(20) The stoichiometry of reaction 1 demands that the second-order rate parameter observed in excess chromium(II) be half the second-order rate parameter observed in excess disulfide.

(21) (a) For a general discussion of this phenomenon see H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed, Reinhold, New York, N.Y., 1959, Chapter 14. (b) For previously observed effects of this phenomenon see T. W. Newton and F. B. Baker, *Inorg. Chem.*, **4**, 1166 (1965); C. Lavallee and T. W. Newton, *ibid.*, **11**, 2616 (1972); D. L. Toppen and R. G. Linck, *ibid.*, **10**, 2636 (1971); C. Lavallee and E. Deutsch, *ibid.*, **11**, 3133 (1972); and references cited in these papers.

(22) [diS] = $[(H_3NC_6H_4S-)_2{}^{2+}]$.

(23) (a) R. V. James and E. L. King, *Inorg. Chem.*, **9**, 1301 (1970); (b) J. P. Birk, *ibid.*, **9**, 735 (1970); (c) J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965).

(24) The data of Figure 2 suggest two mechanisms which, although plausible, are not consistent with the details of the observed data. (1) A mechanism involving a rapid prior equilibrium between chromium(II) and *p*-aminophenyl disulfide demands that in the presence of high concentrations of chromium(II) the observed rate law be rate = $(a/2)[\mathrm{Cr(II)}][\mathrm{diS}]/(1 + b[\mathrm{Cr(II)}])$ where b has the same value as is effective in eq 8 (i.e., 14.5 F^{-1}); this is not the case. (2) A mechanism involving a rapid prior association of two disulfide molecules to form an unreactive dimer leads to a rate law which does not satisfy the data of Table III over the entire range of disulfide concentrations investigated.

(25) (a) G. E. Adams, G. S. McNaughton, and B. D. Michael in "The Chemistry of Ionization and Excitation", G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, pp 281–293; (b) G. E. Adams, G. S. McNaughton, and B. D. Michael, *Trans. Faraday Soc.*, **64**, 902 (1968); (c) G. E. Adams, R. C. Armstrong, A. Charlesby, D. E. Michael, and R. L. Willson, *ibid.*, **65**, 732 (1969); (d) M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, **77**, 990 (1973); (e) J. E. Packer in "The Chemistry of the Thiol Group", Vol. 2, S. Patai, Ed., Wiley, New York, N.Y., 1974, Chapter 11.

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Trends in the Acidities of the Zinc Family Elements

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Quantitative data are presented which provide a thermodynamic basis for trends in the acidities of the zinc family elements and for the reluctance of many two-coordinate mercury compounds to expand their coordination number. A model is presented which accounts for the high preference of mercuric ion or RHg^+ for covalent ligands in acquiring coordination number 2. The ability of the two-coordinate mercury complex to expand its coordination number is also predictable with this model in terms of the properties of the two ligands attached. The bis(hexamethyldisilylamino) compounds of zinc, cadmium, and mercury all undergo extensive reorganization upon adduct formation. They provide a basis for further examination of the concept of reorganization energy in acid–base chemistry. We illustrate how these effects could be incorporated into the E and C parameters. Some recent proposals on this topic which are at variance with the E and C formulation are also discussed.

Introduction

The observed fact that mercury tends to form two-coordinate compounds while zinc and cadmium usually have higher coordination numbers has been of considerable interest for some time.[1,2] Theoretical rationalizations[1,2] have been offered to account for these very complicated (in a thermodynamic sense) observations of reactivity. Accordingly, it was of interest to obtain solvation-minimized enthalpies of adduct formation to ascertain if the proposed explanations were correct. The reduced tendency of mercury to have high coordination numbers should be observed in the bond strengths of coordinated ligands. Since the bis(hexamethyldisilylamino) compounds[3] of zinc, cadmium, and mercury all contain a linear N–M–N system, they are ideally suited to obtaining quantitative data relating to the ability of this family of metals to expand their coordination shell and form coordination number 3. These data can provide a quantitative test of the rationalizations which have been applied to the chemistry of this family of elements.

It is important to the understanding of inorganic chemistry to have quantitative data relating to the strength of bonding of a family of elements of the periodic table. Although much of the descriptive chemistry of the compounds of the elements is presented from the view of chemical periodicity, there is very little quantitative information to support the proposed explanations which are often based upon guesses of bond strengths. Too many important concepts in inorganic chemistry have as their basis qualitative observations about chemical reactivity—an exceedingly complex phenomenon.

The compounds studied here all are soluble in benzene or cyclohexane and are monomeric. They form adducts with a variety of bases. Studies of the zinc and analogous cobalt compounds with pyridine and substituted pyridines have led to the isolation of stable 1:1 adducts[4] which are soluble in nonpolar solvents.

In the course of investigating the trends in the thermodynamics of adduct formation of compounds of the elements of the zinc family, it was also of interest to attempt to incorporate these acids into the E and C approach[5] to chemical reactivity. A very large fraction of the acid–base systems presently contained in the E and C correlation involve hydrogen-bonding interactions, and it is desirable to extend the types of acids which are included in order to establish more adequately the generality of the correlation.

These acids are also of significance to the general area of acid–base chemistry, for they constitute additional examples of systems in which the acid (or base) geometry is extensively distorted in the course of forming an adduct. These linearly coordinated free acids form trigonal-planar adducts. Early workers[6,7] in the field, viewed such geometry changes as an independent, endothermic energy contribution required to get the acid or base ready to form an adduct. According to this view, a very strong donor atom–acceptor atom bond could form, but a small $-\Delta H$ of adduct formation might result because of the large amount of energy required to rearrange the acid or base. In the boron trifluoride–ethyl acetate adduct, for example, a very strong boron–oxygen atom bond might form, but the net $-\Delta H$ of adduct formation would be small because of the energy spent to break the B–F π bonds.

There are important practical consequences associated with the role of reorganization energy. For example, if complexation is assumed to be complete and BF_3 made a larger perturbation on the base coordinated to it than BCl_3, BF_3 would be a better Lewis acid catalyst for an acid-catalyzed reaction of the base than BCl_3 in contrast to the predicted enthalpy of adduct formation. There is considerable evidence to suggest that the above view is not generally correct in acid–base chemistry although it is conceivable that such an efffect could be found in isolated systems. For example, it is found that, in general, not only is BF_3 a poorer acid than BCl_3 but it is also a poorer Lewis acid catalyst.[8] There is even more convincing evidence. We had shown previously[9] that the

Table I. Calorimetric Data for the Reactions of $Zn[N(SiMe_3)_2]_2$ and $Cd[N(SiMe_3)_2]_2$ with Bases

		$Zn[N(SiMe_3)_2]_2$		$Cd[N(SiMe_3)_2]_2$	
Base	Solvent	$-\Delta H$, kcal/mol	K	$-\Delta H$, kcal mol^{-1}	K
Pyridine	Cyclohexane	13.3 ± 0.1^a	995 ± 248^a	10.9 ± 0.1^a	220 ± 15
4-Methylpyridine	Cyclohexane	13.9 ± 0.1^a	290 ± 140	11.1 ± 0.1^a	380 ± 49
Hexamethylphosphoramide	Cyclohexane	11.7 ± 0.2^b	*d*	10.2 ± 0.3^a	4.4×10^4
	Benzene	11.6 ± 0.2^b	*d*		
N,N-Dimethylacetamide	Benzene	9.4 ± 0.1^a	215 ± 10	8.1 ± 0.1^a	120 ± 20
N-Methylimidazole	Cyclohexane	14.4 ± 0.1^b	*d*		
Piperidine[c]	Benzene	14.4 ± 0.2^b	*d*		
Piperidine[c]	Cyclohexane	10.6 ± 0.1^a	330 ± 40^a		

[a] Marginal standard deviation. [b] Estimated deviation of several results. [c] Not used in the calculation of E and C values for the zinc compound; vide infra. [d] Complete complexation of the limiting reagent occurred, within our experimental ability to ascertain.

carbonyl stretching frequency of the BF_3 adduct of ethyl acetate is decreased less than that of the BCl_3 adduct even though the latter acid has the larger $-\Delta H$ of adduct formation and a reported[6,7] smaller reorganization energy. We concluded that the electronic effect attributed to reorganization energy is more properly cast as a polarizability mechanism which influences the acidity of the substance. In this article, we show that the E and C approach to acid–base chemistry can be employed to indicate that a contribution to an acid–base interaction from a reorganization energy must be a linearly dependent quantity for the many acids and bases presently in the E and C correlation. If a system does exist in which some independent contribution from an effect of this sort is present (i.e., one not related to some property of the base or acid employed), it will be an exception to the E and C approach and may be recognized this way.

Experimental Section

Preparation and Purification of Materials. All manipulations were carried out under dry nitrogen and all glassware was thoroughly dried before use. All solvents and bases were rigorously dried as the dialkylamino compounds react with water to give the metal hydroxides or oxides and the free amines. Cyclohexane and benzene were stored over calcium hydride and distilled as needed. The bases were all thoroughly dried and generally distilled from calcium hydride before use.

The bis(hexamethyldisilylamino) compounds of zinc, cadmium and mercury were prepared by the method of Burger, et al.;[3] they were purified by distillation under reduced pressure. NMR spectra in cyclohexane showed only one sharp resonance. Samples of these compounds used in the calorimetry experiments were added to the calorimeter using calibrated syringes.

Calorimetry. The sensitivity of the dialkylamino compounds toward moisture necessitated the design of an all-glass calorimeter that could be evacuated and flushed with dry nitrogen.

The solvent was added to the clean, dried, nitrogen-filled calorimeter (generally 100 ml) via a syringe. The acid was added, using a weighed syringe and the solution magnetically stirred. The general operation of the calorimeter and the calculation of ΔH and K have been previously described.[10,11]

Results

The calorimetric data for the systems studied are shown in Table I. The solvents used in this study were cyclohexane and benzene. The *N*-methylimidazole–zinc system was studied in both cyclohexane and benzene and gave similar results indicating that there are no specific interactions of the acid with either solvent. The *N,N*-dimethylacetamide systems were studied in benzene because polar oxygen donors do not normally produce ideal results in cyclohexane,[12] although the enthalpy of adduct formation of hexamethylphosphoramide with $Zn[N(SiMe_3)_2]_2$ is or was found to be similar in benzene and cyclohexane.

The reactions of $Hg[N(SiMe_3)_2]_2$ with pyridine and tetrahydrothiophene were studied calorimetrically. The heats evolved in these systems were very low and no meaningful molar enthalpy of adduct formation could be calculated using the data obtained. Qualitative studies of the reactions of the mercury compound with the other bases employed in the zinc and cadmium systems indicated that very low heat evolution occurred.

Table II. E_A and C_A Values

Compd	C_A	E_A
$Zn[N(SiMe_3)_2]_2$	$1.07\ (0.04)^a$	5.16 (0.20)
$Cd[N(SiMe_3)_2]_2$	0.79 (0.07)	4.74 (0.29)

[a] Values in parentheses are the marginal standard deviations of the values.

The reaction of $Zn[N(SiMe_3)_2]_2$ with "ether type" bases, e.g., THF, as well as sulfur and phosphine bases, e.g., tetrahydrothiophene and dimethylphenylphosphine, led to results which indicate that very low equilibrium constants pertain. These observations precluded the measurement of the molar enthalpies of adduct formation, using the calorimetric method, for these systems.

Discussion

***E* and *C* Fit.** Using the general procedure previously described,[13] E and C values were calculated for the zinc and cadmium compounds. The values obtained are given in Table II. These results indicate that the zinc compound is a stronger acid than the cadmium compound having higher values of both E_A and C_A.

Since we have not been able to obtain the $\Delta G°$ and $\Delta H°$ values for the interaction of various bases with the mercury compound in this series, the possibility exists that the observed lack of reactivity could be either entropic or enthalpic. Since the mercuric ion is the largest in this similar series of compounds, entropy considerations appear unlikely and we shall attribute the weaker interaction with the mercury compound to a decreased enthalpy of adduct formation.

The only other series of three compounds of different acceptor atoms from the same group in the periodic table studied in detail are the trimethyl compounds of boron, aluminum, and gallium. Trimethylboron has E and C values of 6.14 and 1.70, respectively, and is a very similar though stronger type (comparable C/E ratio) acid as $Zn\{N[Si(CH_3)_3]_2\}_2$. Whereas descent in both groups of elements shows a decrease in the C values for the acceptors studied, the E values for the group 3 elements drastically increase in going from boron to aluminum. Gallium and aluminum have comparable E numbers. The trend is consistent with the polarity of the acid fragment predicted on the basis of electronegativity differences of the B–C as compared to Ga–C and Al–C bonds in the adducts. These quantitative demonstrations of the trends in the properties of these compounds are important to the development of qualitative rationalizations of their reactivity.

The decrease in the overall strength of the acids from zinc to cadmium and probably to mercury is the reverse of what might be expected if steric properties were to dominate successive differences. The disilylamino groups are very large and their bulkiness is probably one of the major factors influencing the monomeric nature of the species, thereby causing

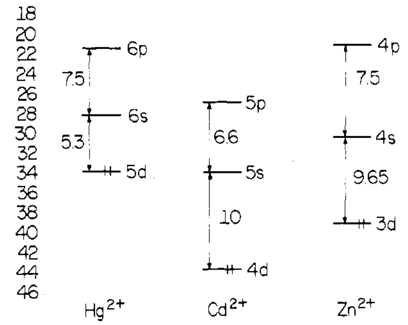

Figure 1. Schematic representation of the atomic orbital energies of the zinc family elements.

the metals in these compounds to have the unusual coordination number of 2. If steric effects were important in adduct formation, one would expect that the larger mercury atom would be more accessible to bases than the smaller zinc atom. Larger enthalpies of interaction with bases should result for the mercury compound. Steric hindrance, although not seeming to influence the properties of the Zn, Cd, and Hg compounds toward the donors studied is certainly a potential complication with these acids. However, even with the bulky donor hexamethylphosphoramide, there are no indications of complications from steric effects in the systems reported here. Steric problems have recently been proposed by Bradley et al.[14] in the study of the triphenylphosphine derivative of $Co[N(SiMe_3)_2]_2$. The cobalt–phosphorus bond length of 2.4 Å is much longer than observed for other triphenylphosphine compounds of cobalt.

The results obtained on the adduct formed between piperidine and the zinc compound are very surprising. The calculated value for the enthalpy using newly[15] obtained E and C values for piperidine[16] ($E = 1.01$ and $C = 9.32$) is −15.2 kcal mol^{-1} compared to a measured value of −10.6 kcal mol^{-1}. An alternative way of saying this which is independent of the E and C approach is that it is surprising that piperidine would have an enthalpy so much lower than would pyridine toward this acid. It is possible that proton transfer has occurred in the adduct producing free or coordinated (or both) $\{(CH_3)_3Si\}_2NH$ and $\{(CH_3)_3Si\}_2NHZnNC_5H_{10}$. If this were the case, the calculated ΔH would be meaningless, for it results from a forced fit of the evolved heat to an inappropriate equilibrium constant expression.

Trends in the Acidity of Compounds of the Zinc Family Elements. Using the information obtained in this study, we are able to propose an explanation for these results which can be extended to rationalize much of the chemical behavior of the compounds of the elements of the zinc family. In developing this model, it is pertinent to consider the orbital energies for the divalent ions of Zn^{2+}, Cd^{2+}, and Hg^{2+} which are schematically represented in Figure 1. The values for the d orbitals are estimated from the ionization potentials of the d^{10} ions (i.e., $d^{10} \rightarrow d^9 + e^-$) and those of the s and p orbitals from the promotion energies[1] $d^{10} \rightarrow d^9s$ and $d^{10} \rightarrow d^9p$, respectively. Based on the energies of the s and p orbitals, one might expect the covalency in the bond, i.e., rough C numbers, for these ions to vary as Cd^{2+}, $Zn^{2+} > Hg^{2+}$ in the formation of tetrahedral species. The reported[17] tendency of bonds to second- and third-row ligands to become weaker as one proceeds down a family of main-group elements, because of poorer orbital overlap, coupled with the s and p orbital energies shown in Figure 1 could result in the sequence of bond energies for $Cd^{2+} \sim Zn^{2+} > Hg^{2+}$. Based on the Pauling ionic radii of the ions of 0.74, 0.97, and 1.10 Å for Zn^{2+}, Cd^{2+}, and Hg^{2+}, one would expect the E values for those ions to decrease in this order. However, there are additional complications to this chemistry. Mercury(II) tends to form divalent complexes and, in so doing, forms bonds that are apparently much stronger and more covalent than those formed by tetrahedral Cd^{2+} and Zn^{2+}. (CH_3Hg^+ was the reference soft acid used by Pearson[18] in his HSAB work.) The tendency of mercury to form two-coordinate compounds has been discussed by Orgel, and his basic ideas will be employed and extended in this discussion.

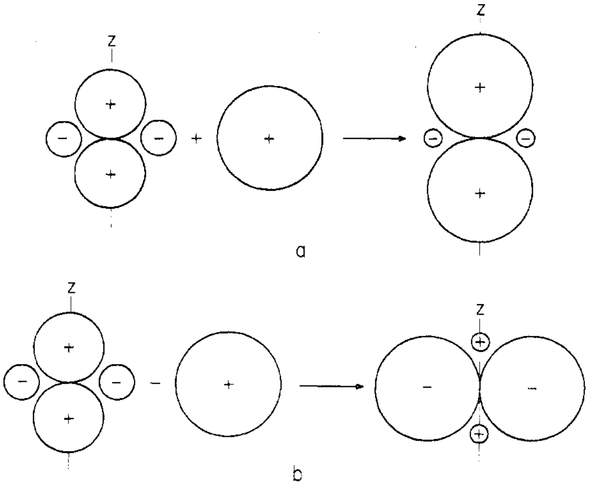

Figure 2. Formation and shapes of d_{z^2}–s hybrid orbitals.

In view of the closeness of the 6s and 5d energy levels of Hg^{2+}, one way in which the polarizability[19] of the mercury ion can be greatly enhanced involves the mixing of these atomic energy levels. The two possible combinations are shown in Figure 2a and b. If the hybrid orbital (Figure 2b) contains the pair of electrons formerly in d_{z^2} and if two ligands are located on d_{z^2}, the net effect of this mixing is to polarize the metal's electron density away from ligands and to concentrate it in the "donut" in the xy plane. The bonding of the two ligands along the z axis involves the hybrid shown in (Figure 2a) and the p_z orbitals. The extent of mixing of d_{z^2} and 4s is variable depending on the two ligands, but when they are very strong donors, as are the methide ions in $(CH_3)_2Hg$, the polarization is extensive. Accordingly, the mercury–carbon bonds are strong, and there is very little tendency for the mercury to attach ligands in the xy plane and increase its coordination number. As the donor strength of these two ligands decreases, the d–s mixing, i.e., the polarization, is not as extensive. Accordingly, we have found[20] that CH_3HgCl will form weak adducts with very strong bases like pyridine. On the other hand, when the two ligands bound to the mercury are weaker donors, e.g., Cl^-, as in $HgCl_2$, the buildup of electron density in the xy plane is not as extensive and the mercury compound is a good Lewis acid which can readily expand its coordination number. However, it is expected that those donors with large E numbers will not interact strongly but will weakly solvate in the xy plane, for the polarizability mechanism described above will not be available for these positions if the ligands on d_{z^2} are better donors. For these complexes, a Cl–Hg–Cl angle greater than 120° is anticipated. When more covalent ligands are employed, they can be expected to replace one of the halides in interacting with d_{z^2} and interact strongly forming a distorted trigonal adduct with a Cl–Hg–Cl angle less than 120° in three-coordinate complexes.

Experimental verification of these predictions is complicated by the fact that in the solid state extensive bridging occurs with mercuric halide adducts producing five- and six-coordinate species.[21] However, the Cl–Hg–Cl angle in the four-coordinate 2:1 adduct of mercuric chloride with triphylarsine oxide is 147°, while that in the near-tetrahedral adduct with 1,4-thioxane is 114°. The 1:1 adduct of mercuric chloride with tetrahydrothiophene contains two-coordinate, $C_4H_8SHgCl^+$ cations and chloride ion. The idea that polarizable donors can take advantage of the polarizability of mercury in HgX_2 when X is a weak ligand is consistent with the thermodynamic data of Farhangi and Graddon,[22] who reported a weak interaction of HgX_2 with C_4H_8O (when X = Cl, $\Delta H = 3.6$ kcal mol^{-1}, and when X = Br, 3 kcal mol^{-1}) but a strong interaction with C_4H_8S ($\Delta H = 16$ kcal mol^{-1} for the chloride and bromide).

The polarizability resulting from d–s mixing will tend to make the mercury ion have a very large *C* number toward those ligands on d_{z^2}. Accordingly, when CH_3HgCl is mixed with a thiol, RSH, hydrogen chloride will be eliminated and Cl^- replaced by the strong donor ligand SR^-. This model accounts for the strong tendency of mercury to bind two polarizable ligands very strongly in a linear fashion and then to become reluctant to expand its coordination number.

An alternative way of looking at this problem is if a two-coordinate mercury(II) compound is to form an adduct, it must do so at the expense of this polarizability mechanism which is bonding the groups on d_{z^2}. Accordingly, it is a weak Lewis acid when the groups on d_{z^2} are strong donors and will tend to form divalent complexes unless the ligands on d_{z^2} are poor donors.

With a much larger d_{z^2}–s atomic orbital energy separation, this polarization mechanism is not as important in zinc(II) and cadmium(II) systems. Accordingly, in the hexamethyldisilylamino systems studied here, we begin with linear divalent ions and attribute the reluctance of the mercury compound to form adducts to the fact that the hexamethyldisilylamino anion is a strong donor. To form an adduct, the electron density would have to be moved out of the *xy* plane by decreasing d_{z^2}–s mixing. The loss in bond energy toward the strong donor anions on d_{z^2} associated with a decrease in d_{z^2}–s mixing that would have to accompany adduct formation is larger than the gain in bond energy from binding added ligands so no adduct formation occurs. It is interesting in light of Figure 1 that both the *C* and *E* numbers of $Cd[NSi(CH_3)_3]_2$ should be lower than those of the analogous zinc compound. The trimethylsilylamine ligands could alter the essentially *n*s and *n*p metal energy levels to different extents for zinc ($n = 3$) and cadmium ($n = 4$). The trend observed between zinc and cadmium is comparable to that found for the main-group elements[17] and could be due to poorer overlap as a consequence of a more diffuse orbital on cadmium.

Reorganization Energies. In view of the extensive studies from this laboratory on spectroscopic changes accompanying adduct formation, we have been very much concerned with the concept of reorganization energies. Certainly for a given adduct formation reaction, e.g., $BF_3 + D \rightarrow BF_3D$, it is possible to write a thermodynamic cycle in which one of the endothermic steps corresponds to converting BF_3 to the same geometry it has in BF_3D. However, we shall attempt to show that such a breakup is unnecessary. In an earlier article from this laboratory,[8] we pointed out that, in order to obtain any[8] of the linear enthalpy–frequency shift relations reported in the literature,[8,23–33] it is essential that the acids (for a constant-base plot) or the bases (for a constant-acid plot) undergo a change in geometry, the energy of which is proportional to the strength of the interaction or to some property of the acceptor or donor.[33] Changes in the B–F bond lengths and F–B–F angles in a series of different-strength BF_3 adducts were offered[8] in support of this idea. The proposed idea[6,7] of an independent quantity for a promotion energy in which the B–F π bonds are broken, leading to a small net $-\Delta H$ but a strong bond between the boron and oxygen, was shown to be inconsistent with the magnitude of the carbonyl frequency shift of the ethyl acetate adducts of BF_3, BCl_3, and $SbCl_5$. Instead, it was proposed that B–F π bonding was decreased and the B–F σ bond weakened in direct proportion to the magnitude of the interaction. The changes that occurred in the tin–proton NMR coupling constants of a series of trimethyltin chloride adducts, as a function of the enthalpy of the interaction,[24] also supported this idea of a reorganization energy that varied in proportion to the strength of interaction (or, possibly, for some systems in proportion to a more complex combination of the *E* and *C* parameters of the base or acid). We and others[34] have concluded that viewing the promotion energy as a constant quantity is, in general, not appropriate. Furthermore, we concluded that variable promotion energies corresponding to many of the effects usually discussed in conjunction with the concept (e.g., breaking B–F π bonds) are best considered as simple contributions to the acid polarizability measured along the bond axis of an incoming base. When the "reorganization energy" is large, the acid will be very difficult to polarize and will be a relatively weaker acid than if this were not the case. The enthalpy will be low. Thus, though an idea of a variable reorganization energy is thermodynamically sound,[35] we claimed it was impractical to consider many of the effects usually discussed in conjunction with this quantity as separate concepts in acid–base chemistry or in spectroscopic correlations.

Kristoff and Shriver[36] have termed the acceptor atom–donor atom bond strength as the "electron pair acceptor strength" and they related this quantity to donor–acceptor bond lengths and force constants. In the boron trifluoride–ethyl acetate adduct discussed above, for example, one would expect BF_3 to make a larger perturbation on the carbonyl stretching vibration relative to $-\Delta H$ than an adduct with a similar enthalpy of formation in which the acid did not undergo a large reorganization. The electron pair acceptor strength differs from a thermodynamic-based acidity by the energy necessary to distort the acid to the geometry it possesses in the complex. The authors proposed "distinguishing between the extent of donor–acceptor interaction (as manifested by a spectroscopic probe) and $\Delta H°$" because the latter contains endothermic contributions from reorganization energies. The statement[36] "spectroscopic probes in general measure the relative strength of the donor–acceptor bond" (which are called[36] electron pair acceptor strengths) "but not the acidity as manifested by ΔH" is also made. These statements are inconsistent with our model.

We have recently[34] concluded that, in general, one is to expect that spectroscopic correlations with enthalpies will have exceptions. The enthalpy depends for σ systems on E_AE_B and C_AC_B. Unless the spectroscopic changes have a similar functional dependence on these properties, exceptions will arise when the *C/E* ratio of the systems studied is varied widely. Thus, exceptions to frequency shift–enthalpy correlations can be interpreted in at least two different ways and only if deviations from such correlations can be found when the *C/E* ratio is constant can a promotion energy contribution be assessed. We do conclude that at present there is no convincing evidence to support the quoted statements and we take exception[37] to them in proposing our models.

The enthalpies we report here on the bis(hexamethyldisilylamino) compounds further substantiate these conclusions. The energy spent in the course of converting the hexamethyldisilylamino groups from a linear free acid[3] toward the trigonal geometry in the adduct[14] must vary with the strength of the interaction and not be an independent variable or a constant. If it were a constant, the enthalpy data on this system would fit the equation[38]

$$-\Delta H + \omega = E_AE_B + C_AC_B$$

where ω is the constant-energy term, significantly better than they fit the *E* and *C* equation[6]

$$-\Delta H = E_AE_B + C_AC_B$$

We have shown[38] that there is no way to incorporate a constant-energy term for an acid into E_A and C_A when the base is varied over a wide range of C_B/E_B ratios. Instead, when there are constant energy contributions to the enthalpy of adduct formation in acid–base systems, this quantity can be independently determined[38] from the enthalpy data.

In our previous discussion of promotion energies,[8] we had not determined how the energy associated with geometry change was incorporated into the E and C equation. We can now show how an endothermic process such as breaking a π bond can be incorporated into an acid parameter if it varies in proportion to some property of the base ($-\Delta H$ of the adduct, C_B, E_B, etc.). In so doing, we indicate how all of the acids in the E and C correlation are inconsistent with an independently varying or constant-promotion energy idea.

Basically, we wish to show that the enthalpy of adduct formation for systems which adhere to the E and C equation can be given by an equation having parameters that permit a varying endothermic contribution, ΔE, from polarizing the acid or base. The following is one possibility

$$-\Delta H = k_{CA}C_A{}^0 k_{CB}C_B{}^0 + k_{EA}E_A{}^0 k_{EB}E_B{}^0$$

Here, k could be unity if there were no reorganization energy and $C_A{}^0$, $C_B{}^0$, $E_A{}^0$, and $E_B{}^0$ would be the E and C parameters for the acid and base in the absence of a reorganization energy. A system with a large reorganization energy would have a small value of k. The k_{CA} values could account for the distortion induced by the covalency in the interaction and the k_{EA} values for the effects of the electric field upon the geometry. The various k's could be viewed as related to $1 - k'$ or $1 - k''$ where k' is the slope of a plot of $\Delta E/C_A{}^0$ vs. a distortion coordinate related to $E_B{}^0$ and $C_B{}^0$ and k'' the slope of a similar plot of ΔE vs. $E_A{}^0$. Here ΔE is the energy required for a certain amount of distortion, and it is presumed that this plot can be approximated by a linear function over the range of distortion that occurs in adducts. Thus, in the $k_AC_A{}^0k_BC_B{}^0$ term, the energy to reorganize a given acid in the course of interacting with several different bases would be variable depending upon the base and would be obtainable in principle from $k'_AC_A{}^0k_BC_B{}^0$ of the term $(1 - k'_A)C_A{}^0k_BC_B{}^0$. When k_A and k_B are large, the acid and base would both be easily polarized and a large interaction would result.

It is clear that we can accomplish the properties described above by simply redefining E_A, C_A, E_B, and C_B as $k_{EA}E_A{}^0$, $k_{CA}C_A{}^0$, $k_{EB}E_B{}^0$, and $k_{CB}C_B{}^0$, respectively. These energy effects can be incorporated into the E and C parameters by the equivalent definitions $E = E^0 - k'E^0$ and $C = C^0 - k''C^0$ for each, the acid and base. Then, for example, our present C_AC_B term of $-\Delta H = E_AE_B + C_AC_B$ becomes

$$C_AC_B = C_A{}^0C_B{}^0 - k_A{}''C_A{}^0C_B{}^0 - k_B{}''C_A{}^0C_B{}^0 + k_A{}''k_B{}''C_A{}^0C_B{}^0 = (1 - k_A{}'')(1 - k_B{}'')C_A{}^0C_B{}^0$$

With $1 - k_A'' = k_{CA}$ and $1 - k_B'' = k_{CB}$, we have $C_AC_B = k_{CA}C_A{}^0k_{CB}C_B{}^0$.

There is no way from enthalpy measurements alone to factor $k_{CA}C_A{}^0$ out of the C_A values we have.

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Registry No. $Zn[N(SiMe_3)_2]_2$, 14760-26-0; $Cd[N(SiMe_3)_2]_2$, 14760-27-1; $Hg[N(SiMe_3)_2]_2$, 14760-28-2; pyridine, 110-86-1; 4-methylpyridine, 108-89-4; hexamethylphosphoramide, 1608-26-0; *N,N*-dimethylacetamide, 127-19-5; *N*-methylimidazole, 616-47-7; piperidine, 110-89-4.

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