4$$

Ideally, values of ΔH_3 are necessary to obtain relative orders of acceptor or donor strenths, but they cannot be evaluated from measurements of ΔH_1 because values of ΔH_4 are not available. Until methods are developed of measuring ΔH_4 directly, it is tempting to assume that values are similar in a series of adducts having similar

structure, but the validity of such an assumption has already been severely questioned (92,87). Although $SiF_4 \cdot 2py$ and $SiCl_4 \cdot 2py$ are molecular with a trans octahedral configuration (90,152), it is not certain that their crystal lattice energies are identical. Therefore, it is not reasonable to attribute the small differences in ΔH_1 in this series to differences in relative acceptor powers of the tetrahalides towards py. This conclusion also applies for the $GeX_4 \cdot 2py$, $SiX_4 \cdot 2iq$ and $GeF_4 \cdot 2$ iq series, even though in some pairs, for example $GeF_4 \cdot 2py$ and $GeCl_4 \cdot 2py$, differences in ΔH_1 are about 6 Kcal/mole.

Previously (122) it had been concluded that relative acceptor powers towards iq are: (i) $SiF_4 > SiCl_4 > SiBr_4$, (ii) $GeF_4 > GeCl_4 > GeBr_4$, (iii) $GeF_4 > SiF_4$, (iv) $SnCl_4 > GeCl_4 > SiCl_4$, and (v) $GeBr_4 > SiBr_4$. The results of the present work show that acceptor powers are approximately the same in series (i), (ii), (iv), and (v). Only order (iii) is reliable, the difference in ΔH_1 values being 8.7 Kcal/mole, which cannot reasonably be attributed to differences in ΔH_4. Order (iii) is also true for py adducts, for which the difference in ΔH_1 values is 11.5 Kcal/mole. Thus, contrary to the earlier work, the only acceptor order that is meaningful is $GeF_4 > SiF_4$ towards py and iq. Interestingly, the same order is obtained for 1:2 complexes with ether ligands (152,153), as well as for 1:1 complexes with TMA (154).

Recently, Beattie and Ozin (155) obtained the stability sequences: $SiF_4 << SiCl_4$, $SiBr_4$ towards TMP, $SiF_4 > SiCl_4 > SiBr_4$ towards TMA and TMP>>TMA towards $SiCl_4$ and $SiBr_4$, all on the basis of vapour pressure measurements. Although they considered several possible rationalizations, including steric effects,reorganization energies and the particiaption, if any, of d-orbitals in bonding, it is still not clear what factors determine the relative acceptor power towards a particular ligand.

Hensen and Sarholz (137) obtained the stability sequence $SiBr_4 \cdot 2py > SiCl_4 \cdot 2py > GeCl_4 \cdot 2py > SiF_4 \cdot 2py$ on the basis of the magnitude of the shift in the $\Pi \rightarrow \Pi^*$ ($^1A_1 - ^1B_1$) transition between the free and complexed py in each case. This order is not supported by the enthalpies of formation of these adducts obtained in this study (table 26) of $SiBr_4 \cdot 2py \sim SiCl_4 \cdot 2py \sim SiF_4 \cdot 2py$. Nor is the Hensen and Sarholz sequence supported by the thermochemical work of Wannagat et al (119,134) which suggests the stability order $SiBr_4 \cdot 2py \sim SiCl_4 \cdot 2py > SiF_4 \cdot 2py$. Evidently the shift in frequency of the $\Pi \rightarrow \Pi^*$ ($^1A_1 - ^1B_1$) transition of py on coordination, is an intrinsic parameter which is not simply related to the overall enthalpy of formation, or thermodynamic stability of these adducts (page 152).

6. Summary and Contribution to Knowledge

1. Enthalpies of reaction of BF_3 with amines for the conditions, g + g → c(CH_3CN solution), were obtained calorimetrically by a technique which involved measurement of the enthalpy of reaction of BF_3 with CH_3CN, the enthalpy of reaction of the $BF_3 \cdot CH_3CN$ formed with the amine added and, the heat of vaporization of the condensed phase amines. Enthalpies are in the order; 4->5-~7->6->3-membered ring base, for the BF_3-cyclicimine $(CH_2)_nNH$ (n = 2 to 6) complexes, and; 4-~7->6-~5->3-membered ring base, for the BF_3-N-methyl cyclicimine (n = 2 to 6) complexes. Enthalpies of formation of BF_3 complexes with methylamines, $(CH_3)_{3-n}NH_n$ (n = 1 to 3), triethylamine, and pyridine complexes are in the orders; DMA~MMA>TMA~NH_3, and; TMA~TEA~py.

2. An explanation of the enthalpy sequences observed was given in terms of steric strain, inductive effects and the partial reorganization of BF_3 in these adducts.

3. Orders of enthalpies of formation of BF_3-amine complexes differed from the corresponding orders of ^{19}F, ^{11}B and ^{1}H nmr chemical shifts.

4. Enthalpies of formation of $CHCl_3$-cyclicimine $(CH_2)_nNH$ (n = 2 to 6) complexes obtained with a ^{1}H nmr technique, are all approximately the same. The calorimetrically measured enthalpies of formation are, however, 5->4-~3->6->7-membered ring.

5. Infrared frequency shifts, $\Delta\nu$(C-D) = ν(C-D) (free $CDCl_3$) - ν(C-D)(complexed $CDCl_3$) and ^1H nmr chemical shifts, $\Delta\delta(^1H) = \delta(^1H)$(free $CHCl_3$) - $\delta(^1H)$(complexed $CHCl_3$), of $CHCl_3$-cyclicimine $(CH_2)_nNH$ (n = 2 to 6) complexes do not correlate with enthalpies of formation determined calorimetrically or by the ^1H nmr technique. Infrared frequency shifts are in the order; 5-~6-~7->4->3-membered ring base, whereas $\Delta\delta(^1H)$ nmr shifts are in the order; 4->5-~6->7->3-membered ring.

6. The enthalpy of hydrolysis of $BI_3 \cdot CH_3CN$ has been measured calorimetrically and the enthalpy of formation of crystalline $BI_3 \cdot CH_3CN$ from its gaseous components has been estimated to be -45.3 Kcal/mole, which is greater than that of $BBr_3 \cdot CH_3CN$.

7. Enthalpies of formation of crystalline $MX_4 \cdot 2L$ complexes (where M = Si, Ge, or Sn; L = py or iq; X = F, Cl, or Br, except X = Cl only when M = Sn) have been redetermined with a more sensitive calorimeter and using improved techniques to exclude water impurity. Contrary to previous results, values do not vary greatly in each series of related adducts, except for the order $GeF_4 \cdot 2L > SiF_4 \cdot 2L > SiF_4 \cdot 2L$.

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