Chemical Reviews

Vol. 69, Number 3 June 1969

QUANTITATIVE ASPECTS OF THE LEWIS ACIDITY OF COVALENT METAL HALIDES AND THEIR ORGANO DERIVATIVES

D. P. N. SATCHELL AND R. S. SATCHELL

Department of Chemistry, University of London, King's College, Strand, London, W.C.2, England, and Department of Chemistry, University of London, Queen Elizabeth College, London, W.8, England

Received April 5, 1968

Contents

I. Introduction

This review concerns quantitative aspects of the acidity of certain covalent halides and their organo derivatives. These compounds can be written generally as MX_n, where X is a halogen atom or an organic radical. M is usually a metal and n its normal valency. Acids MX_n exhibit their acidic properties in equilibria like, or related to, eq 1, in which B represents any base. These equilibria have not received much quantitative study until recently, and most of the data have not been reviewed before. The literature has been surveyed up to the end of 1967, using *Chemical Abstracts* and *Current Chemical Papers* as sources of journal references. The most relevant previous review is that of Stone[1] who, however, confined himself to group III elements and to equilibria occurring in the gaseous phase. Most of the early work was of this nature. The present article concentrates on more recent gaseous phase studies and particularly upon studies using solutions.

$$MX_n + yB \rightleftharpoons MX_nB_y \qquad (1)$$

For reasons explained below, the only quantitative data tabulated here are equilibrium constants, K, which, for eq 1, take the form $K = a_{MX_nB_y}/a_{MX_n}a_B{}^y \simeq C_{MX_nB_y}/C_{MX_n}C_B{}^y$; the many measurements of heats of reaction have not been included. All the constants refer to equilibria occurring in homogeneous, nonaqueous systems. In work with gases concentrations are normally expressed as pressures. In solution, where the distinction between concentration and activity is more important, very few of the available data include activity coefficient corrections, and K normally represents a constant based on concentrations only. Different authors sometimes express K for similar equilibria somewhat differently; to avoid confusion K is defined, and the reaction conditions specified, for each set of data.

The review begins by considering the general nature of acid–base phenomena and the extent to which they have been considered likely to exhibit quantitative regularities. It then deals with the reasons for the delay in the appearance of quantitative data for acids MX_n, discusses the most generally useful type of data, and outlines methods for their measurement, together with the associated difficulties. A section follows in which qualitative predictions about the strengths of acids MX_n are made on the basis of structural and other considerations. Prediction and fact are then compared and quantitative regularities in behavior assessed. The usefulness of some nonthermodynamic, semiquantitative measurements of the acidity of covalent halides is discussed in a final section.

A. DEFINITIONS AND THE NATURE OF ACID–BASE EQUILIBRIA

In 1923 and again, and more fully, in 1938, Lewis[2,3] defined an acid as any substance capable of accepting a pair

---

(1) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

(2) G. N. Lewis, "Valency and the Structure of Atoms and Molecules," Chemical Catalogue Co., Inc., New York, N. Y., 1923.

(3) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

of electrons from a second substance (a Lewis base), the two substances, as a result, forming what is now usually called an adduct, held together by a coordinate covalent (or dative) bond. The adduct thus exists in equilibrium with the free acid and base (eq 2). The polarity of the adduct bond will

$$\underset{\text{acid}}{\mathrm{A}} + \underset{\text{base}}{\mathrm{B}:} \rightleftharpoons \underset{\text{adduct}}{\overset{\delta^-\ \delta^+}{\mathrm{A}:\mathrm{B}}} \qquad (2)$$

vary from case to case, but some sharing of the electrons must always be involved (by definition). In discussing the merits of various acid–base definitions, Lewis pointed out that his own were the most general,[4] but did not expect that a given series of compounds would necessarily exhibit an invariable sequence of relative acid (or base) strength; relative strength was likely to depend upon the reference base (or acid) used. Opponents of Lewis's definitions (and especially supporters of the narrower Brønsted–Lowry[8,9] definitions) always seize upon what they usually refer to as the quantitative deficiencies of Lewis's scheme.[5,6] Thus Lewis's early views on this important matter have, by frequent repetition, achieved the status of a dogma which today imposes even on potentially free-thinking chemists. One object of the present review is to assess in this context the data now available for acids of type MX_n.

Quantitative data for acid–base systems other than those involving proton donors, or metal ions in water, have, until recently, appeared sparsely in the literature. This is true even for systems involving acids like iodine or trinitrobenzene, but is especially true for systems involving covalent metal halides. The main reason for this is that it is often necessary to study the relevant equilibria in the gaseous phase, or in a nonaqueous solvent, under strictly anhydrous conditions, techniques more difficult than those normally available for measuring conventional Brønsted acidity. Scepticism about the quantitative usefulness of Lewis's formulation may also have had a discouraging effect. Lately, however, there has been an upsurge of interest in quantitative aspects of Lewis acidity, stemming in large part from Mulliken's[10] provision of a theoretical foundation for donor–acceptor bonding, but having other roots. Indeed, looking at chemistry as a whole, it is apparent that all definitions of acids and bases, save Lewis's, are now exhibiting a steady, and in some cases a rapid, obsolescence. The current interest in the qualitative subdivision of Lewis acids and bases into so-called "hard" and "soft" species[11] is incidentally doing much to concentrate attention on Lewis's views. Nevertheless, in spite of the growing realization of the importance of Lewis's definitions, a disturbing confusion still exists in some quarters as to the underlying unity of the phenomena which they cover, phenomena which, in fact, embrace all aspects of dative bonding. Thus some authors[12] appear to be under the illusion that adducts formed between bases and weak acids like iodine or trinitrobenzene are somehow (because of the weakness of the interaction and the comparatively great bond lengths involved) essentially different from those adducts involving the same bases with more powerful acids like boron fluoride or stannic chloride. Certainly the former adducts often exhibit different light absorption—the feature with which many investigators using weak acids are primarily concerned—and certainly the exact nature of the bonding will vary from adduct to adduct (sometimes, as we shall see, a double coordinate bond is involved), but the field cannot logically be divided up on any basis of acid strength or adduct stability, for every gradation is discoverable. It may be convenient to discuss some groups of acids separately, as in the present review, but it is misleading to spread the impression that some groups invariably lead to fundamentally different phenomena from others. Covalent metal halides, for example, a class which provides some of the strongest acids known, can occasionally lead to adducts possessing the charge-transfer absorption effects so often found for the adducts of the molecular halogens or of weak organic Lewis acids.[12] And the particular quantitative regularities we shall find in the behavior of acids MX_n are, so far as is known, also typical of cationic acids.[13]

Finally it must always be remembered that Lewis acid–base equilibria are usually more elaborate than eq 1 or 2. Simple equilibria like these are restricted to the gaseous phase and to solvents (*e.g.*, hexane) which do not significantly coordinate with either the acid or the base. More common are equilibria like eq 3 and particularly eq 4. It is in this context that one may see how proton donors fit into Lewis's scheme: they can be considered as adducts of the proton with a base. This is an

$$\underset{\text{acid}}{\mathrm{A_1}} + \underset{\text{adduct}}{\mathrm{A_2{:}B}} \rightleftharpoons \underset{\text{acid}}{\mathrm{A_2}} + \underset{\text{adduct}}{\mathrm{A_1{:}B}} \qquad (3)$$

$$\textit{e.g.},\ \mathrm{BF_3 + R_3N{:}BCl_3 \rightleftharpoons BCl_3 + R_3N{:}BF_3}$$

$$\underset{\text{base}}{\mathrm{B_1}} + \underset{\text{adduct}}{\mathrm{A{:}B_2}} \rightleftharpoons \underset{\text{base}}{\mathrm{B_2}} + \underset{\text{adduct}}{\mathrm{A{:}B_1}} \qquad (4)$$

$$\textit{e.g.},\ \mathrm{R_3N + Et_2O{:}BF_3 \rightleftharpoons Et_2O + R_3N{:}BF_3}$$

$$\mathrm{R_3N + H_2O{:}H^+ \rightleftharpoons H_2O + R_3N{:}H^+}$$

aspect of Lewis's formulations which Lewis himself does not appear to have appreciated. He was perhaps keen to avoid the $A_1 + B_1 \rightleftharpoons A_2 + B_2$ type of format of the Brønsted definitions, which arises because in practice the proton is almost never free. This is less true of other acids, but applies sufficiently to make eq 4 the most common type of acid–base equilibrium. An important implication of this fact is that in meaningful comparisons of acidity the medium must be kept constant and the nature of the equilibrium defined; the relative strengths exhibited by a given series of acids, or bases, in an equilibrium like eq 4 will not necessarily be the same as those shown in an equilibrium like eq 2. Comparisons among hydrogen acids are not free from this difficulty;[14] it is simply that, so far, the vast majority of the data concerning them refer to water as solvent.

In considering particular acids MX_n we shall not include any discussion of processes in which MX_n is decomposed, *e.g.*, as in eq 5 by anion substitution. These are acid–base re-

---

(4) They are the most general because, like the other completely general definitions "free radical," "oxidant," and "reductant," they are based on electronic, and not upon atomic, constitution. Contrary to the views of some[5,6] it makes good sense to speak of the electronic theory (or formulation) of acids and bases.[7]

(5) R. P. Bell, "Acids and Bases," Methuen, London, 1952, pp 84 ff.

(6) R. P. Bell, *Quart. Rev.* (London), 1, 113 (1947).

(7) W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," Dover Publications Inc., New York, N. Y., 1946; 2nd ed, 1961.

(8) J. N. Brønsted, *Rec. Trav. Chim. Pays-Bas*, **42**, 718 (1923).

(9) T. M. Lowry, *Chem. Ind.* (London), **42**, 43 (1923).

(10) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

(11) R. G. Pearson, *ibid.*, **85**, 3533 (1963); for relevant reviews see *Struct. Bonding* (Berlin), 1 (1966).

(12) *E.g.*, G. Briegleb, "Electronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

(13) Y. T. Chen, *Z. Phys. Chem.* (Leipzig), **220**, 231 (1962).

(14) A. I. Shatenstein, "Isotopic Exchange and Replacement of Hydrogen in Organic Compounds," Consultants Bureau, New York, N. Y., 1962.

actions like eq 4, but they do not simply reflect the acidity

$$MX_n + Y^- \rightleftharpoons MX_{n-1}Y + X^- \qquad (5)$$

of the chosen species MX_n.

B. $\Delta G°$ AS A MEASURE OF ACIDITY

To make any quantitative assessment it is necessary to measure something. Different measurements lead to different sorts of information. The most generally useful measurements are those which convey the most information. For this reason the determination of equilibrium constants is the most satisfactory quantitative approach to acidity and basicity. Indeed the vast majority of all existing data, which, of course, mainly refer to hydrogen acids, are measurements of K. Equilibrium constants are invaluable because they provide information about the quantities of the different species present in the equilibrium mixture, information of great practical importance. The main disadvantage of K is that it is a composite quantity ($-RT \ln K = \Delta G°$) containing both entropy (ΔS) and enthalpy (ΔH) effects. It is ΔH that is most directly related to bond strengths, and superficially therefore ΔH would seem likely to be the quantity to provide the clearer comparisons of acid strength. It all depends, however, on what one wants to know. If the only requirement is experimental data for comparison with theoretical estimates of bonding calculated ignoring entropy effects, then clearly ΔH is the useful quantity (this is the main reason, apart from transmitted habits of thought, that it appeals to theoretical and to inorganic chemists[1]), but in most cases what is needed is a measure of an actual equilibrium position in given circumstances. Thus, if in a particular system two acids are competing for a given base, the stronger acid is usually understood to be that which forms the greater amount of adduct. This information is not reliably provided by ΔH, but only by $\Delta G°$. Moreover, in practice, ΔH values are often difficult to interpret in terms of bond strengths, owing to their incorporation of, for example, lattice and/or solvation energies. On balance therefore use of the equilibrium position as the criterion of acid (or base) strength is desirable, as well as being in line with previous practice with hydrogen acids. Only equilibrium constants are listed in this review.

C. METHODS OF MEASUREMENT

Unfortunately, for acids like MX_n, the accurate determination of equilibrium constants is often experimentally difficult. Usually these acids react with water and other hydroxylic substances, such reactions, *e.g.*, eq 6 and 7, leading to new acids and to the effective removal of the acid it is desired to study. For this reason scrupulously anhydrous solvents are

$$AlCl_3 + H_2O \rightleftharpoons AlCl_2OH + HCl \qquad (6)$$

$$BF_3 + H_2O \rightleftharpoons H_2O{:}BF_3 \qquad (7)$$

normally required in solution work. And studies of gaseous phase equilibria bring their own special and additional problems. Experimental techniques will not, however, be discussed, except in so far as method and conditions limit the reliability of the data. The following general considerations apply.

(i) Gaseous phase techniques involve the measurement of equilibrium pressures. When the adduct is only very slightly volatile these pressures are necessarily low and the value of K is correspondingly inaccurate. Because many adducts *are* relatively involatile, gaseous phase studies are circumscribed, but in suitable systems lead to reliable data. Virtually all such measurements refer to acids based on the elements of group III of the periodic table.

(ii) In solution studies useful techniques for determining solute concentrations include cryoscopy, nuclear magnetic resonance, and infrared and especially ultraviolet and visible spectrometry. Very occasionally solubility measurements are used. The first three methods are all limited by the comparatively narrow solute concentration range it is usually possible to employ, and to some extent also, especially cryoscopy, by the temperature range easily available. The data provided by these methods are not therefore normally as accurate as those obtainable either by the best gas-phase measurements or by ultraviolet spectroscopy. The latter is potentially by far the best method available at present. It has the advantage that very low concentrations of reactants can be used, and it is just here that its main danger lies, for it is impossible to render any solvent *completely* anhydrous, and very small masses of water/liter correspond to surprisingly large molarities.[15] In view of the great affinity for water of the more acidic halides, solution work which involves such halides at concentrations $<10^{-4}$ M must be treated with very considerable reserve and must be expected to involve substantial error.

Up to 10 years ago few studies concerned solutions, and most of these involved a cryoscopic technique. Today spectroscopy rightly holds sway. Quite recently, however, a thermal method which leads simultaneously to both ΔH and $\Delta G°$ has been devised.[16] It appears reasonably accurate and promises to be especially useful for systems involving acids and bases which exhibit little spectral change on adduct formation.

II. General Qualitative Expectations about the Acidity of Species MX_n

In discussing the acidity of any species, concern centers on its electron-pair requirements, normally in this review the requirements of M which remain after its characteristic valence behavior has been exhibited in forming MX_n. No parallelism is necessarily to be expected between the acidic behavior of ions M^{n+} and that of the covalent species MX_n.

The following schematic group table, from which irrelevant or little studied elements have been mostly omitted, aids the discussion which follows. This discussion does not pretend to be rigorous, and parts of it will certainly seem naive to some. It aims only to provide a qualitative framework against

Group	IIA	Be	Mg	[Ca	Sr	Ba]
	IIB			Zn	Cd	Hg
	IIIB	B	Al	Ga	In	Tl
	IIIA			Sc	Y	La
	IVB	[C]	Si	Ge	Sn	Pb
	IVA			Ti	Zr	Hf
	VB	[N]	P	As	Sb	Bi
	VA			V	Nb	Ta
	VIB	[O	S]	Se	Te	[Po]
	VIA			Cr	Mo	W
	VIII			{Fe	Co	Ni
				Rn	Rh	Pd
				Os	Ir	Pt

---

(15) (a) I. R. Beattie, *Quart. Rev.* (London), 17, 382 (1963); (b) see T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967), for references to other dangers in spectrophotometric studies.

(16) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 3921 (1966).

which to set the quantitative data given in section III. It constructs this framework at least as rigorously as previous essays in this direction.[17]

A. THE EFFECT OF THE ELECTRONIC CONFIGURATION OF M

Assuming single bonding only between any particular base and MX_n, and so excluding, temporarily, both chelation effects and double bonds between M and any given atom of the base, three broad principles can be formulated.

A. The acidity of a species MX_n can arise, when $n < 4$, from the central atom's desire to complete an outer electron octet by accepting one (or more) pair of electrons from bases. Where two pairs are required the acidity exhibited is likely, other factors being equal, to be less than when a single pair suffices owing to (i) the relatively smaller energy gain on receiving the first pair (which does not complete the octet) and (ii) the accumulation of negative charge on M if two pairs are received.

Acidic behavior will also be observed when, although MX_n already represents a reasonably stable electronic arrangement, M is an element which can expand its outer electron shell (by using d orbitals) to a more stable configuration involving 10, 12, or perhaps 14 electrons. Here the resulting acidity will be expected usually to be less marked, the completion of such large shells normally being energetically less rewarding than the completion of an octet. As for octet completion, the formation of stable larger configurations is likely to be most favorable energetically when only one electron pair is involved.

B. Other factors being equal, the acidity of M will be expected to fall within any group with increasing atomic volume (effectively with increasing atomic number) owing to the relatively weaker attraction between nuclear charge and incoming electron pairs (*cf.* Fajans rules).

C. Since, in general, the energies of different atomic orbitals lie closer together with increasing atomic number (thus facilitating hybridization), and because orbital contraction arising from the electronegativity of the nucleus tends to decrease with increasing atomic number (thus allowing hybridized orbitals more effective overlap), use of d orbitals, especially outer orbitals, therefore will normally become easier and more effective the heavier the element; thus in those groups which must use such orbitals this effect will be expected to counteract to some extent the effects of principle *B*. Sometimes increasing size may also be sterically beneficial (see section II.C.2).

It is evident that the operation of these principles is likely to be seen most clearly in systems where the bonding between MX_n and the base involves the donation of one electron pair only, and thus corresponds formally to a single (σ) bond.

With certain acid–base pairs the possibility exists of more than one electron pair being shared between them. We refer not to the obvious cases of bifunctional acids and bases leading to chelate structures, but to those examples where either (i) the donor center of the base has a further electron pair available and, at the same time, the acid has a suitable vacant orbital to receive this electron pair, so that a π bond results and double dative bonding ($\sigma + \pi$) from base to acid obtains,[18] or (ii) the acid and base can form a dative π bond by reversing their roles, an electron pair being received by the "base" from the "acid."[19] This process has been called "back-bonding." In forming these second bonds any suitable p or d orbitals can be used. The π bond will be weaker than the σ bond, but its existence will stabilize the adduct and so enhance acid–base behavior. It is clear therefore that acids and bases appropriately matched for double bonding will tend to react easily with each other.

A capacity for back-bonding has often been considered an important component of the so-called class (b) acid behavior.[20] Thus class (b) acidic atoms are defined as those which, in contrast to class (a), tend to form their most stable adducts with bases whose donor atoms are drawn from the heavier members of groups V and VI. This behavior could arise in part because phosphorus and sulfur, for instance, may enjoy back-bonding by using vacant, low-lying d orbitals not available to nitrogen and oxygen. However, this type of phenomenological definition seems unsatisfactory because (a) owing to solvation and dielectric constant effects, stability sequences tend to vary with the medium in which they are studied, so that classification is variable; and (b) definitions based on particular chemical properties are inherently less satisfactory than those based on chemical structure. The hard–soft terminology[11] which grew out of observations of similar phenomena, and which tends to include class (a) and (b) behavior, is also very imprecise. Its definitions are based on the fact that some pairs of acids and bases react together more easily than do other pairs. This, as the foregoing paragraphs suggest, may in part be due to back-bonding phenomena. Species which can engage in back-bonding come into the "soft" category. The attraction of the "hard" species for each other has different roots, among which the greater ionic character of their interaction is currently being identified.[11] The troubles with this approach are: (a) any sort of rigid and consistent classification into hard and soft species under all conditions proves impossible while (and this is an aspect of the same fact) supposedly hard acids (*e.g.*, H^+) form very stable adducts with supposedly soft bases (*e.g.*, H^-) which, by definition, they should not; (b) the definitions are again based on behavior and not upon constitution.

Fortunately, as far as the present review is concerned, it is unnecessary to enter more deeply into the current debate on these issues. This is because rather few soft bases have been studied quantitatively with acids MX_n. This is a challenging field still awaiting development, challenging because it includes, in particular, equilibria with carbon bases. In the arguments which follow all that need be remembered is that some acids MX_n can, and probably do, exhibit double bonding with suitable bases. A discontinuity is then likely in data which otherwise reflect only single-bond interactions. It is such discontinuities which provide ammunition for those who question the quantitative usefulness of Lewis's broad definitions. Acid–base double bonding, because it enhances the interaction, has important implications throughout chemistry, not least for the choice of good catalysts for particular reactions.

---

(17) M. Baaz, V. Gutmann, and O. Kunze, *Monatsh. Chem.*, 93, 1162 (1962).

(18) A. Mohammad, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc.*, *B*, 723 (1967).

(19) G. E. Coates, *ibid.*, 2003 (1951).

(20) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), 12, 265 (1958); see, however, L. M. Venanzi, *Chem. Brit.*, 4, 162 (1968).

Returning to the consideration of the acidity of the elements in terms of the principles *A–C* and assuming, in general, that the base will not permit double bonding, we note first that no equilibrium constants referring to the covalent halides of group I elements appear available. In these compounds, MX, three electron pairs are required to complete a new octet. The energy gain in accepting one pair will be relatively small (principle *A*). The absence of equilibrium data is therefore not surprising.

As in group I, so in group II it is the B subgroup elements which provide most of the covalent compounds MX_2. In these compounds (*e.g.*, $ZnCl_2$, CdI_2, etc.) the metal has an outer group of four electrons and therefore seeks a normal maximum of two additional pairs. By principle *A* the observed acidic properties are likely to be only moderate, and it is expected from principle *B* that the order of acidity in comparable compounds will be $Zn > Cd > Hg$.

The elements of group III (electronic configuration s^2p^1) will, of all elements, be those expected by principle *A* to form the most acidic compounds MX_n, for here the central atom requires only a single electron pair to complete an octet. The common covalent compounds of this group (*e.g.*, BF_3, $AlCl_3$, $GaBr_3$, etc.) include, in fact, the majority of the best known Lewis acid catalysts. In the light of principle *B* an order of acidity $B > Al > Ga > In > Tl$ is anticipated for the B subgroup. By the same principle the trivalent compounds of the A subgroup should display acidities $Sc > Y > La$.

Group IV elements in their normal covalent compounds MX_4 succeed in completing the octet. Hence a "saturated" carbon atom will not possess acidic properties under any circumstance (because the first period elements cannot call on d orbitals). Similarly the acidic properties of SiX_4 will be expected to be weak, and this group provides a good example of the operation of principle *C* (although other rationalizations have been suggested[21]). In the B subgroup the opposing effects underlying principles *C* and *B* may be guessed to lead to an acidity maximum at derivatives of tin. In the A subgroup where expansion beyond a ring of eight involves inner d orbitals (which are normally closer in energy to the s and p valence orbitals than are the outer d orbitals), prediction is more difficult, but the order $Ti < Zr \leqslant Hf$ appears sensible since zirconium and hafnium are of very similar size. The use of inner d orbitals by the A subgroup means that the orders $Ti > Ge$ and $Zr > Sn$ will be expected.

Group V elements (s^2p^3) are normally tri- or pentacovalent. Trivalent nitrogen with a complete octet in period 1 will exhibit no acidic properties; indeed it is a powerful base. Trivalent phosphorus can expand the octet, but the tendency to do so will be small. Hence PX_3 compounds will be weak acids. Much the same sort of pattern is therefore to be expected as in group IV, with a maximum acidity at (say) Sb (at Nb in the subgroup) with $V > As$ and $Nb > Sb$. Analogous arguments apply for the elements in their pentacovalent state, except that now the d orbitals are already in play, and completion of a shell of 12 electrons by the acceptance of a single pair is likely (principle A) to be much more favorable energetically than an expansion beyond a stable group of eight, as required in the trivalent series. It follows that the MX_5 compounds should be notably more acidic than the analogous MX_3 compounds, although the additional two X substituents will make reliable comparison difficult in cases when these substituents weaken the acidity of M (see section B.1 below). It is predictable therefore that appropriate SbX_5 and NbX_5 compounds will be powerfully acidic, and more so than any other MX_n species save those derived from group III elements.

For group VI (s^2p^4) the normal covalency is 2, leading to a stable octet. Here again there is an analogy with group IV. The lower members, oxygen and sulfur, are likely to be feebly acidic (oxygen not at all) with the acidity rising to a possible (weak) maximum at Te (and at Mo in the B subgroup). Compounds with abnormal valency (*e.g.*, TeX_4) may well exhibit enhanced acidity. Indeed species TeX_4 only require one electron pair to complete a shell of 12, and in the combined light of principles *A–C* an acidity level somewhat greater than that of the comparable tin compound would be anticipated.

The halogen group (s^2p^5), normally unicovalent, will resemble groups IV and VI in that the lower members will be feebly acidic (fluorine not at all) with the higher members (especially iodine) being able to expand their octet in suitable circumstances, *e.g.*, when attached to an electron-withdrawing substituent.[22] Thus adducts like I_3^- and $C_6H_6 \rightarrow ICl$ are well known.[23] Halogens not being metals, these particular equilibria are not included in the review. However, appropriate covalent metal iodides (*e.g.*, SnI_4, CdI_2) will be expected to exhibit two sorts of acidic site, the central atom and an iodine atom.

Of our schematic periodic table (p 253) only group VIII, the triads, remains. Here predictions are complicated by the frequent use of d orbitals and the resulting variable valence. These elements have been relatively little studied in nonaqueous solvents. Of them all, iron when trivalent is likely to be the strongest acid, with a strength comparable to, or greater than, that of gallium, for it then has the same outer electron configuration as gallium except that the 3d shell is exactly half, instead of completely, full. (Trivalent cobalt and nickel do not enjoy half-filled d shells.) FeX_3 compounds are therefore among the potentially most acidic.

The foregoing comparisons are obviously tentative. However, in their light the following league table giving the top ten potentially acidic structures (omitting the subgroup elements) can be justified: $BX_3 > AlX_3 > FeX_3 > GaX_3 > SbX_5 > InX_3 > SnX_4 > AsX_5 > SbX_3 > ZnX_2$. To readers with any knowledge of the catalytic powers of covalent metal halides,[24] this list will appear reasonably sensible. Naturally, however, factors other than the electronic structure of the central atom play a part. In particular the nature of X influences the absolute magnitude of the observed effects.

B. THE EFFECT OF SUBSTITUENTS ATTACHED TO M

1. Polar Effects

Since the principal function of M is to receive electron pairs, any substituent attached to M which repels electrons relative to hydrogen will be expected to decrease the acidity of M

---

[21] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, London, 1962.

[22] Electron withdrawal tends to stabilize large outer shells of electrons. This is why the maximum valency of an element is often exhibited only in the fluoride. The instability of species like Me_5Sb arises from the reverse effect.

[23] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, 74, 4500 (1952).

[24] See G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y., 1963.

below its value in the corresponding M–H compound. Conversely electron-attracting substituents will increase M's acidity. For substituents which can both withdraw and repel electrons, a balance of effects will be involved. Normally what organic chemists call the inductive polar effects of substituents[25] will be the important ones. Tautomeric electron transfer will often be curtailed by the absence of sufficient overlap between the relevant substituent orbitals and suitable metal orbitals.

2. Steric Effects

Trends expected on purely polar grounds will sometimes be disturbed by steric effects.[26] If the substituents attached to M are bulky, and especially if M is small, these may hinder the close approach of the base or restrict its rotation in the adduct. A similar effect is involved when any rehybridization, necessary on forming the adduct, forces the substituents into positions where they interfere with each other. Steric repulsions and additional restrictions of rotation in the adduct reduce the effective acidity of the acid because forming the adduct becomes less favorable on enthalpy and entropy grounds. Steric effects are not usually very important with H acids because of the small size of the proton, and correlations between Brønsted acidities and basicities and Lewis acid and base behavior can therefore only usually be expected when steric effects are absent also for the latter.

C. THE EFFECT OF THE STRUCTURE OF THE BASE

It is usually only elements of the oxygen, nitrogen, and fluorine groups which have electron pairs available for donation to acids, although unsaturated compounds, especially unsaturated carbon compounds, can also function as bases *via* their π-electron systems. The commonest bases involve a nitrogen, an oxygen, or a halogen atom as donor. In general the behavior of a given acid MX_n toward any series of bases will be expected to parallel that shown by the simplest Lewis acid, the proton, provided that certain complicating features such as double bonding, steric interference, and chelation are absent.

1. Electronic State of the Donor

The importance of the detailed electronic state of the donor atom, in the sense that it may or may not permit double bonding with the acid, has already been emphasized (section II.A). Where double bonding is possible, important quantitative consequences are likely.

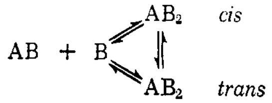
2. Steric Effects

Hindrance of adduct formation due to the presence of bulky substituents around the donor will normally be expected to reduce its basicity, just as similar substituents in an acid reduce its acidity (see section II.B.2). The importance of a given substituent's steric bulk diminishes as the size of the donor and acceptor atoms increases.

3. Successive Coordination

If an acid is capable of forming more than one adduct [*e.g.*, MX_4 acids can lead to both 1:1 (MX_4B) and 1:2 (MX_4B_2) adducts], the effect of the first base species B to coordinate is really to produce a new acid so far as the second base species is concerned. Whether or not MX_4B is a stronger acid than MX_4 will obviously depend upon the various electronic and steric effects the addition of B produces; if M and B are singly bonded MX_4B will be expected normally to be weaker, for some net transfer of negative charge to M will almost inevitably be involved, and steric hindrance, if present, is likely to be more severe in MX_4B than in MX_4. These generalizations are supported by what is known of the stepwise coordination to metal ions in aqueous solutions.[21,27]

In certain AB_2-type adducts the possibility exists of *cis–trans* isomerism. The factors which control the stereochemistry of such adducts are only just becoming understood. There appears no case yet in which the complete equilibrium system eq 8 has been studied quantitatively. Normally it is probable

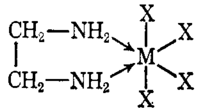


(8)

that one form, either *cis* or *trans*, will be dominant at equilibrium.

4. Polyfunctional Bases

Suitable acids and polyfunctional bases can form chelated



1

adducts, *e.g.*, **1**. Rather little quantitative information is available on this topic for species MX_n in nonhydroxylic solvents. For metal ions in water chelation leads to considerably enhanced stability for the adduct compared with that found for the analogous but unchelated structure.[21]

D. SOLVENT EFFECTS

Because all adducts MX_n:B tend to be dipolar, they are as a class relatively involatile. As noted in section I.C, this often restricts their study in the gaseous phase, since only very low pressures are obtained. Much the same sort of restriction applies to studies in non- or poorly coordinating solvents of low dielectric constant, such as benzene or hexane; adducts tend to be very insoluble in such media. This necessitates working at very low solute concentrations, and although accurate measurements may still be made, the significance of these measurements is impaired by the inevitable presence of basic impurities in the solvent which compete for the acid. Many of the most reliable data therefore refer either to dipolar coordinating solvents or to solvents of appreciable dielectric constant. Such solvents increase solubility by two distinct effects. (i) The higher the dielectric constant the easier is it for dipolar entities to exist together in solution without aggregation and hence precipitation. (ii) Electrostatic solvation of polar species by the weak dipoles of a coordinating

---

(25) C. T. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953

(26) V. Gold, *Progr. Stereochem.*, 3, 169 (1962).

(27) F. J. C. Rossotti, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, London, 1960.

solvent, even when the solvent is of quite low dielectric constant (*e.g.*, ether), tends to spread charge over a larger volume, and this again reduces aggregation and precipitation. Acetone is a solvent which combines effects i and ii.

It is, however, not only the adducts which require a suitable environment. Some acids (*e.g.*, $ZnCl_2$) are soluble only in solvents with which they coordinate acid–base wise, the free energy of this coordination offsetting that lost on destruction of the solid. When this sort of coordination occurs, the reaction studied is no longer a simple acid–base process like eq 1, but a process like eq 4, *e.g.*, eq 9, where S is the solvent.

$$A{:}S + B \rightleftharpoons A{:}B + S \qquad (9)$$

So far as equilibrium constants are concerned, if solvent coordination is not significantly involved, a simple increase in dielectric constant will be expected to favor formation of the adduct AB (*i.e.*, to increase K) since AB will usually be more polar than the uncoordinated acid or base alone. If a solvent coordinates with the acid in competition with the base as in eq 9, an increase in coordinating power at constant dielectric constant (difficult to achieve in practice) will be expected to disfavor the adduct (which is only electrostatically stabilized by the solvent) and therefore to decrease K, since the new solvent will more successfully compete with the base, whereas the stabilization of the adduct will be little changed. When there is a change in both dielectric constant and coordinating power, a balance of effects will be involved.

Although the absolute magnitude of K will be altered by changing the strength of the coordination of the solvent to the acid, the *relative* values of K for a series of bases B, in any given acid–solvent combination, are unlikely to be much affected by its nature, since, in general, the solvent does not coordinate with the bases, so that their inherent, relative coordinating powers toward the acid in different solvents of the same dielectric constant will be much the same. When, however, the behavior of two acids is being compared with reference to a standard base B, any change in the coordinating power of the solvent is very important in determining the *relative* values of K obtained, *i.e.*, the observed relative strengths of the acids toward B. This may be appreciated qualitatively in the following way. In a noncoordinating solvent the behavior will largely reflect that found in the gaseous phase, with the stronger acid in the gaseous phase also being found to engage more of the base in the solution and therefore again being rated the stronger. However, as the coordinating power of the solvent increases, the inherently stronger acid becomes more and more firmly held by the solvent, so that if the reference base B is a significantly weaker base than is the solvent, it will tend to form more adduct with the inherently weaker acid because it is this acid which is the less firmly held by the solvent. Thus the acidity sequence found in the gaseous phase will appear reversed. It may be shown by thermodynamic arguments that, if the dielectric constant effects are taken to be of secondary importance, (i) the sequence of acidity found for the gaseous phase (which reflects behavior in equilibria like eq 1) will normally only be observed in solution when the solvent is a weaker base than is the reference base B, and (ii) under such conditions, provided the entropy effects in the various equilibria are similar, then of two solvents, that which leads to the lower general level of acidity (to the smaller K values) will lead also to the smaller differences in acidity between any two given acids; in short, highly coordinating solvents should often produce a leveling effect.[28]

The interpretation of relative acidities determined in solution studies clearly requires care. It happens that virtually every available datum referring to solution equilibria easily satisfies condition i above, so that the acidity sequences found in the work with solutions will be expected normally to be in qualitative agreement with those observed for gaseous phase equilibria. This, as will be seen, is the case. The ubiquity of leveling effects, which are more dependent on the assumptions about changes in entropy and dielectric constant, may also be judged as the data unfold.

To discover a suitable solvent is one of the most difficult aspects of quantitative work with acids MX_n. To find a series of suitable solvents displaying a range of properties is exceptionally difficult; there seem very few which, even when apparently highly pure, will dissolve species MX_n and their adducts without decomposing them or being discolored by them.

E. EXPECTED CORRELATIONS

In the light of the foregoing sections the following tentative generalizations can be made.

(a) For a series of structurally similar bases a given (standard) acid MX_n should lead, in the absence of steric and double-bonding effects, to a set of relative basicities which correlate closely with the relative basicities these bases exhibit toward other acids MX_n or toward the proton, a species which also receives only a single electron pair.

(b) Similar correlations may occur even when double bonding is present between the base and MX_n, provided that all the bases have the same type of donor center, when a fairly constant secondary effect, unrelated to proton basicity, may be superimposed on their proton-like basicity without much disturbing its quantitative sequence.

(c) When the different bases being compared can engage MX_n in double bonding to very different extents, the relative basicities they exhibit will differ materially from those exhibited toward the proton. In the same way—and this is just inverting the arguments—in comparing two acids MX_n, the same order (indeed much the same magnitude if the environments are similar) of relative acidity should obtain when reference is to standard bases of the same type. When, however, a change in reference base leads to new possibilities of bonding not equally available to both acids, an appreciable change in relative acidity is inevitable.

It is the complications noted in generalization c which underlie queries about the quantitative usefulness of Lewis's very broad definitions. What is usually forgotten by critics is that far-reaching regularities in behavior are nevertheless to be expected. In the next section we examine the extent to which these expectations are realized.

III. Comparison between Prediction and Experiment

A. GROUP II ACIDS

In principle it is possible for 1A:1B, 1A:2B, and perhaps even higher adducts, to form with group II acids, but quantitative measurements have so far been restricted to the 1:1 equilibria only.

---

[28] A. Mohammad and D. P. N. Satchell, *J. Chem. Soc., B*, 527 (1966).

Table I

Zinc Halide–Aniline Equilibria[a]

Aniline derivative	pK_a	$pK\ (pK_{calcd})$ *ZnCl₂*	*ZnBr₂*	*ZnI₂*
		(i) In Diethyl Ether[29] at 20°		
4-Bromo	3.91	$-2.20\ (-2.27)$	$-2.10\ (-2.12)$	
4-Methyl-3-nitro	2.90		$-1.55\ (-1.41)$	$-1.30\ (-1.44)$
3-Nitro	2.50		$-1.00\ (-1.13)$	
2,4-Dichloro	2.00	$-0.71\ (-0.70)$		
2,3-Dichloro	1.83	$-0.47\ (-0.56)$		
2,5-Dichloro	1.50	$-0.28\ (-0.29)$	$-0.48\ (-0.43)$	
4-Nitro	0.99		$-0.08\ (-0.07)$	$+0.20\ (+0.13)$
2-Methyl-4-nitro	0.94	$+0.75\ (+0.17)$		
		(ii) In Acetone[30] at 25°		
4-Methyl-3-nitro	2.90	$-1.90\ (-1.91)$	$-2.40\ (-2.39)$	$-2.02\ (-2.01)$
3-Nitro	2.50	$-1.69\ (-1.74)$	$-1.98\ (-2.07)$	$-1.88\ (-1.83)$
6-Methyl-3-nitro	2.32	$-1.88\ (-1.54)$	$-2.12\ (-1.92)$	$-1.95\ (-1.63)$
4-Chloro-3-nitro	1.93	$-1.37\ (-1.30)$	$-1.52\ (-1.60)$	$-1.39\ (-1.39)$
3-Methyl-4-nitro	1.45		$-1.27\ (-1.21)$	
4-Nitro	0.99	$-0.74\ (-0.70)$	$-0.95\ (-0.84)$	$-0.78\ (-0.78)$
2,6-Dimethyl-4-nitro	0.95		$-0.36\ (-0.81)$	
2-Methyl-4-nitro	0.94		$-1.18\ (-0.80)$	
4-Methyl-2-nitro	0.45		$-0.40\ (-0.40)$	

[a] K refers to eq 10; $pK = -\log\ (C_A/C_BC_{Zn(hal)_2})$, where A = adduct and B = an aniline; pK_{calcd} = pK calculated from correlation equations on p 258; units of K are l. mole^{-1}; $pK_a = -\log$ (dissociation constant of BH^+ in water at 25°) in all tables; uv spectrophotometric method.

1. *Standard Acid-Varying Base Comparisons*

a. Anilines

Table I[29,30] contains equilibrium constants for interaction in ether and in acetone solution between zinc chloride, bromide, and iodide as standard acids, and a series of substituted anilines. Only 1:1 acid–aniline adducts have been reliably observed in these solutions under the concentration conditions (excess of acid) used, and the equilibria very probably take the form of eq 10, where S represents the solvent, which is always present in great excess and doubtlessly coordinates with the solutes as shown in the equation.[24] The equilibrium

$$RC_6H_4NH_2 + Zn(hal)_2S_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RC_6H_4NH_2{:}Zn(hal)_2S + S \quad (10)$$

constant for adduct formation, $K\ (= k_1/k_{-1}C_S = C_{AB}/C_AC_B)$, is defined omitting the large and effectively constant solvent concentration. This type of definition is that used by most authors and is in line with practice for acid–base equilibria in aqueous solution. The data in Table I show that in both acetone and ether, plots for a given acid of pK against pK_a (K_a = the dissociation constant of $RC_6H_4NH_3^+$ in water) are in every case straight lines with slopes of *ca.* 0.7. This means that the basicity range exhibited by the anilines toward zinc halides is compressed compared with that shown by them toward protonation in aqueous solution. This type of result is fairly general throughout the field. The actual correlation equations for $ZnCl_2$, $ZnBr_2$, and ZnI_2 in acetone are $pK = -0.63pK_a - 0.08$, $pK = -0.81pK_a - 0.04$, and $pK = -0.64pK_a - 0.15$, respectively. For $ZnCl_2$ and ZnI_2 in ether the equation is $pK = -0.82pK_a + 0.94$ and for $ZnBr_2$ it is $pK = -0.70pK_a + 0.62$. Since, for the different acids, the slopes of their pK–pK_a plots in a given solvent are not identical, their observed relative acidities depend to some extent on the base used for comparison. In the present systems this effect is small. (It should be noted that the relative acidities of Brønsted acids in nonaqueous solvents also depend on the reference base.[14]) The slope of the pK–pK_a plot for a given acid is also slightly dependent on the solvent used.

Deviations from the rectilinear plots occur for anilines with substituents *ortho* to the amino group, and in particular for bases with *o*-chloro and *o*-methyl substituents. N substitution also leads to discrepant behavior. All such discrepancies doubtlessly arise from steric effects. Save, however, for substitution leading to steric hindrance, it is clear that substituents affect the basicity of anilines toward the zinc halides and toward the proton in much the same way. The correlation equations are therefore useful for the prediction of pK values from available pK_a data. It is clear also from the data that bases stronger than aniline (pK_a = 4.60) will lead to very stable 1:1 adducts with zinc halides in ether (or acetone), and it is probable therefore that with very strong bases some 1:2 adduct formation will be detectable, even when the base is not in excess of the acid.

In acetone the rate of formation of the 1:1 adducts is conveniently measurable, and it is found that both k_1 and k_{-1} in eq 10 are related to K as in $k_1 = G_1K^{\alpha}$ and $k_{-1} = G_2K^{\alpha-1}$, where α, G_1, and G_2 are constants and $G_1/G_2 = C_S$. These equations are similar to the familiar Brønsted relationship for hydrogen acids, for which $0 < \alpha < 1$. In the zinc systems, however, $\alpha > 1$, being 1.5, 1.6, and 1.6 for $ZnCl_2$, $ZnBr_2$, and ZnI_2, respectively. The significance of this result is discussed in ref 30.

Table II[31] contains data for the interaction of cadmium iodide with anilines in acetone solution. The system is excep-

---

(29) D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 4296 (1964).
(30) D. P. N. Satchell and R. S. Satchell, *Trans. Faraday Soc.*, 61, 1118 (1965).
(31) R. S. Satchell, *J. Chem. Soc.*, *B*, 1088 (1967).

Table II

Cadmium Iodide–Amine Equilibria in Acetone Solution[a]

Amine	pK_a	pK' (pK'_{calcd})	pK (pK_{calcd})
4-Methyl-3-nitroaniline	2.90	−0.97 (−0.99)	−1.75 (−1.76)
5-Nitro-1-naphthylamine	2.73	−0.79 (−0.83)	−1.97 (−1.63)
3-Nitroaniline	2.50	−0.72 (−0.63)	−1.46 (−1.45)
6-Methyl-3-nitroaniline	2.32	−0.93 (−0.46)	−1.78 (−1.30)
4-Chloro-3-nitroaniline	1.93	−0.06 (−0.11)	−0.92 (−0.99)
3-Methyl-4-nitroaniline	1.45	~0.3 (+0.33)	−0.63 (−0.62)

[a] K' and K refer to eq 11 and 12, respectively; pK' (and pK) = $-\log (C_A/C_BC_{CdI_2})$, where A = the relevant adduct and B = amine;[31] pK_{calcd} = pK calculated from correlation equations on p 259; units of K' and of K are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

Table III

Zinc Halide–Benzamide Equilibria in Diethyl Ether Solution[a]

		pK (pK_{calcd})[34]	
Benzamide deriv	pK_a[34,35]	$ZnCl_2$	$ZnBr_2$
4-Methoxy	−1.80	−3.56 (−3.27)	
2-Methyl	−1.88	−3.14 (−3.20)	
4-Methyl	−2.01	−3.17 (−3.10)	−3.17
N-Methyl	−2.13	−2.34 (−3.01)	
Hydrogen	−2.16	−2.96 (−2.98)	
4-Fluoro	−2.24	−2.83 (−2.92)	
3-Methoxy	−2.35	−2.94 (−2.83)	
4-Chloro	−2.47	−2.72 (−2.74)	−2.56
3-Bromo	−2.75	−2.52 (−2.52)	
3-Nitro	−3.07	−2.21 (−2.26)	
4-Nitro	−3.23	−2.17 (−2.14)	−2.17

[a] K refers to eq 13; pK = $-\log (C_A/C_BC_{Zn(hal)_2})$, where A = adduct and B = substituted benzamide; pK_{calcd} = pK calculated from correlation equation on p 259; units of K are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

tionally interesting in that it provides evidence[32] for the existence of two equilibria, eq 11 and 12. In eq 11 iodine is acting

$$RNH_2 + CdI_2S_2 \rightleftharpoons RNH_2{:}ICdIS_2 \qquad \text{fast, } K' \qquad (11)$$

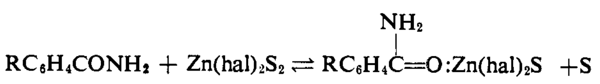
$$RNH_2 + CdI_2S_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNH_2{:}CdI_2S + S \qquad \text{slow, } K \qquad (12)$$

as the acceptor atom (*cf.* section II.B). Equilibrium 12 is analogous to those studied with the zinc systems, and the data for K display the behavior typical of the latter. Thus, except for sterically hindered bases, pK = −0.79pK_a + 0.53. This equilibrium, like the zinc equilibria, is established relatively slowly,[31] the rate constants k_1 and k_{-1} being similarly related to K, with $\alpha = 1.66$.

K' of eq 11 is related to pK_a for the base by pK' = −0.91pK_a + 1.65; here the slope of the pK–pK_a plot is close to unity. A careful reexamination of the zinc halide–acetone–aniline systems reveals some slight evidence for the presence of equilibria like eq 11 there also.[33]

b. Amides

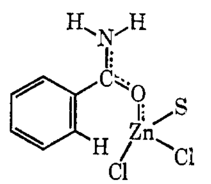
Table III[34,35] contains equilibrium constants for the interaction of zinc chloride and bromide with various benzamides in ether solution. Here again only 1:1 adducts were observed, eq 13. Nuclear magnetic resonance spectra[34] show that co-



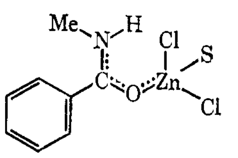
$$RC_6H_4CONH_2 + Zn(hal)_2S_2 \rightleftharpoons RC_6H_4\overset{NH_2}{\overset{|}{C}}{=}O{:}Zn(hal)_2S + S \qquad (13)$$

ordination is *via* the carbonyl, and not *via* the amino group. As for the aniline equilibria, pK is rectilinearly related to pK_a where K_a is now the dissociation constant of (amide–H)$^+$ in water. For $ZnCl_2$ the relationship is pK = −0.79pK_a − 4.69. A significant point is that considering their behavior toward the proton (*i.e.*, considering their pK_a values which probably, although not certainly, also refer to interaction at oxygen[36,37]) amides are relatively much (*ca.* 4 × 10^6-fold) stronger bases toward zinc halides than are anilines. This finding is compatible with interaction *via* the carbonyl group in amides and may arise from some double bonding to zinc, employing the metal's vacant d orbitals and the second lone pair of electrons on the carbonyl oxygen atom. The proton is unable to accept such electrons, and the nitrogen atom in an aniline does not have such electrons available, hence the relatively great basicity of the carbonyl compounds toward the metal halides (*cf.* section II.C.1; the argument here would be stronger if separate ΔH and ΔS values were available, but the increase in basicity is very large).

For benzamides, as for anilines, steric disturbance of the pK–pK_a plots is found with N-methyl derivatives. However, in contrast to the anilines, *o*-methylbenzamides do not show this effect. These findings may be rationalized in terms of the metal–oxygen double bonding suggested above as follows. Since amides often enjoy partial carbon–nitrogen double-bond character, the most effective double bond from the oxygen to zinc will probably occur when the nitrogen, carbon, oxygen, and zinc atoms are coplanar. Under such conditions, were the zinc center to assume a *trans* configuration with respect to the amine group (**2**), a halogen atom would interfere sterically with the *o*-hydrogen atom of the benzamide. Zinc must therefore take up the *cis* position as in **3**. Substitution of methyl for hydrogen in the *ortho* position will therefore



2



3

produce no new steric effect. However, for an N-methyl substituent to avoid steric collision with a halogen atom, the N-methyl group must lie *trans* with respect to the oxygen atom as in **3**, whereas the free amides normally prefer the *cis* configuration.[38,39] Thus the effects of differently sited methyl groups on the observed K values can be understood

---

(32) R. S. Satchell and D. P. N. Satchell, *Chem. Ind.* (London), 2129 (1966).

(33) R. S. Satchell, unpublished data.

(34) R. S. Satchell, submitted for publication.

(35) J. T. Edward, H. S. Chang, K. Yates, and R. Stewart, *Can. J. Chem.*, **38**, 1518 (1960).

(36) T. Birchall and R. J. Gillespie, *ibid.*, **41**, 2642 (1963).

(37) M. Liler, *Spectrochim. Acta*, **23A**, 139 (1967).

(38) J. E. Worsham and M. E. Hobbs, *J. Amer. Chem. Soc.*, **76**, 206 (1954).

(39) L. A. LaPlanche and M. T. Rogers, *ibid.*, **86**, 337 (1964).

Table IV

Zinc Halide–Ketone Equilibria in Diethyl Ether Solution[a]

Ketone	*pK*$_a$	*pK* *ZnCl*$_2$	*pK* *ZnBr*$_2$
Perinaphthenone[18]	−1.38	−1.48	−1.72
4,4′-Dimethoxybenzophenone[40]	−4.3	−0.39	−0.51
4-Methoxyacetophenone[40]	−4.8	−0.52	−0.52

[a] $\mathrm{p}K = -\log (C_A/C_BC_{\mathrm{Zn(hal)_2}})$, where A = 1:1 adduct and B = ketone; units of *K* are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

as the consequence of the postulated adduct bonding. Moreover **3** implies that the N-methyl adduct will show only *one* N–H peak in its proton magnetic resonance spectrum. This is found to be the case.[34]

It is noteworthy that, apart from the N-methyl derivatives discussed above, the general effect of substituents on these metal halide equilibria is much the same as their effect on the protonation of the amides—in spite of the considerable differences in bonding probably involved in the two cases.

c. Ketones

Table IV[18,40] contains the few data available for ketones. Tests of correlations are not worthwhile but, as expected, the more positive is pK_a the more negative is pK. As for benzamides, the ketones are appreciably (4–60 × 10^3-fold) more basic toward the metal halides than are nitrogen bases of the same pK_a. Again double bonding from oxygen to the metal is a possible cause.[18]

2. *Standard Base-Varying Acid Comparisons*

a. Anilines

Table I shows that changing the halogen substituent has little effect on the strength of zinc acids. In ether, the strengths are very similar and (p 258) to some extent dependent on the reference base. Similar remarks apply to acetone solutions, where $ZnBr_2 > ZnI_2 > ZnCl_2$. On the basis of inductive effects only, the expected order would be $ZnCl_2 > ZnBr_2 > ZnI_2$. The small over-all difference between the halides may reflect a contribution from the type of double bonding[41] thought to underlie the unexpected relative acidities of the boron halides, nonbonding electrons from the halogen atoms partially occupying the vacant zinc d orbitals, the magnitude of this acidity-reducing effect having the same sequence as the acidity-increasing inductive electron withdrawal, and the two effects tending therefore to nullify each other.[42] Halogen substituents are known to exhibit opposing electronic effects in many contexts.

Comparison of Tables I and II shows the zinc halides to be more powerful acids than cadmium iodide in acetone solution. This is as expected (section II.A). The difference, however, is small, the values of *K* referring to the same base differing by a factor of *ca.* 2 for $ZnCl_2$ and 4 for $ZnBr_2$.

Table V

Zinc Dialkyl–Bipyridyl Equilibria in Benzene Solution[a]

R	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9	n-C_5H_{11}
$10^{-3}K$	0.746	4.00	1.89	0.855	1.08
R	n-C_6H_{13}	n-C_7H_{15}	n-C_8H_{17}	n-C_9H_{19}	
$10^{-3}K$	1.19	1.39	1.18	1.22	

[a] $K = C_A/C_BC_{\mathrm{ZnR_2}}$, where A = 1:1 adduct and B = bipyridyl;[43,44] units of *K* are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

b. Amides

Toward amides, which may employ double bonding from oxygen to zinc (p 259), one might, perhaps, anticipate some opening out of the narrow acidity range exhibited by the zinc halides toward nitrogen bases. Table III shows, however, that the chloride and bromide remain about equally strong.

Although no accurate equilibrium constants have yet been obtained for mercuric halides, it can be said[38] that they are very much weaker acids than are the zinc halides toward amides (*e.g.*, $HgBr_2$ and 3-methoxybenzamide give p$K \gg -1.8$).

c. 2,2′-Bipyridyl

Besides the data in Tables I–IV, the only other systematic work with group II acids concerns zinc di-*n*-alkyls in equilibrium with bipyridyl in benzene solution (Table V[43,44]). Bipyridyl acts as a chelating base and leads therefore to 1:1 adducts only. The relatively small, and apparently haphazard, change in *K* observed on changing the *n*-alkyl group from CH_3 to C_9H_{19} is probably compatible with the combined inductive, steric, and hyperconjugative effects of the groups, but a convincing rationalization is not yet available. This comment applies to all sequences which only involve the alteration of aliphatic or alicyclic hydrocarbon structures, except for a few compounds where the steric effects are so large as clearly to be dominant.

d. Ethers

A study[45] of the competition between diethyl ether and tetrahydrofuran for three dialkylmagnesium compounds has led to some qualitative equilibrium constants of somewhat uncertain interpretation.

e. Chloride Ions

Both zinc and mercuric chloride have been examined as acceptors for chloride ions. These data are discussed in section III.F.

3. *Solvent Effects*

Toward anilines zinc halides provide more acidic systems in acetone than in ether (Table I). Acetone (ϵ = 20.7) has the higher dielectric constant, which will favor adduct formation, but may (Table XXVII) coordinate to zinc more strongly than does ether (ϵ = 4.3). The latter effect would explain the slower establishment of the equilibria in acetone[30] but should reduce the level of acidity. These matters are considered further in section III.C.1.c.

---

[40] A. Mohammad, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc.*, *B*, 727, (1967).

[41] Analogous to the double bonding suggested above for added oxygen ligands.

[42] F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

[43] K. H. Thiele and P. Zaunneck, *Organometal. Chem. Rev.*, **1**, 331 (1966).

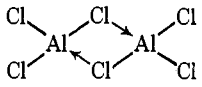
[44] For similar but less well-defined data, see J. G. Noltes and J. Boersina, *J. Organometal. Chem.*, **9**, 1 (1967).

[45] C. A. Hollingsworth, E. W. Smalley, and S. K. Podder, *Inorg. Chem.*, **3**, 222 (1964).

B. GROUP III ACIDS

More data exist for acids derived from group III elements than for any other group. This is a reflection partly of the inherent interest in a group which includes the most typical, and some of the strongest, Friedel–Crafts catalysts, and partly of the fact that certain of the acids (especially the boron acids) can be studied in the gaseous phase. Most of the data referring to the gaseous phase have been reviewed before,[1] and only their essential features will be stressed here. The motive behind many of the early gaseous phase measurements was not the quantitative study of Lewis acidity for its own sake, but the establishment of steric hindrance effects.[26]

Throughout this group 1A:1B adduct formation will normally be expected. Owing to the marked tendency of many MX_3 acids to dimerize *via* bridge structures (*e.g.*, 4) in noncoordinating media, 2A:1B adducts are likely in some circumstances. However, none of the available equilibrium constants involve this or any stoichiometry, but 1:1. Studies of acid dimerization are not included. We shall begin by considering the elements separately.



4

1. *Boron Acids*

a. Standard Acid–Varying Base Comparisons

Trimethylboron. Most of the older data for the gaseous phase refer to trimethylboron. These are in Table VI[46–51] together with a few more recent measurements with this acid. The equilibria take the general form of eq 14. The trends among the different series of related bases are mostly to be interpreted

$$\text{base} + \text{BMe}_3 \rightleftharpoons \text{base:BMe}_3 \qquad (14)$$

in terms of steric strains and repulsions (especially important for BMe_3) preventing adduct formation. We are not here primarily concerned with such phenomena, except to note that where they exist they will be expected to disturb correlations with data for the same bases in which steric effects do not intrude. It is important to realize that it was the implicit assumption that such correlations would exist which underlay the whole of the early work on the interpretation of anomalies as steric in origin. At the time this was largely an act of faith.

Certain relevant points stand out from the data in Table VI. First, comparison of the unhindered phosphine and amine equilibria shows phosphines to be the distinctly weaker bases. This is sensible: they are known to be weak proton acceptors, and double bonding from boron to empty phosphorus d orbitals is hardly to be expected (*cf.* section II.C.1 and p 262). The more extensive adduct formation with trimethylphosphine than with trimethylamine is probably the result of the larger size of the phosphorus atom reducing the steric repulsions.

Table VI

Equilibria in the Gaseous Phase Involving Trimethylboron[a]

Base	*K*	*Ref*
NH_3	0.22	46
CH_3NH_2	28.6	46
$(CH_3)_2NH$	46.7	46
$(CH_3)_3N$	2.12	46
$(CH_3)_3N$ (with $(CD_3)_3B$)	1.70	50
$C_4H_9(CH_3)_2N$	0.098	48
$C_2H_5NH_2$	1.42	46
$(C_2H_5)_2NH$	0.82	46
$(C_2H_5)_3N$	0	46
c-$C_7H_{13}N$	51.0	46
CH_3NH_2	28.6	46
$C_2H_5NH_2$	14.2	46
n-$C_3H_7NH_2$	16.7	46
n-$C_4H_9NH_2$	21.3	46
n-$C_5H_{11}NH_2$	24.1	46
n-$C_6H_{13}NH_2$	25.6	46
i-$C_3H_7NH_2$	2.72	46
sec-$C_4H_9NH_2$	2.68	46
t-$C_4H_9NH_2$	0.11	46
$(CH_3)_2NH$	46.7	46
$(CH_2)_2NH$	35.2	46
$(CH_2)_3NH$	3010	46
$(CH_2)_4NH$	286	46
$(CH_2)_5NH$	47.6	46
$(CH_2)_4PH$	0.11 (at 60°)	51
$(CH_2)_5PH$	0.21 (at 60°)	51
C_5H_5N	3.32	46
2-$CH_3C_5H_4N$	0 (at 55°)	46
3-$CH_3C_5H_4N$	7.25	46
4-$CH_3C_5H_4N$	9.52	46
PH_3	0 (at −78°)	47
CH_3PH_2	0 (at 20°)	46
$(CH_3)_2PH$	0.10	46
$(CH_3)_3P$	7.81	46
$C_2H_5(CH_3)_2P$	4.00	49
$(CH_2{=}CH)(CH_3)_2P$	0.65	49
$(CH_3)_3N$	2.12	46
$(CH_3)_3P$	7.81	46
$(CH_3)_3As$	0.63 (at 0°)	47
$(CH_3)_3Sb$	0 (at −78°)	47

[a] K refers to eq 14; $K = P_A/P_BP_{BMe_3}$, where A = adduct and B = base; units of K are atm^{-1}; temperature, 100° unless otherwise stated; vapor pressure method.

Secondly a plot of pK against pK_a for the unhindered pyridines is linear. However, there are only three points. That is why the early work on steric effects was largely an act of faith. Thirdly, the small and apparently haphazard changes in K exhibited by the series of primary aliphatic amines[52] are remarkably similar to the changes in the acidity of zinc dialkyls induced by the same n-alkyl substituents, though, of course, the effects are in the reverse direction so far as the magnitude of K is concerned. As noted, no convincing explanation is available of these subtle variations (section III.A.2.c). Finally the complete replacement of

---

(46) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(47) R. H. Harris, Ph.D. Thesis, Purdue University, 1952.

(48) H. C. Brown and R. B. Johannesen, *J. Amer. Chem. Soc.*, **75**, 16 (1953).

(49) H. D. Kaesz and F. G. A. Stone, *ibid.*, **82**, 6213 (1960).

(50) P. Love, R. W. Taft, and T. Wartik, *Tetrahedron*, **5**, 116 (1959).

(51) H. L. Morris, M. Tamres, and S. Searles, *Inorg. Chem.*, **5**, 2156 (1966).

(52) See also R. W. Taft, *U.S. Govt. Res. Develop. Rept.*, **40** (5), 15 (1965); *Chem. Abstr.*, **63**, 1248 (1965).

Table VII

Equilibria Involving Triethylboron in the Liquid Phase[a]

Base	*K*
Me_3P	Small
Me_2PNMe_2	0.35
$MeP(NMe_2)_2$	9.09
$P(NMe_2)_3$	48.3

[a] The equilibria are $Me_3N + B{:}BEt_3 \rightleftharpoons B + Me_3N{:}BEt_3$; $K = C_B C_{Me_3N:BEt_3}/C_{Me_3N}C_{B:BEt_3}$, where B = base; temperature, 0°; no additional solvent; vapor pressure method.[54]

Table VIII

Boron Fluoride- and Diborane-Ether Equilibria in the Gaseous Phase[a]

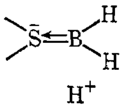
Ether	*K*	*Ref*
	(i) Boron Fluoride	
$(CH_3)_2O$	5.88	56
$(C_2H_5)_2O$	2.44	56
$(i\text{-}C_3H_7)_2O$	22.2 (at 50°)	55
$(CH_2)_4O$	69.4	57, 58
$2\text{-}CH_3C_4H_7O$	41.5	58
$2,5\text{-}(CH_3)_2C_4H_6O$	48.5	58
$(CH_2)_5O$	29.5	57, 58
$2\text{-}CH_3C_5H_9O$	3.00	60
$2,6\text{-}(CH_3)_2C_5H_8O$	0.89	58
$(CH_3)_2S$	0.17 (at 60°)	59
$(C_2H_5)_2S$	0.53 (at 60°)	59
$(CH_2)_4S$	0.25 (at 60°)	59
$(CH_2)_5S$	0.51 (at 60°)	59
	(ii) Diborane	
$(CH_3)_2O$	0 (at 20°)	60
$(CH_3)_2S$	1.12 (at 60°)	61
$(CH_3)_2Se$	0 (at 20°)	61
$(C_2H_5)_2S$	1.09 (at 60°)	62
$(CH_2)_4S$	0.91 (at 60°)	62

[a] Values of K ($P_A/P_BP_{BF_3}$ or $P_A/P_BP_{B_2H_6}{}^{1/2}$) refer to the equilibria $B + BF_3 \rightleftharpoons B{:}BF_3$ and $B + 0.5B_2H_6 \rightleftharpoons B{:}BH_3$; B = an ether and A = adduct; units of K are atm^{-1} or atm$^{-1/2}$; temperature, 100° unless stated otherwise; vapor pressure method.

protium by deuterium in BMe_3 leads to a sizable secondary isotope effect.[50]

There exist no very reliable data for trimethylboron in solution equilibria.[53] A few liquid phase measurements with the triethyl derivative and some phosphorus bases are in Table VII.[54] No solvent was used.

Ethers as Bases. Data for the gaseous phase interactions of boron fluoride and of diborane with a variety of open-chain and cyclic ethers, and certain of their sulfur and selenium analogs, are in Table VIII.[55–62] Steric effects are likely to be involved in some of the interactions, although to an uncertain extent. The pK_a values for ethers and thioethers are not yet known with much certainty,[63] but in so far as they are known, they are in general qualitative agreement with the relative basicities shown toward the boron acids, so that in these cases the steric effects are probably slight. The only definite anomaly in Table VIII is the greater basicity of dimethyl thioether compared with dimethyl ether toward borane, an acid with very small steric requirements. Borane is actually more acidic than boron fluoride toward dimethyl thioether, whereas with other types of base the reverse is true. Boron acids will not normally be expected to be able to donate electrons to the empty d orbitals of the donor elements of the high periods, so that proton-like behavior will usually be expected (section II.C.1) and is, indeed, found for all boron acids (save borane) except in examples where steric repulsions obviously[64] underlie the anomaly (p 261). The unusual nature of borane, however, leads to the possibility[1] of structures like **5**. Consequently diborane will only be expected to display acidity paralleling proton acidity toward bases derived from the same donor atom (section II.E). The data[62] for dimethyl thioether and tetrahydrothiofuran suggest, however, that even this is not yet certain. The apparent behavior of the thioethers toward borane[62] and boron fluoride[59] is not easy to rationalize. Perhaps more work is needed here.



5

No other reliable equilibrium constants are available for boron acids and ethers interacting in the gaseous phase, although data for boron chloride[59] show that this acid is much stronger than is boron fluoride.

Almost all the data for ethereal bases in the liquid phase refer to boron fluoride as the standard acid. They are listed in Tables IX,[65–67] X,[68] and XI[69] and are of recent origin. The measurements referring to ether mixtures in the absence of another solvent (Table IX) show trends in keeping with the relative basicities revealed in the gaseous phase equilibria (Table VIII). The same is true of the measurements in benzene solution (Table X). Thus dimethyl ether is clearly more basic than diethyl ether, and in cyclic compounds the basicity order is 5 > 6 > 3 in terms of ring size. If changes in the O–D stretching frequencies[63] are accepted as a reliable guide to pK_a values, the data for the cyclic ethers lead to a good pK–pK_a plot, with steric disturbances only of importance for the 2-chloro derivatives. The main discrepancies between Tables VIII and X involve the thio derivatives. As mentioned above

---

(53) H. C. Brown and D. Gintis, *J. Amer. Chem. Soc.*, **78**, 5378 (1956).

(54) R. R. Holmes and R. P. Carter, *Inorg. Chem.*, **2**, 1146 (1963).

(55) H. C. Brown and R. M. Adams, *J. Amer. Chem. Soc.*, **64**, 2557 (1942).

(56) D. E. McLaughlin and M. Tamres, *ibid.*, **82**, 5618 (1960).

(57) D. E. McLaughlin, M. Tamres, and S. Searles, *ibid.*, **82**, 5621 (1960).

(58) D. E. McLaughlin, M. Tamres, S. Searles, and S. Nutkina, *J. Inorg. Nucl. Chem.*, **17**, 112 (1961).

(59) H. L. Morris, N. I. Kulevsky, M. Tamres, and S. Searles, *Inorg. Chem.*, **5**, 124 (1966).

(60) H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, **60**, 290 (1938).

(61) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(62) T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **81**, 2989 (1959).

(63) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(64) For an alternative view, see R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 1621 (1967).

(65) R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, **59**, 1962 (1963).

(66) A. C. Rutenberg, A. A. Palko, and J. S. Drury, *J. Amer. Chem. Soc.*, **85**, 2702 (1963).

(67) M. Okada, K. Suyama, and Y. Yamashita, *Tetrahedron Letters*, **28**, 2329 (1965).

(68) H. E. Wirth and P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962).

(69) E. Gore and S. S. Danyluk, *ibid.*, **69**, 89 (1965).

Table IX

Boron Fluoride in Liquid Ether Mixtures[a]

R_2O	*K*	*Ref*
Dimethyl ether	2.5, 3.3 (at 26°)	65, 66
Ethyl methyl ether	2.0 (at 26°)	66
Tetrahydrofuran	32	67
2-Methyltetrahydrofuran	13	67
2-Chlorotetrahydrofuran	0.58	67
Tetrahydropyran	12	67
1,4-Dioxane	1.5	67
2-Methyl-1,3-dioxolane	0.56	67
4-Methyl-1,3-dioxolane	0.34	67
4-Chloromethyl-1,3-dioxolane	0.0041	67

[a] *K* refers to the equilibrium $Et_2O:BF_3 + R_2O \rightleftharpoons Et_2O + R_2O:BF_3$; $K = C_{Et_2O}C_{R_2O:BF_3}/C_{R_2O}C_{Et_2O:BF_3}$; temperature, 20° unless stated otherwise; nmr method.

Table X

Boron Fluoride Equilibria in Benzene Solution[a]

B_1	*B_2*	*K*
Me_2O	Et_2O	4.5
MeOEt	Et_2O	3.2
MeOEt	Me_2O	0.43
n-Pr_2O	Et_2O	0.20
i-Pr_2O	Et_2O	0.03
$(CH_2)_2O$	Et_2O	1.6
$(CH_2)_4O$	Et_2O	~500
$(CH_2)_5O$	Et_2O	37
$(CH_2)_5O$	Me_2O	11
$(CH_2)_4S$	Et_2O	0.016
Et_2S	Et_2O	~0.0003
MeOH	Me_2O	10
MeOH	Et_2O	34
EtOH	Me_2O	24
EtOH	Et_2O	75

[a] *K* refers to the equilibrium $B_1 + B_2:BF_3 \rightleftharpoons B_2 + B_1:BF_3$; $K = C_{B_2}C_{B_1:BF_3}/C_{B_1}C_{B_2:BF_3}$; temperature, 27°; ir spectrophotometric method.[68]

the gaseous phase measurements for these compounds are difficult to understand.

Table XI

Boron Halide–Ether Equilibria in Dichloromethane Solution[a]

R_2O	*$B(hal)_3$*	*K*
Me_2O	BF_3	3.36
Et_2O	BF_3	171
i-Pr_2O	BF_3	107
Me_2O	BCl_3	91
Et_2O	BCl_3	473

[a] *K* refers to the equilibrium $R_2O + B(hal)_3 \rightleftharpoons R_2O:B(hal)_3$; $K = C_{R_2O:B(hal)_3}/C_{R_2O}C_{B(hal)_3}$; units of *K* are l. mole^{-1}; temperature, 23°; nmr method.[69]

Table XI[69] concerns equilibria more directly analogous to the gaseous phase reactions. Apart from confirming the greater strength of boron chloride compared with boron fluoride, these data for dichloromethane solutions appear very anomalous. It may be that one or more of the reactants is undergoing decomposition.

Table XII

Reactions of Dimethylaminodiborane with Bases in the Gaseous Phase[a]

B	*$10^{-3}K$*	*Temp, °C*
Me_3N	0.11	24
Me_3P	6.3	24.5
Me_2PH	Small	25
C_5H_5N	14	25
2-MeC_5H_4N	4.0	28.5

[a] *K* refers to the equilibrium $Me_2NB_2H_5 + \mathbf{B} \rightleftharpoons A$, where B = base and A = 1:1 adduct (detailed structure unknown; measurements referring to a few other related equilibria are given in ref 70); $K = P_A/P_BP_{Me_2NB_2H_5}$; units of *K* are atm^{-1}; vapor pressure method.[70]

Table XIII

Equilibria between Trimethylamine and Boron Fluoride Derivatives in the Gaseous Phase[a]

R	CH_3	C_2H_5	*n*-C_3H_7	$-CH{=}CH_2$
K	31.0	20.2	16.3	122

[a] *K* refers to the equilibrium $RBF_2 + Me_3N \rightleftharpoons Me_3N:BF_2R$; $K = P_{Me_3N:BF_2R}/P_{RBF_2}P_{Me_3N}$; units of *K* are atm^{-1}; temperature, 150°; vapor pressure method.[71]

Table XIV

Equilibria between Boron Fluoride and Some Phosphorus and Related Bases in the Gaseous Phase[a]

B	*K*	*Ref*
CH_3PH_2	~0	46
$(CH_3)_2PH$	0.095	46
$(CH_3)_3P$	15.0	46
$(CH_3)_3As$	2.5 (at 5°)	47
$(CH_3)_3Sb$	~0 (at −78°)	47
$(CH_3)_3N$	Large	72
$(CH_2)_4PH$	0.38 (at 60°)	51
$(CH_2)_5PH$	0.80 (at 60°)	51

[a] *K* refers to the equilibrium $B + BF_3 \rightleftharpoons B:BF_3$; $K = P_{B:BF_3}/P_BP_{BF_3}$; units of *K* are atm^{-1}; temperature, 100° unless stated otherwise; vapor pressure method.

Miscellaneous Gaseous Phase Data. Measurements of some derivatives of diborane and of boron fluoride in the gaseous phase are in Tables XII,[70] XIII,[71] and XIV.[46,47,51,72] The trends in *K* are generally understandable in the light of our earlier discussions and confirm trends shown by data in Tables VI and VIII. The electron-withdrawing effect of the vinyl group presumably outweighs any steric embarrassment this group produces. For a more detailed evaluation of the early gaseous equilibrium measurements the reader should consult ref 1.

Bases Other Than Ethers. The results of studies with other types of base, normally with boron fluoride as the standard acid in ethereal solvents, are in Tables XV–XVII.[73–76] In all these cases an equilibrium like eq 15 is involved; other

---

(70) A. B. Burg and J. S. Sandhu, *Inorg. Chem.*, **4**, 1467 (1965).

(71) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 6233, (1960); see also ref 1 for a few related data.

(72) A. B. Burg and A. A. Green, *J. Amer. Chem. Soc.*, **65**, 1838 (1943).

(73) R. S. Satchell and D. P. N. Satchell, *Chem. Ind.* (London), 1520 (1965).

(74) R. S. Satchell and D. P. N. Satchell, *J. Chem. Soc.*, *B*, 36 (1967).

(75) B. M. J. Ellul and R. B. Moodie, *ibid.*, 253 (1967).

(76) R. B. Moodie, *Chem. Ind.* (London), 1269 (1961).

Table XV

Boron Fluoride–Amine Equilibria in Diethyl Ether Solution[a]

Amine	*pK_a*	*pK (pK_{calcd})*
3-Nitroaniline	2.50	−2.65 (−2.69)
6-Methyl-3-nitroaniline	2.32	−2.03 (−2.52)
4-Chloro-3-nitroaniline	1.93	−2.12 (−2.14)
2,5-Dichloroaniline	1.50	−1.16 (−1.73)
3-Methyl-4-nitroaniline	1.45	−1.81 (−1.68)
4-Nitroaniline	0.99	−1.46 (−1.24)
N,N-Dimethyl-4-nitroaniline	0.92	+0.13 (−1.17)
N-Phenylaniline	0.78	+0.11 (−1.05)
4-Nitro-1-naphthylamine	0.38	−0.55 (−0.65)
3,5-Dinitroaniline	0.22	−0.45 (−0.50)
2-Nitroaniline	−0.29	+0.02 (+0.01)

[a] K refers to eq 15; pK = −log ($C_A/C_BC_{BF_3}$), where A = adduct and B = amine;[73,74] pK_{calcd} = pK calculated from correlation equation on p 264; units of K are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

than 1:1 stoichiometry for boron acids appears most unusual,

$$R_2O{:}BF_3 + B \rightleftharpoons B{:}BF_3 + R_2O \qquad (15)$$

but can, of course, occur in a trivial sense with bifunctional bases.

Toward boron fluoride in diethyl ether, anilines display behavior analogous to that observed with the zinc halides and a good correlation, pK = −0.96pK_a − 0.29, exists for the unhindered anilines.[74] Steric effects are particularly pronounced for N substituents. Boron fluoride–aniline adducts, carrying at least one hydrogen atom on nitrogen, disproportionate slowly to the tetrafluoroborate and the arylaminoboron difluoride.[74]

Table XVII

Boron Fluoride–Ketone Equilibria in Diethyl Ether Solution[a]

Ketone	*pK_a*	*pK at 25°* [18, 40]	*pK at 20°* [76]
Perinaphthenone	−1.38	−1.13	
4,4′-Dimethoxybenzophenone	−4.30	+2.15	
4-Methoxyacetophenone	−4.80	+0.63	+0.92
4-Methylacetophenone	−5.47		+1.73
Acetophenone	−6.15		+2.19

[a] K refers to eq 15; pK = −log ($C_A/C_BC_{BF_3}$), where A = adduct and B = ketone; units of K are l. mole^{-1}; uv spectrophotometric method.

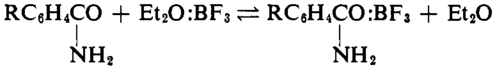
Table XVI

Boron Fluoride–Benzamide Equilibria[a]

Benzamide deriv	*pK_a*	*pK (pK_{calcd}) in diethyl ether*[34] *at 25°*	*pK (pK_{calcd}) in tetrahydrofuran*[75] *at 26°*
4-Methoxy	−1.80		−2.35 (−2.22)
2-Methyl	−1.88	∼−3.4 (−3.45)	
4-Methyl	−2.01		−1.99 (−1.96)
N-Methyl	−2.13	−1.25 (−3.18)	
3-Methyl	−2.15		−1.83 (−1.78)
Hydrogen	−2.16	−3.1 (−3.14)	−1.78 (−1.77)
4-Phenyl			−1.70
4-Fluoro	−2.24		−1.63 (−1.67)
4-Chloro	−2.47	−2.87 (−2.80)	−1.35 (−1.38)
4-Bromo	−2.47		−1.32 (−1.38)
3-Chloro	−2.59		−1.10 (−1.23)
3-Fluoro			−1.17
3-Bromo	−2.75	−2.53 (−2.49)	−1.09 (−1.03)
3-Nitro	−3.07	−2.14 (−2.13)	−0.64 (−0.63)
4-Nitro	−3.23	−1.86 (−1.95)	−0.40 (−0.43)

[a] K refers to eq 15; pK = −log ($C_A/C_BC_{BF_3}$), where A = adduct and B = benzamide derivative; pK_{calcd} = pK calculated from correlation equations on p 264; units of K are l. mole^{-1}; uv spectrophotometric method.

Data for benzamides are available for two ethereal solvents. Good pK–pK_a correlations are found with both; in tetrahydrofuran pK = −1.25pK_a − 4.47, and in diethyl ether pK = −1.11pK_a − 5.54. These data are unusual in that they involve the opening out of the basicity range exhibited by the amides, in comparison with the range they exhibit toward the proton in water. The formulation[75] of these correlations in $\rho\sigma$ terms reveals that σ leads to a marginally better representation than does σ^+. The significance of this result is difficult to assess. In benzamides, where coordination is *via* the carbonyl group as in eq 16 (see section III.A.1.b), steric hindrance arises from N-methyl but not from *o*-methyl substitution.[34] The relatively great enhancement of the basicity



$$\underset{NH_2}{RC_6H_4CO} + Et_2O{:}BF_3 \rightleftharpoons \underset{NH_2}{RC_6H_4CO}{:}BF_3 + Et_2O \qquad (16)$$

of benzamides, compared to anilines of the same pK_a, found in the zinc acid equilibria (section III.A.1.b) is also observed with boron fluoride. This is surprising since the same explanation cannot hold for boron acids, these having no acceptor d orbitals. However, an enhancement due to =N—H···F—B= hydrogen bonding may be particularly important for boron fluoride. This is discussed below in connection with the other keto bases. A few measurements involving amides and boron chloride in cyclohexane solution have been reported recently.[77]

Only five ketones have been examined with boron fluoride (Table XVII). For the three acetophenones a satisfactory pK–pK_a plot is obtained, but it is likely[40] that some special stabilizing effect such as hydrogen bonding (**6**) is involved for these compounds since 4,4′-dimethoxybenzophenone (pK_a = −4.3) is a very much *weaker* base toward boron fluoride than is 4-methoxyacetophenone (pK_a = −4.8). A structure **7**, similar to **6**, can be written for the corresponding benzamide adducts. For amides this hydrogen-bond stabilization (if real)

---

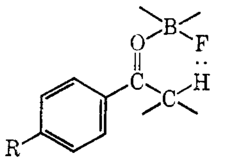
(77) M. Nakagawa, *Kogyo Kagaku Zasshi*, 67, 523 (1964).

Table XVIII

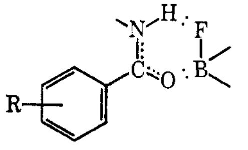
Equilibria between *p*-Fluorobenzonitrile and BX_3 Acids in Dichloromethane Solution[a]

BX_3	BF_3	BCl_3	BBr_3	p-$FC_6H_4BCl_2$
K	76	Large	Large	6.0

[a] K refers to the equilibrium $p\text{-}FC_6H_4CN + BX_3 \rightleftharpoons p\text{-}FC_6H_4CN{:}BX_3$; $K = C_A/C_BC_{BX_3}$, where A = adduct and B = $p\text{-}FC_6H_4CN$; units of K are l. mole^{-1}; temperature, 25°; nmr method.[80]



6



7

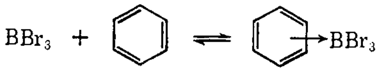
seems almost as important as the double bonding to zinc acids, whereas with ketones it is less important (as shown by comparison with anilines as standard bases). This is a sensible result: $\equiv C{-}H\cdots F{-}$ interaction will be materially weaker than $=N{-}H\cdots F{-}$ interaction. If the benzamide adducts have structure **7**, steric hindrance will be expected to arise with N- but not with *ortho*-substituted compounds. This is exactly in keeping with the experimental findings (*cf.* section III.A.1.b, where for the corresponding equilibria involving $ZnCl_2$ analogous steric effects receive a similar but distinct explanation). The foregoing rationalizations are obviously tentative, but do explain the facts.

The opening out of the basicity range of the amides toward boron fluoride compared with their behavior toward the proton in water (p 264) may also be due to the hydrogen-bonded adduct structure, an effect absent from the proton equilibria.

Data exist for the reactions of several covalent halides, including those of boron, with three derivatives of azobenzene in acetonitrile solution.[78] Although few relevant experimental details are given, the values of the equilibrium constants obtained make it clear that the reagent concentrations must have been such that the inevitable traces of water in the solvent were in serious competition with the azobenzenes for the acids. Corrections were attempted (in two cases only) for this effect. There are several other features of this work [the stoichiometry of the adducts, the exact nature of the equilibria, and the extent of the involvement of the solvent ($SbCl_5$ disproportionates in acetonitrile)] which make us wary. Later work[79] with similar systems using 1,2-dichloroethane invites some of the same criticisms.

Equilibria involving *p*-fluorobenzonitrile with certain boron acids in methylene chloride solution are described in Table XVIII.[80] The data confirm the relatively great strengths of boron chloride and bromide compared with the fluoride.

Infrared evidence[81] suggests that boron bromide in an excess of benzene engages in eq 17, with $K = 4.8 \pm 0.8$ l. mole^{-1} at 25°.



(17)

b. Standard Base-Varying Acid Comparisons

Comparisons among boron acids are few. Data for equilibria in the gaseous phase involving thioethers[59] clearly indicate that boron chloride is much more acidic than boron fluoride, but the low volatility of the boron chloride adducts made measurement difficult and the constants are not included in Table VIII. Only one or two other comparisons are available for the halogen derivatives. Measurements with *p*-fluorobenzonitrile in dichloromethane[80] support the order $BCl_3 \gg BF_3$, but the azobenzene equilibria[78] suggest an order $BF_3 > BBr_3 > BCl_3$. However, as noted, these latter data must be treated with reserve. Purely thermal measurements (ΔH) usually yield the order $BBr_3 > BCl_3 > BF_3$, and this is rationalized in terms of more inductive withdrawal by the lighter halogens but also more, and dominant, boron–halogen double bonding (section III.A.2.a). It is possible that the balance between these effects is partly a function of the strength of the coordinating base for back-bonding is not necessarily altogether absent in the adduct.

As expected, successive replacements of fluorine atoms by methyl groups in boron fluoride lead to a steady reduction in acidic properties (Table XIV). The electronic effects are probably somewhat obscured in the available examples by steric repulsions. Sensibly also, substitution of hydrogen for fluorine in boron fluoride materially reduces acidity unless the base atom has accessible d orbitals (see section III.B.1.a.).

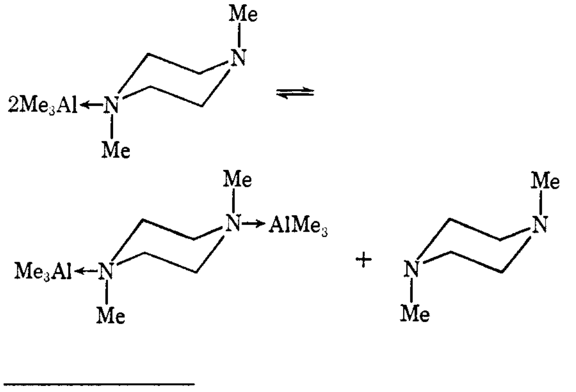
c. Solvent Effects

Table XVI shows that solutions of boron fluoride in tetrahydrofuran are less acidic than comparable solutions in diethyl ether. Toward protons tetrahydrofuran is probably more basic than is diethyl ether.[63] Their dielectric constants are similar. The observed data are therefore compatible with our expectations (section II.D).

2. Aluminum Acids

a. Standard Acid-Varying Base Comparisons

A few semiquantitative data[19,82] refer to the dimeric acid $Al_2(CH_3)_6$. In the gaseous phase this acid leads to adducts like $(CH_3)_2O{:}Al(CH_3)_3$ with the dimethyl derivatives of oxygen, sulfur, selenium, and tellurium, the order of basicity being, as expected, O > S > Se > Te. In *n*-hexane solution the equilibrium constant[83] for eq 18 is $K = 0.28$ at 25°. Another organoaluminum acid with which a few measurements have



(18)

---

(78) V. Gutmann and A. Steininger, *Monatsh. Chem.*, **96**, 1173 (1965).

(79) A. Steininger and V. Gutmann, *ibid.*, **97**, 171 (1966).

(80) R. W. Taft and J. W. Carter, *J. Amer. Chem. Soc.*, **86**, 4199 (1964).

(81) A. Finch, P. N. Gates, and D. Steele, *Trans. Faraday Soc.*, **61**, 2623 (1965).

(82) N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 316 (1942).

(83) K. H. Thiele and W. Brüser, *Z. Anorg. Allg. Chem.*, **348**, 179 (1966).

Table XIX

Equilibria Involving Triphenylaluminum in Deuteriochloroform Solution[a]

Base	*n*-$Bu_2$0	PhCN	Et_3N
K	0.67	~1	~3.3

[a] *K* refers to eq 19; $K = C_BC_{Ph_3Al:OEt_2}/C_{Et_2O}C_{Ph_3Al:B}$, where B = base; temperature, 43°; nmr method.[84]

Table XX

Aluminum Halide–Amine Equilibria in Diethyl Ether Solution[a]

Amine	pK_a	pK (pK_{calcd}) *$AlCl_3$*[85]	 *$AlBr_3$*[86]
4-Methyl-3-nitroaniline	2.90	−2.59 (−2.49)	
3-Nitroaniline	2.50	−2.18 (−2.25)	
6-Methyl-3-nitroaniline	2.32	−1.76 (−2.14)	−2.61 (−2.89)
4-Chloro-3-nitroaniline	1.93	−1.71 (−1.91)	
3-Methyl-4-nitroaniline	1.45	−1.77 (−1.62)	−2.16 (−2.24)
4-Nitroaniline	0.99	−1.45 (−1.34)	−1.88 (−1.89)
2-Methyl-4-nitroaniline	0.94	−1.35 (−1.31)	−1.76 (−1.86)
4-Methyl-2-nitroaniline	0.45	−1.20 (−1.02)	−1.57 (−1.49)
4-Nitro-1-naphthylamine	0.38		−1.54 (−1.44)
2-Nitroaniline	−0.29	−0.62 (−0.58)	−0.77 (−0.93)
6-Methyl-2-nitroaniline	−0.71	0.00 (−0.32)	−0.27 (−0.62)
2-Chloro-4-nitroaniline	−0.94		−0.05 (−0.44)

[a] *K* refers to eq 20; $pK = -\log (C_A/C_BC_{Al(hal)_3})$, where A = adduct and B = amine; pK_{calcd} = pK calculated from correlation equations on p 266; units of *K* are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

Table XXI

Equilibria Involving Trimethylgallium in the Gaseous Phase[a]

Base	*K*	*Base*	*K*
Me_3N	Large	Me_2O	0.935
Me_3P	33.3 (at 130°)	Me_2S	~0.4
Me_3As	0.746	Me_2Se	0.658
Me_3Sb	0	Me_2Te	~0.4

[a] *K* refers to the equilibrium $Me_3Ga + B \rightleftharpoons B{:}GaMe_3$; $K = P_{B:GaMe_3}/P_BP_{Me_3Ga}$, where B = base; units of *K* are atm^{-1}; temperature, 100° unless stated otherwise; vapor pressure method.[19]

Table XXII

Gallium Halide–Aniline Equilibria in Diethyl Ether Solution[a]

Aniline derivative	pK_a	pK (pK_{calcd}) *$GaCl_3$*	 *$GaBr_3$*
4-Methyl-3-nitro	2.90	−2.83 (−2.88)	−3.03 (−2.98)
3-Nitro	2.50	−2.48 (−2.49)	−2.55 (−2.58)
6-Methyl-3-nitro	2.32	−1.77 (−2.31)	−1.80 (−2.39)
3-Methyl-4-nitro	1.45	−1.78 (−1.45)	−1.78 (−1.51)
4-Nitro	0.99	−1.51 (−0.99)	−1.50 (−1.05)
2-Methyl-4-nitro	0.94	−0.80 (−0.94)	−0.83 (−1.00)
4-Methyl-2-nitro	0.45	−0.46 (−0.46)	−0.48 (−0.50)
3,5-Dinitro	0.22	−0.26 (−0.23)	−0.29 (−0.27)

[a] *K* refers to eq 22: $pK = -\log (C_A/C_BC_{Ga(hal)_3})$, where A = adduct and B = aniline derivative; pK_{calcd} = pK calculated from correlation equations on p 266; units of *K* are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.[88]

been made is triphenylaluminum. The constants for equilibrium 19 occurring in deuteriochloroform solution, where B = *n*-Bu_2O, PhCN, or Et_3N, are in Table XIX.[84] The value

$$Ph_3Al{:}OEt_2 + B \rightleftharpoons Ph_3Al{:}B + Et_2O \tag{19}$$

for triethylamine is surprisingly small compared with those for the other bases, but steric repulsions doubtlessly intrude.

The majority of the data for aluminum acids refer to the interaction of the chloride and bromide with anilines in diethyl ether solution (Table XX[85,86]). As for the zinc halides and boron fluoride, the values of p*K* for unhindered anilines engaging in eq 20 are linearly related to their pK_a values, with

$$RC_6H_4NH_2 + Al(hal)_3{:}Et_2O \rightleftharpoons RC_6H_4NH_2{:}Al(hal)_3 + Et_2O \tag{20}$$

$pK = -0.75pK_a - 1.15$ for aluminum bromide and $pK = -0.60pK_a - 0.75$ for aluminum chloride.

b. Standard Base–Varying Acid Comparisons

Table XX shows that, toward anilines in diethyl ether, aluminum bromide is roughly twice as acidic as is the chloride ($\Delta pK \approx 0.3$). This factor is slightly dependent on the reference base, owing to the somewhat different slopes of the p*K*–pK_a plots, but for the basicity range studied the bromide is clearly the stronger acid. The data suggest that with very weak anilines this may not remain true. Aluminum bromide is also considered to be marginally stronger than the chloride toward azobenzenes.[78,79]

3. Gallium Acids

a. Standard Acid–Varying Base Comparisons

Table XXI contains equilibrium constants for trimethylgallium in the gaseous phase. They are not always very accurate, and probably reflect some steric effects, but contain no unusual features; nitrogen and oxygen bases are stronger toward trimethylgallium than the corresponding phosphorus and sulfur compounds. The same picture emerges from experiments[87] with GaH_3 in benzene solution at 30°. The equilibrium

$$(CH_3)_3P{:}GaH_3 + (CH_3)_3N \rightleftharpoons (CH_3)_3N{:}GaH_3 + (CH_3)_3P \tag{21}$$

constant for eq 21 is *K* = 2.94, showing the nitrogen base to be the stronger.

More extensive studies are available for gallium chloride and bromide in ether (Tables XXII[88] and XXIII). Toward anilines, in equilibria like (22), the gallium halides behave analogously to those of zinc, boron, and aluminum: linear

$$Et_2O{:}Ga(hal)_3 + RC_6H_4NH_2 \rightleftharpoons RC_6H_4NH_2{:}Ga(hal)_3 + Et_2O \tag{22}$$

p*K*–pK_a plots are found, except that certain *ortho*-substituted bases exhibit steric hindrance. For gallium chloride $pK = -0.99pK_a + 0.01$ and for the bromide $pK = -1.01pK_a - 0.05$. A few data for 1:1 adduct formation with amide

---

(84) T. Mole, *Aust. J. Chem.*, 16, 801 (1963).

(85) A. Mohammad and D. P. N. Satchell, *J. Chem. Soc.*, *B*, 331 (1968).

(86) A. Mohammad and D. P. N. Satchell, *ibid.*, 726 (1967).

(87) N. N. Greenwood, E. J. F. Ross, and A. Storr, *ibid.*, 1400 (1965).

(88) A. Mohammad and D. P. N. Satchell, *ibid.*, *B*, 403 (1967).

Table XXIII

Equilibria between Gallium Halides and Carbonyl Bases in Diethyl Ether Solution[a]

B	*pK*$_a$	*pK* *GaCl*$_3$	*pK* *GaBr*$_3$
Perinaphthenone[18]	−1.38	< −4.0	
4,4′-Dimethoxybenzophenone[40]	−4.3	−0.54	−0.60
4-Methoxybenzophenone[40]	−4.8	−0.57	−0.57
3-Nitrobenzamide[34]	−3.07	∼ −2.6	
4-Nitrobenzamide[34]	−3.23	−2.53	−2.49

[a] *K* refers to the equilibrium $Et_2O{:}Ga(hal)_3 + B \rightleftharpoons B{:}Ga(hal)_3 + Et_2O$; $pK = -\log (C_A/C_BC_{Ga(hal)_3})$, where A = adduct and B = a ketone or an amide; units of *K* are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

Table XXIV

Equilibria between Gallium Halides and Ethers in Solution[a]

B	*GaX*$_3$	*K*	
Et_2O	$GaCl_3$	24	$K' = 1.9$
Et_2S	$GaCl_3$	55	
Et_2O	$GaBr_3$	18	$K' = 1.4$
Et_2S	$GaBr_3$	25	

$K'(GaCl_3) = 2.05^b$ $K'(GaBr_3) = 2.87^b$

[a] K' refers to eq 23 and $K' = C_{Et_2O}C_{Et_2S:GaX_3}/C_{Et_2S}\cdot C_{Et_2O:GaX_3}$; *K* refers to the equilibrium $B + GaX_3 \rightleftharpoons B{:}GaX_3$, and $K = C_{B:GaX_3}/C_{B:}C_{GaX_3}$, where B = Et_2O or Et_2S; *K* is in mole fraction units; no additional solvent; temperature, 25°; nmr method.[89] [b] Direct determination (not *via K*).

and keto bases are in Table XXIII. The observed values of *K* for both types of base are in line with the trend in the pK_a values, but as with the zinc halides (section III.A.1.b and c) the ketones are 6–25 × 10^4- and the amides 5 × 10^5-fold more basic than expected on the basis of their pK_a values, if the behavior of anilines is taken as standard. No doubt a similar explanation applies.

Data, obtained in rather concentrated solutions, for interaction between gallium chloride and bromide and both diethyl ether and diethyl sulfide, in the absence of additional solvent, are in Table XXIV.[89] It appears that the sulfur compound is *ca.* twofold the *more* basic toward these halides. This result contrasts with the other available comparisons of period 1 with period 2 elements as ligands for gallium. Further work appears necessary to clarify this issue. Table XXIV shows that for the equilibrium 23, $K' = C_{Et_2O}C_{Et_2S:GaCl_3}/C_{Et_2S}C_{Et_2O:GaCl_3} \approx 2.0$. Treating diethyl ether as the solvent and omitting its

$$Et_2O{:}GaCl_3 + Et_2S \rightleftharpoons Et_2S{:}GaCl_3 + Et_2O \qquad (23)$$

molarity from the equilibrium constant as in our other quoted constants in this solvent, we find $K = K'/C_{Et_2O} \simeq 0.2$ l. mole^{-1} (*i.e.*, p$K \simeq 0.7$). Taking pK_a for diethyl sulfide as *ca.* −5.0 we conclude that this thioether is *ca.* 2 × 10^4-fold more basic toward gallium chloride than would be expected on the basis of the data for anilines. Clearly thioethers, as well as ketones, are relatively much more basic toward covalent halides than are anilines.

Finally in this section some interesting equilibria, of rather uncertain nature, between gallium bromide and alkyl bromides in nitrobenzene have been reported.[90]

b. Standard Base-Varying Acid Comparisons

The data for ketones, anilines, and amides indicate that gallium bromide and chloride are almost equally acidic, with, if anything, the bromide a shade the stronger. Experiments with azobenzenes also suggest very similar acidities for these halides.[78,79] The equilibria with ethers place the chloride first, although the data in Table XXIV are not entirely self-consistent; in any event the two acids exhibit similar strengths in this context too. For the elements boron, aluminum, and gallium we can now distinguish for their halides the sequences $BF_3 \ll BCl_3$ ($<BBr_3$); $AlCl_3 < AlBr_3$; $GaCl_3 \simeq GaBr_3$. These are in keeping with much experimental evidence[16] which suggests that the efficiency of metal–halogen double bonding is likely to decrease with increasing size of the metal. It will be of interest to extend work to both the indium acids and to the iodides.

4. *Indium and Other Group III Acids*

Virtually no data are yet available for these acids (see, however, ref 59).

5. *Comparisons within Group III Elements*

Existing gaseous phase measurements[1] provide little unambiguous, quantitative information about the relative acidities of boron, aluminum, gallium, and indium acids, compounds involving steric interference having mostly been studied. The best available comparisons refer to the halides in diethyl ether solution with anilines, ketones, and amides as reference bases. Toward anilines (Tables XV, XX, XXII) the observed order of acid strength (over the basicity range studied) is $AlBr_3 > BF_3 \simeq AlCl_3 \simeq GaBr_3 \simeq GaCl_3$ with the over-all difference being quite small. Because the slopes of the various p*K*–pK_a plots are not identical, the only clear-cut distinction is between $AlBr_3$ and the others. Since boron chloride is much more acidic than is the fluoride (section III.B.1.b) the order for the chlorides is almost certainly $BCl_3 > AlCl_3 \geq GaCl_3$. A similar sequence is likely for the bromides. This result meets with our expectations (section II.A).

Toward ketones (Tables XVII and XXIII) the order of acid strength found is always $GaBr_3 \simeq GaCl_3 > BF_3$. Where possible complications arising from hydrogen bonding are absent, the factor separating the gallium and boron acids is *ca.* 600 in ether solution. Toward benzamides (Tables XVI and XXIII) where hydrogen bonding is probably always present for boron fluoride, a similar picture emerges with $GaBr_3 \simeq GaCl_3 > BF_3$, but the factor separating the boron and gallium acids is only *ca.* 4. The effects underlying these sequences have been discussed earlier (section III.B.1.a).

C. GROUP IV ACIDS

Of the many data concerning this group, the majority refer to tin acids. As with group II, both 1A:1B and 1A:2B adduct stoichiometry is feasible. Few equilibrium studies have provided data for the 1:2 structures, most having been made under concentration conditions where acid was in considerable excess of base. As yet there appear to have been no equilibrium measurements with silicon or germanium derivatives. These compounds appear, from qualitative evidence, to show relatively very feeble acidic properties.[15]

---

(89) N. N. Greenwood and T. S. Srivastava, *J. Chem. Soc., A*, 703 (1966).

(90) S. U. Choi, *Daehan Hwakak Hwoejee*, 7, 65 (1963); *Chem. Abstr.*, 59, 12618 (1963).

Table XXV

Stannic Chloride–Benzonitrile Equilibria in Benzene Solution[a]

R	K_{11}	K_{12}
Hydrogen	4.2	2.0
p-Methoxy	15.5	3.4
m-Methyl	6.8	1.4
p-Fluoro	3.4	2.2
p-Chloro	2.9	1.5
p-Nitro	0.8	Small
p-Chloro	2.9[b]	1.6[b]

[a] K_{11} and K_{12} refer to eq 24 and 25, respectively; $K_{11} = C_{B:SnCl_4}/C_BC_{SnCl_4}$ and $K_{12} = C_{(B:)_2SnCl_4}/C_BC_{B:SnCl_4}$, where B = RC_6H_4CN; units of K_{11} and K_{12} are *l*. mole^{-1}; temperature, 30° (for other temperatures see ref 92); ir spectrophotometric method.[91,92] [b] In 1,2-dichloroethane.

Table XXVI

Stannic Chloride–Cyclic Ether Equilibria in Benzene Solution[a]

Base	$10^{-3}K$
Tetrahydrofuran	600
2-Methyltetrahydrofuran	1
2,5-Dimethyltetrahydrofuran	0.3
Tetrahydropyran	8
4-Methyltetrahydropyran	2.5

[a] *K* refers to the equilibrium $2B + SnCl_4 \rightleftharpoons (B:)_2SnCl_4$; $K = C_{(B:)_2SnCl_4}/C_B{}^2C_{SnCl_4}$, where B = base; units of *K* are l.^{2} mole^{-2}; temperature, 25°; calorimetric method.[93]

Table XXVII

Various Stannic Chloride Equilibria in Benzene Solution[a]

Base	K_{11}	K_{12}	*Method*	*Ref*
9-Fluorenone	6.6[b]		IR	92
Diisobutyl ketone	33.8[b]		IR	92
Ethyl pivalate	4.2[b]		IR	92
Ethyl formate	19	17	UV	94
Ethyl acetate	61	6	UV	94
Ethyl propionate	21	5	UV	94
Ethyl chloroformate	0.13		UV	94
Ethyl chloroacetate	1.1	0.1	UV	94
Ethyl dichloroacetate	0.45		UV	94
Diethyl carbonate	10.5	3	UV	94
Diethyl ether	3.5	15	UV	94
Tetrahydrofuran	3000	750	UV	94
2,5-Dimethyltetrahydrofuran	50	200	UV	94
Acetone	80	25	UV	94
Cineole (with $SnBr_4$)[c]				

[a] K_{11} and K_{12} refer to similar equilibria and have the same definitions as in Table XXV, except that B represents an ether, a ketone, or an ester; units of K_{11} and K_{12} are l. mole^{-1}; temperature, 25° unless stated otherwise [b] At 30°; see ref 92 for data at other temperatures. [c] See ref 95.

1. Tin Acids

a. Standard Acid–Varying Base Comparisons

We take first the work in which both 1:1 and 1:2 adducts have been observed. For stannic chloride and a series of benzonitriles in benzene (Table XXV) an infrared technique detected both 1:1 and 1:2 adducts, but the accuracy obtained with the latter was less than with the former.[91,92] Since benzene is a poorly coordinating solvent, the observed equilibria were considered to be (24) and (25), and to involve five-coordinate tin.

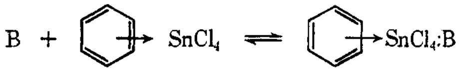
$$RC_6H_4CN + SnCl_4 \overset{K_{11}}{\rightleftharpoons} \underset{\textbf{8}}{RC_6H_4CN:SnCl_4} \qquad (24)$$

$$RC_6H_4CN:SnCl_4 + RC_6H_4CN \overset{K_{12}}{\rightleftharpoons} (RC_6H_4CN:)_2SnCl_4 \qquad (25)$$

The relative values of K_{11} and K_{12} (K_{11} always > K_{12}) indicate that species **8** is less acidic than is stannic chloride itself; this is sensible.

Thermal data have led to equilibrium constants for various cyclic ethers interacting with stannic chloride in benzene (Table XXVI). The authors[93] considered that only 1:2 adducts were involved in their systems, but this has been questioned.[94] The data in Table XXVI suggest that steric effects are important for the methyl-substituted compounds. Sensibly, tetrahydropyran is less basic than tetrahydrofuran.

Spectroscopic data for equilibria in benzene between stannic chloride and an assortment of ethers, ketones, and esters are in Table XXVII;[92,94,95] both 1:1 and 1:2 constants have been evaluated in many cases. The agreement between Tables XXVI and XXVII for tetrahydrofuran is poor. The experimental method used to obtain most of the constants given in Table XXVII (removal by added base of the charge-transfer absorption arising from the interaction between $SnCl_4$ and benzene) suggests that the formulation of equilibria 24 and 25 given earlier, in terms of five-coordinate tin, may be unsound in detail; solvent benzene presumably[95] occupies at least one coordination site as in eq 26. Indeed approximate equilibrium


(26)

constants for the 1:1 charge-transfer interaction eq 27 have been determined for four simple aromatics (Table XXVIII[103,104]), the values of which indicate that the majority of the tin

$$RPh + SnCl_4 \rightleftharpoons RPh \rightarrow SnCl_4 \qquad (27)$$

is coordinated to the solvent.[105] Stannic iodide in benzene also forms appreciable amounts of 1:1 adduct.[106] In this case

---

(91) T. L. Brown and M. Kubota, *J. Amer. Chem. Soc.*, **83**, 331 (1961).

(92) J. Laane and T. L. Brown, *Inorg. Chem.*, 3, 148 (1964).

(93) F. J. Cioffi and S. T. Zenchelsky, *J. Phys. Chem.*, 67, 357 (1963).

(94) J. J. Myher and K. E. Russell, *Can. J. Chem.*, 42,1555 (1964).

(95) T. N. Sumarokova, *Zh. Fiz. Khim.*, **38**, 316 (1964).

(96) The charge-transfer spectra may, however, arise from "contact" charge-transfer interactions.[97] Many workers[98,99] are skeptical about the reality of acid–base adduct formation between even the most acidic of covalent halides and simple aromatic molecules. Certainly color changes and other spectral effects are often produced, but the extent to which these arise from small quantities of impurities appears sometimes to be debatable. X-Ray examinations[100] of isolatable "adducts" suggest that if there is any acid–base bonding, it involves the halogen as the acceptor center.[101,102] The few equilibrium constants available for aromatics will nevertheless be taken here at their face value.

(97) J. B. Ott, J. R. Coates, R. J. Jensen, and N. F. Margelsom, *J. Inorg. Nucl. Chem.*, 27, 2005 (1965).

(98) F. Fairbrother, J. F. Nixon, and H. Prophet, *J. Less-Common Metals*, 9, 434 (1965).

(99) H. H. Perkampus and G. Orth, *Angew. Chem.*, **78**, 908 (1966).

(100) D. D. Eley, J. H. Taylor, and S. C. Wallwork, *J. Chem. Soc.*, 3867 (1961).

(101) See, however, S. U. Choi and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 903 (1966).

(102) J. Gerbier, *C. R. Acad. Sci. Paris., Ser. B*, **262**, 1611 (1966).

(103) S. Minc, Z. Kecki, and B. Izdebska, *Roczniki Chem.*, **39**, 625 (1965).

(104) Z. Kecki and B. Izdebska, *ibid.*, **40**, 1529 (1966).

(105) See also H. Tsubomura, *Bull. Chem. Soc. Jap.*, 27, 1, (1954).

(106) J. F. Murphy and D. E. Baker, *Can. J. Chem.*, **43**, 1272 (1965).

Table XXVIII

Stannic Chloride–Aromatic Hydrocarbon Equilibria[a]

ArH	*K*
Ethylbenzene	2.5
o-Xylene	1.4
m-Xylene	1.8
p-Xylene	1.1

[a] K refers to eq 27; $K = C_{\mathrm{A}}/C_{\mathrm{ArH}}C_{\mathrm{SnCl_4}}$, where A = adduct; units of K are l. mole^{-1}; excess of ArH acted as solvent; temperature, 20°; uv spectrophotometric method.[103, 104]

Table XXIX

Stannic Chloride–Carboxylic Acid Equilibria in *o*-Dichlorobenzene Solution[a]

R	K_{12}	K_a
t-Bu	112	8.9×10^{-6}
n-Bu	82	1.5×10^{-5}
i-Bu	70	1.4×10^{-5}
Et	43	1.3×10^{-5}
Me	20	1.8×10^{-5}
$PhCH_2$	16	4.9×10^{-5}
$ClCH_2CH_2$	1.8	1.0×10^{-4}
$ClCH_2$	0.14	1.4×10^{-3}
Cl_2CH	<0.01	5.1×10^{-2}
Ph	52	6.3×10^{-6}
$2\text{-}MeC_6H_4$	174	1.2×10^{-4}

[a] K_{12} refers to eq 29: $K_{12} = C_{\mathrm{(RCOOH)_2:SnCl_4}}/C_{\mathrm{(RCOOH)_2}}C_{\mathrm{SnCl_4}}$; units of K are l. mole^{-1}; temperature, 28°; K_a = acid dissociation constant of RCOOH in water at 25°; ir spectrophotometric method.[108]

it has been proposed that the iodine atoms provide a more acidic center than does the tin atom (*cf.* section II.A).

Table XXVII again indicates that, except with two ethers, $K_{12} < K_{11}$. If these two anomalies are genuine they are to be cherished; they imply that $Et_2O:SnCl_4$ and $C_6H_{12}O:SnCl_4$ are stronger acids than is $C_6H_6 \rightarrow SnCl_4$. An explanation of this in terms of a dominant drive toward the octahedron does not seem at all convincing in view of the rest of the data.

The measurements for the various esters (coordination presumably *via* the carbonyl group) in Table XXVII seem compatible with our general expectations for substituent effects.[107]

Table XXIX[108] deals with carboxylic acids. Equilibrium data for this important class of base are still not available for any covalent halide other than stannic chloride. The data are also unique in that $K_{11} < K_{12}$; indeed no estimate of K_{11} was obtained, it being so small. In *o*-dichlorobenzene solution the equilibrium may be represented, ignoring possible coordination of solvent to the tin, by either eq 28 or eq 29. Equation 29 represents interaction with the acid dimer (present in substantial amounts in rapid equilibrium with the monomer in *o*-dichlorobenzene[109]). In Table XXIX K_{12} represents K_{29}, the quantity directly measured; K_{28} can be calculated from the dimerization constants.[109] The reason that 1:2 adducts are predominant in these systems is almost certainly because a half-opened, cyclic dimer acts as a chelating ligand.[108] The strengths of the relevant carboxylic acids as bases toward the proton are not all known,[63] and those which are, are not known with much certainty, but there appears little correlation between pK_{12} and pK_a. Perhaps this is not too surprising in view of the participation of the dimer, rather than the monomer. There exists, more reasonably, a good correlation[110] for the eight substituted acetic acids between pK_{12} and σ^* (Taft's constant which reflects inductive effects). More data for aromatic acids are needed before a similar test can be applied to them.

$$2RCOOH + SnCl_4 \rightleftharpoons (RCOOH)_2SnCl_4 \qquad (28)$$

$$(RCOOH)_2 + SnCl_4 \rightleftharpoons (RCOOH)_2SnCl_4 \qquad (29)$$

Table XXX

Equilibria between Tin Acids and Carbonyl Bases in Diethyl Ether Solution[a]

		pK		
B	pK_a	$SnCl_4$	$SnBr_4$	$PhSnCl_3$
Perinaphthenone[18]	−1.38	−2.66	−1.55	−1.41
4-Nitrobenzamide[34]	−3.23	−2.80		

[a] K refers to eq 30; $pK = -\log\,(C_{\mathrm{A}}/C_{\mathrm{B}}C_{\mathrm{SnX_4}})$, where A = adduct and B = a ketone or an amide; units of K are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.

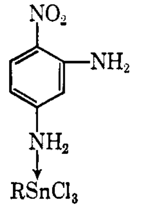
In these carboxylic acid equilibria we have the combination of both chelation and coordination *via* oxygen. This circumstance results in pivalic acid dimer being almost as strong a base as *o*-nitroaniline (*cf.* Tables XXIX and XXXI).

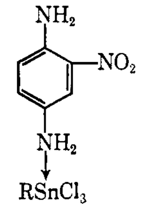
Data for one ketone and one benzamide interacting with stannic chloride and bromide in dilute ethereal solution are in Table XXX. Here it is assumed (and data in Table XXVII support this) that the observed 1:1 equilibria have the form of eq 30. Little is deducible from Table XXX, save that compared with anilines as standard (see below), ketones and benzamides are relatively much more basic than their pK_a values would suggest. As we have seen this is true for group II and group III acids also and doubtlessly has the same explanation.

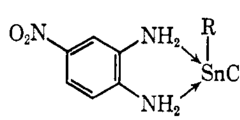
$$R_2C{=}O + SnCl_4(Et_2O)_2 \rightleftharpoons R_2C{=}O{:}SnCl_4Et_2O + Et_2O \qquad (30)$$

The remaining data for tin acids almost all refer to reaction with anilines in one or more solvents (Tables XXXI–XXXVI).[111–114] In ethereal solvents the observed 1:1 equilibria will take the form of eq 31. In aromatic solvents the extent of involvement of the solvent is uncertain. The three diamines (Table XXXV) also lead only to 1:1 adducts under the conditions used.[113,114] The adduct spectra show their structures are

$$RC_6H_4NH_2 + SnX_4(Et_2O)_2 \rightleftharpoons RC_6H_4NH_2{:}SnX_4(Et_2O) + Et_2O \qquad (31)$$


9


10


11

---

(107) See also Y. N. Vol'nov, *Zh. Fiz. Khim.*, 31, 2312 (1957).

(108) D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 61, 1132 (1965).

(109) D. P. N. Satchell and J. L. Wardell, *ibid.*, 61, 1199 (1965).

(110) J. L. Wardell, Ph.D. Thesis, London, 1965.

(111) D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 4134 (1964).

(112) D. P. N. Satchell and J. L. Wardell, *ibid.*, 4300 (1964).

(113) J. L. Wardell, *J. Organometal. Chem.*, 9, 89 (1967).

(114) J. L. Wardell, *ibid.*, 10, 53 (1967).

Table XXXI

Stannic Halide–Aniline Equilibria in *o*-Dichlorobenzene Solution[a]

		pK (pK_{calcd})			
		$SnCl_4$		$SnBr_4$	
Aniline derivative	pK_a	20° [111]	25° [28]	20° [111]	25° [26]
4-Methyl-3-nitro	2.90	−3.60 (−3.81)	−3.71		
3-Nitro	2.50	−3.60 (−3.63)	−3.68		
6-Methyl-3-nitro	2.32	−3.35 (−3.54)			
3-Methyl-4-nitro	1.45	(−3.13)	−3.54		−0.84[b]
4-Nitro	0.99	−3.18 (−2.92)			−0.55[b]
2-Methyl-4-nitro	0.94	−2.38			−0.25[b]
4-Methyl-2-nitro	0.45	−2.50 (−2.66)		+0.60[b]	
3,5-Dinitro	0.22	(−2.55)	−2.37		
2-Nitro	−0.29	−2.30 (−2.31)			
6-Methyl-2-nitro	−0.71	−0.80[b] (−0.85)			
2-Chloro-4-nitro	−0.94	−0.70[b] (−0.72)			
4-Chloro-2-nitro	−1.03	−0.70[b] (−0.67)			
5-Chloro-2-nitro	−1.54	−0.34[b] (−0.40)			
2,5-Dichloro-4-nitro	−1.78	+0.15[b] (−0.27)			
6-Chloro-2-nitro	−2.43	−0.06[b] (+0.08)			
N-Phenyl-4-nitro	−2.48	−0.96[b] (+0.11)			
N-Phenyl-2-nitro	−2.96	+0.26[b] (+0.37)			
2,6-Dichloro-4-nitro	−3.20	+0.53[b] (+0.50)			

[a] K refers to the equilibrium $B + Sn(hal)_4 \rightleftharpoons B{:}Sn(hal)_4$; $pK = -\log (C_A/C_BC_{Sn(hal)_4})$, where A = adduct and B = an aniline derivative; pK_{calcd} = pK calculated from correlation equations on p 270; units of K are l. mole^{-1}; uv spectrophotometric method. [b] These adducts show charge-transfer absorptions.

Table XXXII

Stannic Halide–Aniline Equilibria in Diethyl Ether Solution[a]

		pK (pK_{calcd})		
		$SnCl_4$	$SnBr_4$	
Aniline derivative	pK_a	25° [28]	20° [112]	25° [28]
4-Methyl-3-nitro	2.90	−2.70 (−2.69)	−2.27 (−2.12)	
3-Nitro	2.50	−2.38 (−2.43)	−1.53 (−1.70)	
6-Methyl-3-nitro	2.32	−2.10 (−2.31)	−0.91 (−1.50)	
3-Methyl-4-nitro	1.45	−1.78 (−1.74)	(−0.57)	−0.24
4-Nitro	0.99	−1.60 (−1.44)	+0.08 (−0.08)	−0.02
2-Methyl-4-nitro	0.94	−1.44 (−1.41)	+0.38 (−0.03)	+0.28
4-Methyl-2-nitro	0.45	−1.04 (−1.09)	+0.50 (+0.50)	
3-Chloro-4-nitro	0.27		+0.62 (+0.69)	
3,5-Dinitro	0.22	−0.90 (−0.94)		

[a] K refers to eq 31; $pK = -\log (C_A/C_BC_{Sn(hal)_4})$, where A = adduct and B = an aniline derivative; pK_{calcd} = pK calculated from correlation equations on p 270; units of K are l. mole^{-1}; uv spectrophotometric method.

Table XXXIII

Stannic Chloride–Aniline Equilibria in Various Aromatic Solvents[a]

Aniline derivative	*Solvent*	ϵ	pK
N-Phenyl-4-nitro	*m*-DCB	5.04	−0.46
N-Phenyl-4-nitro	Chlorobenzene	5.62	−0.72
N-Phenyl-4-nitro	*o*-DCB	9.93	−0.96
N-Phenyl-4-nitro	*o*-DCB + 25% (v/v) toluene	8.04	−0.95
N-Phenyl-4-nitro	*o*-DCB + 50% (v/v) toluene	6.16	−0.91
N-Phenyl-4-nitro	*o*-DCB + 75% (v/v) toluene	4.27	−0.72
N-Phenyl-4-nitro	*o*-DCB + 90% (v/v) toluene	3.13	−0.61
N-Phenyl-4-nitro	Toluene	2.38	−0.54
6-Methyl-2-nitro	*o*-DCB	9.93	−0.80
6-Methyl-2-nitro	Toluene	2.38	−0.62

[a] K and pK have the same definitions as in Table XXXI; units of K are l. mole^{-1}; temperature, 20°; ϵ = dielectric constant; DCB = dichlorobenzene; uv spectrophotometric method.[111]

9, **10**, and **11**. In all these systems, except those involving the diamine compounds, good pK–pK_a correlations are found for the unhindered bases. For stannic chloride, stannic bromide, and phenyl trichlorotin in ether the equations are $pK = -0.65pK_a - 0.80$, $pK = -1.07pK_a + 0.98$, and $pK = -0.80pK_a + 1.40$, respectively. With stannic chloride in *o*-dichlorobenzene the data fit two distinct relationships,[30] one for the stronger bases (giving adducts with simple anilinium type spectra) and one for the weaker bases (leading to adducts exhibiting some additional charge-transfer absorption[111]). The equations are respectively $pK = -0.47pK_a - 2.45$ and $pK = -0.54pK_a - 1.23$. Charge-transfer spectra are also observed[112,118] for certain of the adducts in ethereal solvents, but are associated there with no breaks in the pK–pK_a plots. It seems clear that in the *o*-dichlorobenzene system a fairly sharp discontinuity occurs in some aspect of the

Table XXXIV

Stannic Halide–Aniline Equilibria in Various Solvents[a]

Aniline derivative	*Solvent*	*pK*	
		$SnCl_4$	$SnBr_4$
3-Nitro	DCB	−3.68	
3-Nitro	DCB + 5% (v/v) Et_2O	−3.24	
3-Nitro	DCB + 10% (v/v) Et_2O	−2.89	
3-Nitro	DCB + 30% (v/v) Et_2O	−2.87	
3-Nitro	DCB + 70% (v/v) Et_2O	−2.60	
3-Nitro	Et_2O	−2.38	
3-Methyl-4-nitro	DCB	−3.54	−0.84
3-Methyl-4-nitro	DCB + 30% (v/v) Et_2O		−0.78
3-Methyl-4-nitro	DCB + 70% (v/v) Et_2O		−0.46
3-Methyl-4-nitro	Et_2O	−1.78	−0.24
3-Methyl-4-nitro	DCE	−2.83	−0.55
4-Nitro	DCB	−3.18	−0.55
4-Nitro	DCB + 30% (v/v) Et_2O		−0.41
4-Nitro	DCB + 70% (v/v) Et_2O		−0.20
4-Nitro	Et_2O	−1.60	−0.02
4-Nitro	DCE	−2.74	−0.29
2-Methyl-4-nitro	DCB	−2.38	−0.25
2-Methyl-4-nitro	DCB + 30% (v/v) Et_2O		−0.17
2-Methyl-4-nitro	DCB + 70% (v/v) Et_2O		+0.16
2-Methyl-4-nitro	Et_2O	−1.44	+0.28

[a] K and pK have the same definitions as in Table XXXI; units of K are l. mole^{-1}; temperature, 25°; DCB = *o*-dichlorobenzene and DCE = 1,2-dichloroethane; uv spectrophotometric method.[28]

N→Sn bonding at a certain basicity level, a discontinuity which does not occur in more basic solvents in spite of spectral evidence that the energetics of the bonding are changing in much the same way.

Table XXXV

Alkyltin Trichloride–Aniline Equilibria in Diethyl Ether Solution[a]

Aniline derivative	pK_a	*pK (pK*$_{calcd}$*) for R =*					
		n-Bu	*p-Ph*C_6H_4	*Me*	*p-Me*C_6H_4	*Ph*	*p-Cl*C_6H_4
4-Methyl-3-nitro	2.90	+0.10	+0.06	−0.35	−1.10	−0.93 (−0.92)	−0.70
3-Nitro	2.50	+0.47		−0.03	−0.78	−0.62 (−0.60)	−0.39
6-Methyl-3-nitro	2.32			+0.40	−0.36	−0.21 (−0.46)	−0.01
4-Chloro-3-nitro	1.93					−0.05 (−0.14)	
2,5-Dimethyl-4-nitro	1.52					+0.33 (+0.18)	
3-Methyl-4-nitro	1.45					+0.22 (+0.24)	
4-Nitro	0.99					+0.44 (+0.61)	
2-Methyl-4-nitro	0.94					+0.62 (+0.65)	
4-Amino-3-nitro	>4	−1.62	−1.80	−1.90	−1.98	−2.30	−2.71
2-Amino-4-nitro	2.70	−1.66	−1.95	−1.95		−2.70	−3.30
3-Amino-4-nitro	1.01	−0.66		−0.75	−0.21	−0.66	−1.36

[a] K refers to eq 31; $pK = -\log(C_A/C_B C_{RSnCl_3})$, where A = adduct and **B** = an aniline; pK_{calcd} = pK calculated from the correlation equation on p 270; units of K are l. mole^{-1}; temperature, 25°; uv spectrophotometric method.[113, 114]

In view of their pK_a values, diamines exhibit anomalously large pK values. This is because[113] (a) the *o*-diamine is a chelating base, and (b) pK_a is determined in aqueous solutions, where hydrogen bonding will reduce the electron-donating effect of the second amine group compared with its effect in ether.

A few other data,[115] referring mainly to the 1:1 interaction between trimethyltin chloride and a variety of O and S donors in carbon tetrachloride are in Table XXXVII.[116–118] It is clear that toward this tin acid the sulfur atom is a weaker base than is oxygen.

Table XXXVI

Phenyltin Trichloride + 4-Methyl-3-Nitroaniline Equilibria in Different Solvents[a]

Solvent	*pK*
Et_2O	−0.93
DCB + 80% (v/v) Et_2O	−0.95
DCB + 60% (v/v) Et_2O	−0.96

[a] K and pK have the same definitions as in Table XXXV; units of K are l. mole^{-1}; DCB = *o*-dichlorobenzene; temperature, 25°; uv spectrophotometric method.[113]

b. Standard Base-Varying Acid Comparisons

Tables XXXI and XXXII show that, toward a given nitrogen base, stannic chloride is a much stronger acid than is stannic bromide. An approximate value of p$K \simeq 0.2$ for the 2-chloroaniline–SnI_4 equilibrium[111] allows us to obtain (by stepwise comparison) a sequence of relative acidities (K) in *o*-dichlorobenzene, $SnCl_4$:$SnBr_4$:SnI_4:: 2 × 10^4:20:1; in ether $SnCl_4$:$SnBr_4$::40:1. The effect of monoalkyl, or aryl, substitution in stannic chloride is illustrated in Tables XXXV and XXXVIII.[119,120] In 1:1 equilibria with the nonchelating base 1,4 diamino-3-nitrobenzene in ether, species $RSnCl_3$ display the reasonably intelligible sequence of relative acidities *n*-Bu (1) < *p*-Ph_2 (1.5) < Me (1.9) < *p*-MeC_6H_4 (2.3) < Ph (3.8) < *p*-ClC_6H_4 (12). All these acids are much weaker than stannic chloride itself. The effect of substituents on the acid strength is, however, not necessarily as straightforward a phenomenon for equilibria in coordinating solvents as it is in noncoordinating environments. Thus to a first approximation in the gaseous phase provided, as is usual in the absence of steric hindrance, that a substituent's effect on ΔS does not outweigh its electronic effect on ΔH, it is possible to predict its effect on the acidity from its known electronic properties. When, however, what is really involved is a competition between solvent and base for the acid, confident predictions are more difficult because there are now more contributions to ΔS, and it is necessary to know whether the substituent change affects ΔH for

---

(115) See also M. Vancea and M. Volusniuc, *Acad. Rep. Populare Romine, Filiala Cluj, Studii Cercetari Chem.*, **11**, 233 (1960); *Chem. Abstr.*, **57**, 5570 (1962).

(116) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964).

(117) T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, **87**, 5015 (1965).

(118) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 5730 (1966).

(119) M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Organometal. Chem.*, **4**, 308 (1965).

(120) G. Matsubayaski, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **28**, 2937 (1966).

Table XXXVII

Equilibria Involving Trialkyltin Halides[a]

R_3M(hal)	*Base*	*K*	*Temp, °C*	*Solvent*	*Method*	*Ref*
Me_3SnCl	Pyridine	1.85	26	X	Ir	16
Me_3SnCl	Acetone	0.417	26	X	Nmr	16
Me_3SnCl	Acetonitrile	0.557	26	X	Nmr	16
Me_3SnCl	N,N-Dimethylacetamide	0.400	26	X	Nmr	16
Me_3SnCl	N,N-Dimethylacetamide	0.370	27	X	Ir	117
Me_3SnCl	N,N-Dimethylthioacetamide	0.476	26	X	Nmr	16
Me_3SnI	N,N-Dimethylacetamide	1.56	26	X	Nmr	118
Me_3SnCl	N,N-Dimethylthioacetamide	1.49	−70	Y	Nmr	16
Me_3SnCl	Acetone	0.909	26	Z	Calorimetry	16
Me_3SnCl	Hexamethylphosphoramide	385	26	Z	Calorimetry	16
Me_3SnCl	Tetramethylene sulfoxide	0.179	35	X	Ir	116
Et_3SnCl	Tetramethylene sulfoxide	0.175	35	X	Ir	116
Et_3PbCl	Tetramethylene sulfoxide	0.196	35	X	Ir	116

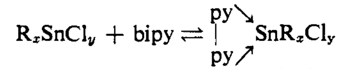
[a] *K* refers to the equilibrium $R_3M(hal) + B \rightleftharpoons B{:}MR_3(hal)$; $K = C_{B:MR_3(hal)}/C_BC_{R_3M(hal)}$, where B = base and M = Sn or Pb; units of *K* are l. mole^{-1}; solvents X, Y, and Z are carbon tetrachloride, dichloromethane, and isooctane respectively; see ref 16, 117, and 118 for values of *K* at other temperatures.

Table XXXVIII

Alkyltin Chloride–2,2′-Bipyridyl Equilibria in Acetonitrile Solution[a]

R_xSnCl_y	$SnCl_4$	n-$C_4H_9SnCl_3$	$(CH_3)_2SnCl_2$
$10^{-3}K$	$>10^4$	$>10^4$	2
R_xSnCl_y	$(C_2H_5)_2SnCl_2$	$(n$-$C_3H_7)_2SnCl_2$	$(n$-$C_4H_9)_2SnCl_2$
$10^{-3}K$	3	1.2	1.1

[a] *K* refers to the equilibrium



$$R_xSnCl_y + \text{bipy} \rightleftharpoons \begin{matrix}\text{py}\searrow \\ | \quad\ SnR_xCl_y \\ \text{py}\nearrow\end{matrix}$$

$K = C_A/C_{bipy}C_{R_xSnCl_y}$, where bipy = bipyridyl and A = adduct; units of *K* are probably l. mole^{-1}; temperature, 25°; uv spectrophotometric method.[119, 120] Values of *K* for $(n$-$C_4H_9)_2SnCl_2$ in various solvents are given in ref 119.

Table XXXIX

Titanium Chloride Equilibria in Solution[a]

B	K_{11}	K_{12}	*Temp, °C*	*Solvent*	*Ref*
Phenanthrene[b]	0.16		20	CCl_4	123
Anisole	0.077	6×10^{-4}	25	n-C_5H_{12}	97
Diphenyl ether	0.022		25	n-C_5H_{12}	97

[a] K_{11} and K_{12} refer respectively to the equilibria $TiCl_4 + B \rightleftharpoons B{:}TiCl_4$ and $B{:}TiCl_4 + B \rightleftharpoons (B{:})_2TiCl_4$; $K_{11} = C_{A_{11}}/C_BC_{TiCl_4}$ and $K_{12} = C_{A_{12}}/C_BC_{A_{11}}$, where B = base and A_{11} and A_{12} are the 1:1 and the 1:2 adducts. respectively; units of K_{11} and K_{12} are l. mole^{-1}; uv spectrophotometric method. [b] Data at other temperatures are given in ref 123.

the coordination of the solvent more or less than it affects ΔH for coordination of the base. In the system just discussed the results are "intelligible" because it is normally assumed, as a first approximation, that ΔS can be ignored and that the dominant contribution to ΔH will be that due to coordination of the base (section II.D). Under such conditions the predictions which apply for noncoordinating media will be valid: electron withdrawal will increase acidity, and so on (section II.B).

If the situation is straightforward for $RSnCl_3$ in ether with 1,4-diamino-3-nitrobenzene, it is clearly not so straightforward with simpler anilines (Table XXXV). The complexities which can arise are well illustrated in a study of the interaction, in acetonitrile solution, of stannic chloride, and of certain alkyltin chlorides, with the chelating base bipyridyl. The equilibrium constants for 1:1 adduct formation (Table XXXVIII) are superficially sensible, except for the position of the diethyl compound, but independent measurements of ΔH show that a complicated balance of effects is actually involved.[120] Some reservation must unfortunately be attached to the equilibrium constants in Table XXXVIII (for which it has also been necessary to guess the units) owing to the apparent absence of any proper attempt to exclude moisture, and to the often very low acid concentrations used.

c. Solvent Effects

Tables XXXIII, XXXIV, and XXXVI list the relevant data, which are scant. The trends in p*K* in the purely aromatic solvents (Table XXXIII) are understandable (apart from *m*-dichlorobenzene solutions which behave anomalously): lower dielectric constant and increased coordinating power will be expected to lead to a reduction in *K* (section II.D). This table also shows how the relative basicities of two bases toward a given acid can depend upon the solvent.

In ether–aromatic hydrocarbon mixtures, provided that a fair proportion of ether is present, this component, owing to its powerful coordinating ability, is likely to dominate the solvent's behavior. Thus the small change in p*K* found is reasonable (Table XXXVI).

The data in Table XXXIV show that for the stannic halides (i) the reduction of dielectric constant and increase in coordinating properties reduces acidity, (ii) this effect is greatest for the strongest acids, and (iii) of two solvents that which leads to the lower over-all level of acidity leads also to a smaller difference in acidity between given acids; *i.e.*, strongly coordinating solvents lead to a leveling effect. Certain likely assumptions lead to the prediction of just these effects (section II.D).

2. *Other Group IV Acids and Intra-Group Comparisons*

Apart from the work with tin acids, the only other measurements concerning the B subgroup elements refer to trimethyllead chloride. These are in Table XXXVII. They show that the lead compound is surprisingly little less acidic than the corresponding tin compound. The acidity sequence for group IVB is perhaps therefore Si < Ge << Sn ⩾ Pb. This is much as predicted (section II.A).

Table XL

Zirconium Halide–Ethyl Acetate Equilibria in Benzene Solution[a]

$Zr(hal)_4$	$ZrCl_4$	$ZrBr_4$	ZrI_4
K_{12}	2000	50	2.9

[a] K_{12} refers to eq 33; $K_{12} = C_{A_{12}}/C_{A_{11}}C_E$, where A_{12} and A_{11} represent respectively the 1:2 and the 1:1 adducts, and E is the ester; K is in mole fraction units; temperature, 5°; cryoscopic and dielectric polarization methods.[124]

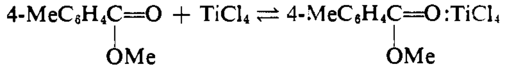
Table XLI

Equilibria Involving Phosphorus Oxychloride in Nitrobenzene Solution[a]

MCl_4	K_{11}	K_{12}
$TiCl_4$	270	8.5
$ZrCl_4$	Large	160
$HfCl_4$	Large	189

[a] K_{11} and K_{12} refer respectively to the equilibria $POCl_3 + MCl_4 \rightleftharpoons PCl_3O{:}MCl_4$ and $POCl_3 + PCl_3O{:}MCl_4 \rightleftharpoons (PCl_3O{:})_2MCl_4$: $K_{11} = C_{A_{11}}/C_{POCl_3}C_{MCl_4}$ and $K_{12} = C_{A_{12}}/C_{A_{11}}C_{POCl_3}$, where A_{11} and A_{12} are the 1:1 and 1:2 adducts, respectively; units of K are kg mole^{-1}; temperature, 5.8°; cryoscopic method.[125,126]

In the A subgroup the equilibrium between titanium chloride and *p*-tolyl acetate leads,[121] in dichloroethane, to the 1:1 adduct (eq. 32). At 25 and 60° the values of K are 400 ± 80



$$4\text{-}MeC_6H_4\underset{\displaystyle OMe}{\underset{|}{C}}{=}O + TiCl_4 \rightleftharpoons 4\text{-}MeC_6H_4\underset{\displaystyle OMe}{\underset{|}{C}}{=}O{:}TiCl_4 \qquad (32)$$

and 85 ± 10 l. mole^{-1}, respectively. An infrared method was used. No sign of a 1:2 equilibrium was reported. Mixtures of titanium chloride and ethyl propionate are considered to lead exclusively to the 1:2 adduct.[122] Other measurements with titanium chloride and organic bases are in Table XXXIX.[97,123]

Data for zirconium halides, obtained cryoscopically in benzene, are in Table XL.[124] These refer to eq 33. The extent to which the solvent coordinates to zirconium in the 1:1 adduct

$$(MeCO_2Et)_2Zr(hal)_4 \rightleftharpoons (MeCO_2Et)Zr(hal)_4 + MeCO_2Et \qquad (33)$$

is uncertain. It is clear that in this equilibrium the order of acidity is $ZrCl_4 > ZrBr_4 > ZrI_4$.

Titanium, zirconium, and hafnium chlorides have been compared in an equilibrium with phosphorus oxychloride in nitrobenzene solution.[125–128] The cryoscopic method used showed that both 1:1 and 1A:2B adducts were involved. The data are in Table XLI. They show that the 1:1 adducts are more stable than the 1:2 adducts, and that the order of acidity is Ti < Zr $\lessapprox$ Hf. These findings are entirely in line with our predictions.

Table XLII

Phosphorus and Arsenic Chlorides in Equilibria with Crystal Violet in Chloroform Solution[a]

MCl_n	$AsCl_3$	PCl_3	PCl_5
$10^{-3}K$	1.1	46	19

[a] K refers to the equilibrium $MCl_n + cv \rightleftharpoons A$; $K = C_A/C_{cv}\,C_{MCl_n}$, where cv = crystal violet and A = 1:1 adduct: units of K are l. mole^{-1}; temperature, 25° (ref 129 and 130 contain data for other temperatures); uv spectrophotometric method.[129, 130]

Table XLIII

Antimony Trichloride–Aniline Equilibria in Diethyl Ether Solution[a]

Aniline derivative	K_{11}[b]	K_{13}
4-Methyl-3-nitro	0.95	2.85
3-Nitro	0.30	1.51
6-Methyl-3-nitro	0.18	0.71

[a] K_{11} and K_{13} refer to the equilibria $B + SbCl_3 \rightleftharpoons B{:}SbCl_3$ and $B + 3SbCl_3 \rightleftharpoons B{:}(SbCl_3)_3$; $K_{11} = C_{A_{11}}/C_BC_{SbCl_3}$ and $K_{13} = C_{A_{13}}/C_B(C_{SbCl_3})^3$, where A_{11} and A_{13} represent respectively the 1:1 and 1:3 adducts and B is an aniline; units of K_{11} and K_{13} are l. mole^{-1} and l.^{3} mole^{-3}, respectively; temperature, 20°; uv spectrophotometric method.[110,134] [b] These values supersede those in ref 134.

D. GROUP V ACIDS

Surprisingly little work concerns this group. Phosphorus and arsenic are generally considered to be rather weak acids, but have been little studied. In chloroform solution phosphorus and arsenic trichlorides and phosphorus pentachloride form 1:1 adducts with crystal violet. The K values given in Table XLII[129,130] indicate (surprisingly) that arsenic is a weaker acceptor than is phosphorus, and that the pentahalide is of only comparable acidic strength to the trihalide. These results need confirmation. Phosphorus tribromide and bromine also lead to a 1:1 adduct in chlorinated hydrocarbons[131] (eq 34). At 25°, K (l. mole^{-1}) has values of 400 and 330 in carbon tetra-

$$PBr_3 + Br_2 \rightleftharpoons PBr_5 \qquad (34)$$

chloride and in ethylene dichloride, respectively. The extent of dissociation of the pentachloride is much smaller. Semiquantitative measurements[132,133] with liquid mixtures of phosphorus trichloride and tribromide or of methylphosphorus dichloride with trimethylamine, at low temperatures, indicate an order of acidity $PCl_3 > PBr_3 \simeq MePCl_2$ in equilibria like (35). This sequence, like those obtained with group III halides, suggests

$$Me_3N + PX_3 \rightleftharpoons Me_3N{:}PX_3 \qquad (35)$$

that double bonding between M and halogen in $M(hal)_n$ is of reduced importance for elements M in the second and later periods. Steric effects may, however, also play a part in these phosphorus equilibria.

Data for the equilibria between antimony trichloride and anilines in diethyl ether are in Table XLIII.[134] Evidence for both 1:1 and 3A:1B adducts was found, but not for a 2A:1B stoichiometry. The data lead to good pK-pK_a plots for both the observed interactions. The structure of the 3:1 adducts is uncertain. There exist a few other scattered data for antimony trichloride. Thus methyl benzoate and anisole have both been

---

(121) J. Gohring and B. P. Susz, *Helv. Chim. Acta*, **49**, 486 (1966).

(122) G. Leclere and G. Duyckaerts, *Spectrochim. Acta*, **22**, 403 (1966).

(123) H. L. Krauss and H. Huetmann, *Z. Naturforsch.*, **18b**, 976 (1963).

(124) Y. B. Kletenik and O. A. Osipov, *Zh. Obshch. Khim.*, **29**, 1375, 1423 (1959).

(125) B. A. Voitovich, *Zh. Neorgan. Khim.*, **5**, 1981 (1960).

(126) B. A. Voitovich, *Titan i Ego Splavy, Akad. Nauk SSSR, Inst. Met.*, **5**, 188 (1961); *Chem. Abstr.*, **57**, 15873 (1962).

(127) See also E. M. Larsen and L. J. Wittenberg, *J. Amer. Chem. Soc.*, **77**, 5850 (1955).

(128) See also D. I. Tsckhovol'skaya, *Zh. Neorgan. Khim.*, **9**, 1387 (1964).

(129) A. Basinski and E. Kwiatkowski, *Roczniki Chem.*, **41**, 175 (1967).

(130) E. Kwiatkowski, *J. Chem. Soc.*, **38**, 169 (1964).

(131) A. I. Popov and N. E. Skelly, *J. Amer. Chem. Soc.*, **76**, 3916 (1954).

(132) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960).

(133) R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, **2**, 384 (1963).

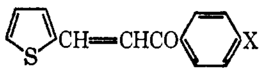
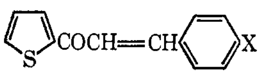
(134) D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 739 (1965).

Table XLIV

Equilibria between Antimony Pentachloride or Ferric Chloride Dimer and Chalcone Analogs in Benzene Solution[a]

12	pK		
	Fe_2Cl_6	$SbCl_5$	$(pK)_{CCl_3COOH}$
$X = NO_2$	−2.95		−1.32
X = Cl	−3.82	−2.92	−1.40
X = H	−4.20	−3.17	−1.58
$X = C_6H_5$	−4.36	−3.11	−1.48
$X = CH_3$	−4.50	−3.32	−1.65
$X = OC_2H_5$	−4.61	−3.91	−1.80
$X = OCH_3$	−4.53	−4.02	−1.94
13			
X = Cl	−3.78	−2.78	−1.36
X = H	−4.18	−3.11	−1.50
$X = C_6H_5$	−4.41	−3.20	−1.46
$X = CH_3$	−4.30	−3.45	−1.59
$X = OCH_3$	−4.48	−3.72	−1.84

[a] *K* refers to eq 36 and 38; p*K* = $-\log (C_A/C_BC_{MCl_n})$, where A = adduct and

B =  or 

12 13

and MCl_n = $SbCl_5$ or Fe_2Cl_6; units of *K* are l. mole⁻¹; for $(pK)_{CCl_3COOH}$, see text; temperature, 20° (?); uv spectrophotometric method.[137]

Table XLV

Antimony Pentachloride–Ester Equilibria in 1,2-Dichloroethane Solution[a]

R	*K*	*R*	*K*
CH_2Cl	3.8×10^3	C_2H_5	3.0×10^6
$CHCl_2$	4.9×10	$i\text{-}C_4H_9$	8.8×10^5
CCl_3	1.7	$t\text{-}C_4H_9$	2.3×10^2

[a] *K* refers to the equilibrium $SbCl_5 + EtOCOR \rightleftharpoons R(EtO)C{=}O{:}SbCl_5$; $K = C_A/C_{SbCl_5}C_{ester}$, where A = adduct; units of *K* are l. mole⁻¹; temperature, 25°; calorimetric method.[138]

Table XLVI

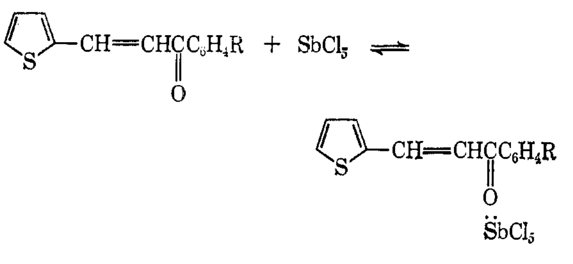
Various Antimony Pentachloride Equilibria in 1,2-Dichloroethane Solution[a]

B	*pK*	*B*	*pK*
Tributyl phosphate	−10.45	Acetonitrile	−2.85
Trimethyl phosphate	−9.28	Dimethyl sulfone	−2.72
Tetrahydrofuran	−6.92	Diphenyl sulfone	−2.36
Tricresyl phosphate	−6.80	Benzonitrile	−2.15
Triphenyl phosphate	−6.80	Azobenzene	−7.70
Water	−5.26	*p*-Nitroazobenzene	−5.23
Acetone	−4.85	Azoxybenzene	−4.40
Ethyl acetate	−4.83	Benzanthrone	−4.40
Sulfolane	−4.92	9,10-Phenanthraquinone	−3.52

[a] *K* refers to an equilibrium similar to eq 37; p*K* = $-\log (C_{B:SbCl_5}/C_BC_{SbCl_5})$, where B = base; units of *K* are l. mole⁻¹; temperature, 20°; uv spectrophotometric method.[139]

found to lead to 1:1 adducts in ether.[135] At 23°, *K* (l. mole⁻¹) has the value 0.80 for the former base and 2.7 for the latter. In carbon tetrachloride anisole is reported to give a 1A:2B adduct.[135] In nitrobenzene solution, aniline and pyridine give 1:1 adducts, and at 25°K (l. mole⁻¹) has the value 2×10^4 for the former and 1.2×10^6 for the latter base.[136]

Antimony pentachloride forms 1:1 adducts with a series of chalcones (Table XLIV[137]). In these compounds the carbonyl group probably acts as the donor center (eq 36). The extent of involvement of the benzene solvent in (36) is unknown. pK_a values are not available for these ketones, but the p*K* data



$$\text{C}_4\text{H}_3\text{S}{-}\text{CH}{=}\text{CH}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{C}_6\text{H}_4\text{R} + \text{SbCl}_5 \rightleftharpoons \text{C}_4\text{H}_3\text{S}{-}\text{CH}{=}\text{CH}\underset{\underset{\underset{\text{SbCl}_5}{\ddot{}}}{\underset{\text{O}}{\|}}}{\text{C}}\text{C}_6\text{H}_4\text{R} \qquad (36)$$

correlate well with $(pK)_{CCl_3CO_2H}$values determined for 1:1 adduct formation between the same ketones and trichloroacetic acid in benzene.[137] Substituents R have their anticipated effects on p*K*, and altogether this system is entirely in keeping with our expectations, although alarmingly small acid concentrations seem to have been used.

Antimony pentachloride has also been shown to form 1:1 adducts with a series of substituted ethyl acetates, equilibrium constants being determined in 1,2-dichloroethane solution by a calorimetric method (Table XLV[138]). The carbonyl group is almost certainly the basic center in these esters, and the *K* values are compatible with the anticipated polar and steric effects of the substituents.[138] The pentachloride apparently forms 1:1 adducts with a wide assortment of compounds in 1,2-dichloroethane, and in another study[139] p*K* values (Table XLVI) were determined by noting the effect on the indicator equilibrium (37), in which B represents an azobenzene, when the compound in question was added. However, in this work

$$B + SbCl_5 \rightleftharpoons B{:}SbCl_5 \qquad (37)$$

important corrections were necessary for water present in the solvent,[140] and the values in Table XLVI should probably be treated with considerable reserve, especially in view of their enormous range, and of the fact that the value for ethyl acetate differs from that anticipated from data in Table XLV by a factor of at least 40.

A freezing-point technique has been used to show that antimony, niobium, and tantalum pentahalides form 1:1 adducts with phosphorus oxychloride in nitrobenzene solution. The corresponding p*K* values (Table XLVII[141]) show the order of acidity to be Sb < Nb < Ta, with tantalum clearly more effective than niobium. It happens that niobium and tantalum have almost the same atomic size, so that this sequence was to be anticipated (section II.A). The remainder of the data discussed above suggest the sequence As < P << Sb. Much work remains to be done with group V acids before our predictions about them can be adequately tested.

---

(135) G. Michel and G. Duyckaarts, *Spectrochim. Acta*, 21, 279 (1965).

(136) I. M. Kolthoff, D. Stŏcesocá, and T. S. Lee, *J. Amer. Chem. Soc.*, 75, 1834 (1953).

(137) O. F. Boberov, V. N. Tolmachev, and V. F. Lavrushin, *Dopovidi Akad. Nauk Ukr. RSR*, 1315 (1966); *Chem. Abstr.*, 66, 60470*a* (1967).

(138) G. Olofsson, *Acta Chem. Scand.*, 21, 1892 (1967).

(139) V. Gutmann and U. Mayer, *Monatsh. Chem.*, 98, 294 (1967).

(140) See also V. Gutmann, A. Steininger, and E. Wychera, *ibid.*, 97, 460 (1966).

(141) B. A. Voitovich and A. S. Barabanova, *Zh. Neorgan. Khim.*, 6 2098 (1961).

Table XLVII

MCl_5–$POCl_3$ Equilibria in Nitrobenzene Solution[a]

MCl_5	$SbCl_5$	$NbCl_5$	$TaCl_5$
K	40	63	150

[a] K refers to the equilibrium $MCl_5 + POCl_3 \rightleftharpoons PCl_3O{:}MCl_5$; $K = C_A/C_{MCl_5}C_{POCl_3}$, where A = adduct; units of K are kg mole^{-1}; temperature. 5.8°; cryoscopic method.[141]

Table XLVIII

Equilibria Involving $M(py)_2X_2$ Acids in Organic Solvents[a]

(i) In Chloroform Solution[143] (M = Co)

X	Cl	Br	I	NCO	NCS	NCSe
K	12.6	9.04	2.32	23.2	83×10^3	$>10^6$

(ii) In Nitromethane Solution[143] (M = Co)

X	Cl	NCS	NCSe
K	0.40	3.55×10^3	27.8×10^3

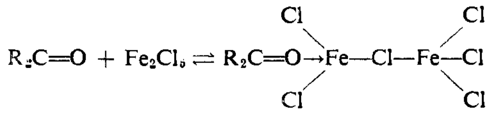
(iii) In Chlorobenzene Solution[142] (X = Cl)

M	Co	Ni
K	8.6	6.1×10^4

[a] K refers to the equilibrium $M(py)_2X_2 + 2py \rightleftharpoons M(py)_4X_2$; $K = C_{M(py)_4X_2}/(C_{py})^2C_{M(py)_2X_2}$, where py = pyridine: units of K are l.^{2} mole^{-2}; temperature, 20° (data at 30° are given in ref 142); uv spectrophotometric and solubility methods.

E. GROUP VIII ACIDS

Few systematic data concern this group. Ferric chloride has been used in a study similar to that detailed for antimony pentachloride in Table XLIV. In benzene, ferric chloride exists effectively as the dimer, and the observed equilibria probably take the form of eq 38. The ionic structure suggested for the adduct by the Russian authors[137] is unlikely to be soluble in benzene. These data for ferric chloride dimer (Table XLIV) display features similar to those found with antimony pentachloride and show these two acids to be of comparable strength, with ferric chloride somewhat the stronger. An isolated datum suggests that, in nitrobenzene solution, ferric chloride also forms a more stable adduct with phosphorus oxychloride than does titanium chloride[126] (Table XLI).



$$R_2C{=}O + Fe_2Cl_6 \rightleftharpoons R_2C{=}O\rightarrow\underset{Cl}{\overset{Cl}{Fe}}{-}Cl{-}\underset{Cl}{\overset{Cl}{Fe}}{-}Cl \qquad (38)$$

The tendencies of four-covalent cobalt and nickel to expand their coordination to the octahedron have been investigated, in chlorobenzene, chloroform, and nitromethane solutions, with pyridine (py) as the entering base and pyridine, and either halide or cyanate as the resident ligands (Table XLVIII[142,143]). It is clear that, compared with cobalt, nickel much prefers the octahedral form and is therefore the stronger acceptor. The reasons for this are uncertain, and explanations[142] based on crystal field theory have been criticized.[144] There is no doubt that a serious contradiction is involved in discussing acid–base effects in purely ionic terms. It is, however, an approach much favored by inorganic chemists. Table XLVIII shows that for $Co(py)_2X_2$ compounds the order of acidity is perhaps $Co(py)_2(NCSe)_2 > Co(py)_2(NCS)_2 > Co(py)_2(NCO)_2 > Co(py)_2Cl_2 > Co(py)_2Br_2 > Co(py)_2I_2$. When the entering ligand is 2-methylpyridine, very great steric hindrance is encountered.[143]

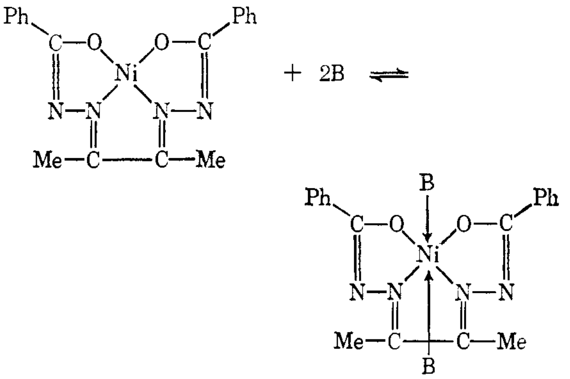
Table XLIX

Equilibria between Nitrogen Bases and Diacetyl(bisbenzoylhydrazone)nickel(II) in Benzene Solution[a]

B	pK_a	pK (pK_{calcd})
Pyridine	5.23	−3.78 (−3.88)
3-Methylpyridine	5.68	−3.90 (−4.09)
2-Methylpyridine	5.97	−0.48
4-Methylpyridine	6.02	−4.45 (−4.24)
2,5-Dimethylpyridine	6.40	−0.54
2,6-Dimethylpyridine	6.75	−1.05
2,4-Dimethylpyridine	6.77	−1.02
Quinoline	4.85	−2.08
Isoquinoline	5.40	−3.78 (−3.95)
Piperidine	11.12	−5.70
Pyrolidine	11.27	−6.84

[a] K refers to eq 39; $pK = -\log (C_A/C_B{}^2C_{NiX_4})$, where B = base and NiX_4 = diacetyl(bisbenzoylhydrazone)nickel(II); units of K are l.^{2} mole^{-2}; pK_{calcd} calculated from $pK_{calcd} = -0.46pK_a - 1.47$; temperature, 25° (data at other temperatures are given in ref 145); uv spectrophotometric method.[145]

The equilibrium between four-covalent, planar nickel and the octahedral form has also been examined in benzene solution using reaction 39, where B is a nitrogen base. For pyridines not carrying 2-substituents (*i.e.*, free from steric hindance) a good correlation is found between pK (Table XLIX) and pK_a. This result is reminiscent of those obtained with more conventional acids MX_n. Compared with pyridines as standards, piperidine and pyrolidine are much less basic than their pK_a values would suggest. This is doubtlessly because they are saturated bases and cannot receive the metal's d electrons in double bonding. In all, this system shows many of the features we have been emphasizing throughout the review.



(39)

Finally, in this group, we have some equilibria involving platinum. In eq 40 ac-Ph represents phenyl acetylene and R is a ring substituent. The data (Table L[146]) show, as expected,

$$(Ph_3P)_2Pt\leftarrow\text{ac-PhR} + \text{ac-Ph} \rightleftharpoons (Ph_3P)_2Pt\leftarrow\text{ac-Ph} + \text{ac-PhR} \qquad (40)$$

that the greater the electron withdrawal from the acetylenic center, the bigger the value of K. The electronic effects appear largely inductive.

---

(142) N. Libus and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).

(143) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(144) L. I. Katzin, *J. Chem. Phys.*, **35**, 467 (1961).

(145) L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 848 (1958).

(146) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

Table L

Phenylacetylenes in Equilibrium with Bis(triphenylphosphine)platinum(0) in Cyclohexane Solution[a]

R	$3\text{-}NO_2$	$4\text{-}NO_2$	4-Br	4-Cl	2-Cl	3-MeO	H
K	125	105	10	10	3	6	1
R	4-MeO	2-MeO					
K	1	0.5					

[a] K refers to eq 40; $K = C_{(Ph_3P)_2Pt:B}C_{RB}/C_{(Ph_3P)_2Pt:RB}C_B$, where RB = $RC_6H_4C{\equiv}CH$; temperature, 29°; uv spectrophotometric method.[146]

Table LI

Stannic Bromide–Triphenylmethyl Bromide Equilibria in Various Solvents[a]

Solvent	K_1	10^7K_2
Benzene	0.14	4.6
Dibromoethane	4.3	5.6
Bromobenzene	3.8	6.1
Chlorobenzene	3.0	17
Ethyl bromide	8.6	1600

[a] K_1 and K_2 refer to the equilibria $Ph_3CBr + SnBr_4 \rightleftharpoons [Ph_3C]^+[SnBr_5]^- \rightleftharpoons [Ph_3C]^+ + [SnBr_5]^-$; $K_1 = C_{\text{ion pair}}/C_{Ph_3CBr}C_{SnBr_4}$ and $K_2 = C_{(Ph_3C)^+}C_{(SnBr_5)^-}/C_{\text{ion pair}}$; units of K_1 are l. mole^{-1} and of K_2 l.$^{-1}$ mole; temperature, 15°; uv spectrophotometric method.[147]

Table LII

Triphenylmethyl Chloride–MCl$_n$ Equilibria in Acetic Acid Solution[a]

(i) RCl = $4\text{-}CH_3C_6H_4CPh_2Cl$

MCl_n	$SbCl_3$	$HgCl_2$	$BiCl_3$	$SnCl_4$	$FeCl_3$	$SbCl_5$
K	0.0083	0.021	0.088	7.55	238	437

(ii) RCl = Ph_3CCl

MCl_n	$SnCl_4$	$FeCl_3$
K	0.601	22.2

[a] K refers to the equilibrium $RCl + MCl_n(AcOH)_x \rightleftharpoons ([R]^+[MCl_{n+1}]^-)(AcOH)_{x-y} + y\text{AcOH}$; $K = C_{[R]^+[MCl_{n+1}]^-}/C_{RCl}C_{MCl_n}$, where RCl = a triphenylmethyl chloride derivative; units of K are l. mole^{-1}; temperature, 20°; uv spectrophotometric method.[150]

Table LIII

Triphenylmethyl Chloride–MCl$_n$ Equilibria in Phosphorus Oxychloride Solution[a]

	K in	
MCl$_n$	*PhPOCl$_2$*	*POCl$_3$*
$FeCl_3$	130	290
$SbCl_5$	39.4	110
$SnCl_4$	15.5	85
BCl_3	10.8	100
$TiCl_4$	5.3	16
$ZnCl_2$	5.3	12
$HgCl_2$	0.23	$\simeq$0.01
$AlCl_3$	0.19	14
$SbCl_3$	0.024	$\simeq$0.01
PCl_5	0.003	<0.001

[a] K refers to the equilibrium $Ph_3CCl + MCl_n \rightleftharpoons [Ph_3C]^+\text{-}[MCl_{n+1}]^-$, the extent of solvent involvement being unknown; $K = C_{[Ph_3C]^+[MCl_{n+1}]^-}C_{MCl_n}C_{Ph_3CCl}$; units of K are l. mole^{-1}; temperature, 20°; uv spectrophotometric method.[152,153]

Table LIV

Antimony Pentachloride–Triphenylmethyl Chloride Equilibrium in Various Solvents[a]

Solvent	K
Sulfuryl chloride	$>10^5$
Thionyl chloride	$>10^5$
1,2-Dichloroethane	$>10^5$
Benzoyl chloride	$>10^5$
Acetonitrile	$\simeq 10^5$
Propanediol-1,2-carbonate	3.4×10^2
Phenylphosphorus oxyfluoride	1.3×10^2
Phosphorus oxychloride	1.1×10^2
Phenylphosphorus oxychloride	3.9×10
Trimethylphosphoric acid	2.5
Dimethylformamide	5×10^{-2}
Dimethyl sulfoxide	4×10^{-2}
Pyridine	$<10^{-2}$

[a] K refers to the equilibrium $Ph_3CCl + SbCl_5 \rightleftharpoons [Ph_3C]^+[SbCl_6]^-$; units and definition of K as in Table LIII; temperature, 20° (?); uv spectrophotometric method.[154]

F. ACIDITY OF COVALENT METAL HALIDES TOWARD HALIDE IONS

Triphenylmethyl halides are useful sources of halide ions for interaction with covalent metal halides because the characteristic spectra of the resulting triphenylmethyl carbonium ions make it possible to follow the equilibria spectroscopically. In a solvent, SH, which does not solvolyze the acid (eq 41) or lead to disproportionation (eq 42), the relevant equilibrium may be eq 43. The main difficulties with these systems have

$$M(hal)_n + xSH \rightleftharpoons M(hal)_{n-x}S_x + xHhal \qquad (41)$$

$$2M(hal)_n \rightleftharpoons [M(hal)_{n-1}]^+[M(hal)_{n+1}]^- \rightleftharpoons [M(hal)_{n-1}]^+ + [M(hal)_{n+1}]^- \qquad (42)$$

$$Ph_3C(hal) + HS \rightarrow M(hal)_n \rightleftharpoons [Ph_3C]^+[M(hal)_{n+1}]^- + SH \rightleftharpoons [Ph_3C]^+ + [M(hal)_{n+1}]^- + SH \qquad (43)$$

been to be certain (a) of the extent to which the ion pair in eq 43 is dissociated, and (b) that effects 41 and 42 are absent. Apart from the pioneering work of Fairbrother and Wright,[147] who used the only mildly acidic stannic bromide in various halohydrocarbon solvents (Table LI), much of the other early work (*e.g.*, that in nitromethane[148]) is suspect for these reasons.[149] Even the data referring to acetic acid as solvent (Table LII[150]), where it is probably safe enough to assume that the ion-pair dissociation is very small, are somewhat suspect because acetic acid is known to solvolyze some covalent halides. Subsequent work by other authors[151] does not really succeed in allaying fears that the ion-pair dissociation has not been properly allowed for, or, for at least some of the acids, that processes 41 and 42 are also occurring. The most reliable of these later data are probably in Table LIII.[152,153] The particular equilibrium involving antimony pentachloride has also been measured in a series of solvents (Table LIV[154]), although here again the extent of solvent involvement in the various cases is effectively unknown. All the work mentioned above

---

(147) F. Fairbrother and B. Wright, *J. Chem. Soc.*, 1058 (1949).

(148) J. W. Bayles, A. G. Evans, and J. A. G. Jones, *ibid.*, 1020 (1957).

(149) E. Price and N. N. Lichtin, *Tetrahedron Lett.*, 18, 10 (1960).

(150), J. L. Cotter and A. G. Evans, *J. Chem. Soc.*, 2988 (1959).

(151) For a review through 1961, see M. Baaz and V. Gutmann, "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y., 1963.

(152) M. Baaz, V. Gutmann, and J. R. Masaguer, *Monatsh. Chem.*, 92 582 (1961).

(153) M. Baaz, V. Gutmann, and J. R. Masaguer, *ibid.*, **92**, 590 (1961).

(154) V. Gutmann and E. Wychera, *Inorg. Nucl. Chem. Lett.*, **2**, 257 (1966).

suffers the additional serious disadvantage that, for the strongest acids, stoichiometric acid concentrations $\lesssim 10^{-4}\ M$ were employed (section I.C).

Tables LII and LIII are in general agreement, except for the relative placings of $FeCl_3$ and $SbCl_5$. These, however, are the acids for which the data are likely to be least accurate. The real surprise of Table LIII, in the light of both our predictions and of other experimental work, is the low place occupied by aluminum chloride. In no other context does this acid exhibit a strength less than that of the chlorides of zinc, mercury, and tin. Moreover the acidity of boron chloride is relatively less than one might have predicted, although here the size of the base (Cl^-) may lead to steric effects. These interesting anomalies need verification.[155] There is, however, evidence that aluminum chloride is a poorer catalyst for the racemization of 1-phenylethyl chloride than is zinc chloride.[156] It seems likely that the relative ease of donation of *two* electron pairs from Cl^- to the metal atom underlies these sequences.[157]

IV. *Other Quantitative Approaches to Lewis Acidity*

Besides direct measurement of the thermodynamic quantities $\Delta G°$ and ΔH discussed above, other quantitative estimates of acidity (or basicity) so far proposed are relatively crude. Their main attraction is the ease with which they can be made. There is the use of (a) infrared shifts, (b) parameters derived from nuclear magnetic resonance spectra, (c) Dq values for suitable complex ions, and (d) rate constants of catalyzed reactions.

(a) By comparing infrared shifts with equilibrium constants[62,158] it has been established that the change in the O–D stretching frequency ($\Delta\nu_{OD}$ in cm^{-1}) of CH_3OD, on hydrogen bonding to different bases, serves as a rough measurement of the thermodynamic basicity of these bases in water. It is found that $\Delta\nu_{OD}$ is linearly related to $\log K_b$ where K_b $(= 1/K_a)$ is the equilibrium constant for eq 44. By analogy it has been suggested[159] that the shift in the carbonyl stretching

$$B + H_3O^+ \rightleftharpoons BH^+ + H_2O \qquad (44)$$

frequency ($\Delta\nu_{C=O}$) of any suitable carbonyl compound, on adduct formation with, in particular, a covalent metal halide (eq 45), is a semiquantiative measure of the acidity of the halide. However, comparison of such shifts with equilibrium

$$R_1R_2C{=}O + MX_n \overset{K}{\rightleftharpoons} R_1R_2C{=}O{:}MX_n \qquad (45)$$

constants shows this suggestion to be unfounded.[18] One probable reason is that the mass of the metal atom of the acid species, as well as its acid strength, is a factor in determining $\Delta\nu_{C=O}$, and this mass changes greatly among the halides studied. Methods using other oxygen bases are likely to be, and indeed show evidence of being, equally unsatisfactory.[160,161] On the other hand, comparisons of $\Delta\nu_{C=O}$ for a series of substituted carbonyl bases with a *single* acid[138,162] may well be found generally to correlate with both $\log K$ and $\log K_b$; here the dominant variable is the electron release of the substituent, which itself will often be well removed from the site of coordination. Thus carbonyl shifts may provide a swift, semiquantitative measure of the basicity of keto and other compounds toward a particular acid, in the sense that the actual determination of some equilibrium constants, together with the associated shifts, will then permit the approximate estimation of others simply by observing the shift and using an interpolation from a straight-line plot. Even so, the usefulness of shift methods of this sort is likely to be low (and very much lower than that of the $\Delta\nu_{O-D}$ method for proton basicity which can be used for a wide range of base structures) since such shifts depend on the type of compound involved, and particular ketones, esters, amides, and other bases will all need different correlation equations.

(b) When covalent metal halides are added to dimethylformamide in nitropropane (or in dichloromethane) coordination to the carbonyl group occurs, and the positions of both the N-methyl proton and the aldehyde proton resonances are altered;[163] there is, so to speak, a shift in the chemical shift. That this shift will prove to be related to the corresponding equilibrium constants for adduct formation is most unlikely in this case, if only because of the important steric hindrance observable in systems with this general structure (Table III). With reference bases free from steric effects, nuclear magnetic resonance may prove a useful approach, for various types of empirical parameter are available.[80,164–170] However, all these methods still require proper testing; there exist as yet no adequate comparisons with equilibrium constants and almost all the data refer to acids derived from group III elements.

(c) Dq values for complexes of Ni^{2+} with various bases may reflect the corresponding equilibrium constants, but this is not yet known.[171] This type of correlation appears likely to be of very limited applicability for assessing acidity.

(d) Many reactions, most notably the many varieties of Friedel–Crafts reaction, are catalyzed by covalent halides. Relative rates of reaction under given conditions have often been used, in lieu of better data, to assess relative acid strength. This sort of approach is very unsatisfactory because, at least in the past, it has been uncertain that the different acids exhibited the same kinetic reaction orders, and therefore possibly operated by the same mechanism, in the various cases compared. For instance in the racemization of α-phenylethyl chloride, an apparently simple reaction, even closely related covalent halides exhibit very different reaction orders.[172,173]

The significance and reliability of all the above approaches is, at present, at best uncertain. Many more comparisons with K values are necessary before any of the measurements can be accepted as leading to reliable correlations. It is not very

---

(155) See also H. Spandau and E. Brunneck, *Z. Anorg. Allg. Chem.*, **278**, 197 (1955).

(156) R. M. Evans and R. S. Satchell, unpublished data.

(157) See also P. A. McCusker and M. S. Kennard, *J. Amer. Chem. Soc.*, **81**, 2976 (1959), for equilibria involving the interaction, in ether solution, of ferric chloride derived from its hydrogen chloride adduct.

(158) W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941).

(159) M. F. Lappert, *J. Chem. Soc.*, 542 (1962).

(160) N. Kulevsky and L. Sveum, *J. Inorg. Nucl. Chem.*, **27**, 2111 (1965).

(161) M. J. Frazer, W. Gerrard, and W. Twaits, *ibid.*, **25**, 637 (1963).

(162) J. C. Jaccard and B. P. Susz, *Helv. Chim. Acta*, **50**, 97 (1967).

(163) S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1965).

(164) P. N. Gates and E. F. Mooney, *J. Chem. Soc.*, 4648 (1964).

(165) E. J. McLauchlan and E. F. Mooney, *Spectrochim. Acta*, **23A**, 1227 (1967).

(166) T. D. Coyle and F. S. Stone, *J. Amer. Chem. Soc.*, **83**, 4138 (1961).

(167) A. Lieb, M. T. Emerson, and J. P. Oliver, *Inorg. Chem.*, **4**, 1825 (1965).

(168) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

(169) J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 884 (1964).

(170) H. E. Swift, C. P. Poole, and J. F. Itzel, *J. Phys. Chem.*, **68**, 2509 (1964).

(171) D. W. Meek, "The Chemistry of Non-Aqueous Solvents," Vol. I, Academic Press, New York, N. Y., 1966.

(172) R. S. Satchell, *J. Chem. Soc.*, 5963 (1963).

(173) R. S. Satchell, *ibid.*, 5464 (1964).

profitable just to measure the change in some parameter and *assume* it correlates with acid strength, but that is about the level of sophistication reached by much of the available work in this area.

V. Conclusions

The equilibrium constants assembled in this review come from a wide variety of sources; they have been variously calculated and enjoy very different accuracies. Nevertheless, considered as a whole, they lead to several distinct and important conclusions. These conclusions are to be compared with the expectations advanced in section II.E.

1. There is much quantitative evidence that acids MX_n and protons exhibit parallel behavior toward any series of bases throughout which the donor center is of the same chemical type. Under such conditions equilibrium data fit equations of the form $pK = apK_a + b$. Indeed, within such series, except where steric hindrance intrudes, all the various effects (change in K and in K_a, change in vibration frequency, etc.) produced by a change of substituent in the *base* tend to correlate with each other. This is so even for systems where opportunities exist for double bonding between the metal and the donor center.[174] The value of a is not obviously related to, nor does it greatly depend upon, acid strength. Normally a lies between 0.7 and 1.0.

2. Comparisons between series of bases with different donor centers show that oxygen compounds tend to be relatively much more basic than nitrogen compounds toward acids MX_n then they are toward the proton. This fact may be due to double bonding between metal and base in the oxygen adducts, both electron pairs on oxygen being employed. Since few available data refer to sulfur and phosphorus bases, the relatively great basicity of such bases, compared with their respective oxygen and nitrogen analogs, toward certain metals (basicity which is apparent in other contexts, and which is there sometimes also thought to be due to double bonding—arising from the possibility of back-bonding), remains to be established so far as the present systems are concerned.

3. Most quantitative comparisons of the relative acidities of compounds MX_n are compatible with expectations based on the electronic structure and size of M, on the nature of the ligands X, and on the assumption of single bonding between MX_n and the reference base. Moreover, the order of relative acidity is largely independent of the reference base, although exceptions do exist. When further results become available for carbon, sulfur, phosphorus, and halogen bases, relative acidity may then be seen to be more dependent on the reference base than appears at present; but such irregularities, which will arise if changed opportunities for bonding, especially double bonding, provided by the new reference base are not equally available to all the acids, appear unlikely to prove so prevalent as seriously to undermine the foregoing generalizations. This is because the actual number of MX_n–base pairs which will permit *dominant* double-bonding effects is likely to be rather small.

4. Species MI_n can act as bifunctional acids, a behavior pattern unlikely to be restricted entirely to iodides.

5. Correlation equations, relating rate constants of acid–base processes involving species MX_n to the corresponding equilibrium constants, take the same form as the Brønsted relationship for the hydrogen acids, $k = GK^{\alpha}$, except that $\alpha > 1$.

6. Relative acidity and basicity depend upon the reaction medium in ways which, as yet, can only be rationalized rather superficially.

7. Short cuts to the relative acidities of species MX_n have not yet proved to be either direct or profitable.

8. Before a complete picture can emerge, many more data are needed, especially for acids derived from elements of groups V, VI, and VIII, and generally for carbon, sulfur, phosphorus, and halogen bases.

---

(174) Double bonding—or whatever the phenomenon is called—will only be expected to disturb such correlations (i) if the electronic requirements of the second bond are opposed to those of the primary donor–acceptor interaction, and (ii) if the second bond makes the dominant contribution to the adducts' stability. The latter condition will not normally obtain, a point not realized by all authors.[175]

(175) L. D. Pettit, A. Royston, C. Sheringham, and R. J. Whewell, *Chem. Commun.*, 1179 (1967).