but that the ring proton signals depend on both anion and concentration. The $-\mathrm{CH}=$ resonances shift to lower field by -0.03 to -0.13 ppm upon increasing the concentration from 1 g/100 ml to 10 g/100 ml. The concentration dependence is greatest for the smallest cation studied, $\mathrm{B(acac)_2^+}$, and it increases with decreasing size of the anion (*cf.* in Table I, the series $[\mathrm{B(acac)_2}]\mathrm{X}$; X = $\mathrm{SbCl_6^-}$, $\mathrm{AuCl_4^-}$, $\mathrm{HCl_2^-}$). By relating the ring proton chemical shift for a given $[\mathrm{M(acac)}_n]\mathrm{X}$ compound to the shift for the corresponding $[\mathrm{M(acac)}_n][\mathrm{SbCl_6}]$, one finds that the $-\mathrm{CH}=$ resonances shift to lower field as the anion varies in the order $\mathrm{SbCl_6^-} \sim \mathrm{AuCl_4^-} < \mathrm{I_3^-} \sim \mathrm{ClO_4^-} < \mathrm{HCl_2^-} < \mathrm{Br^-} \sim \mathrm{Cl^-}$; this is the order of decreasing anion size. Again, the effect is more pronounced, the smaller the cation.

The anion and concentration dependence can be understood in terms of ion pairing. Location of an anion near the $-\mathrm{CH}=$ proton would increase the electric field at the proton by an amount which depends on the distance from the proton to the center of the anion; thus, $\Delta\sigma$ should become more negative as the anion size decreases. The concentration dependence of $\Delta\sigma$ reflects increasing dissociation of ion pairs with decreasing solute concentration.

Because the methyl resonances are independent of anion and concentration, it is tempting to suggest that the anion in the ion pair is located near the $-\mathrm{CH}=$ proton rather than near the methyl groups. A simple calculation indicates, however, that the methyl resonances will be rather insensitive to ion pairing because the electric field due to the anion is nearly perpendicular to the C–H bonds; location of the anion along the threefold axis of the methyl group gives a change in $\Delta\sigma$ of only *ca.* -0.02 ppm on going from $[\mathrm{M(acac)}_n][\mathrm{SbCl_6}]$ to $[\mathrm{M(acac)}_n]\mathrm{Cl}$. The anion may in fact prefer to be near the $-\mathrm{CH}=$ proton, but our data are equally consistent with an ion pair in which there is no strongly preferred site for the anion. What one can say is that the anion is not located exclusively along the threefold axis of the octahedral complexes (or along the two C'_2 axes of $\mathrm{B(acac)_2^+}$), since such a location predicts a positive change in $\Delta\sigma$ as the size of the anion decreases.[39]

Acknowledgment. The support of this research by National Science Foundation Grant GP-7851 is gratefully acknowledged.

(39) A referee has suggested that some of the variations in chemical shifts observed in this work may represent solvation effects since deuteriochloroform is known to hydrogen bond to certain metal acetylacetonates: T. S. Davis and J. P. Fackler, Jr., *Inorg. Chem.*, **5**, 242 (1966). We have recorded nmr spectra of $[\mathrm{B(acac)_2}][\mathrm{SbCl_6}]$ and $[\mathrm{Si(acac)_3}][\mathrm{SbCl_6}]$, and of the isoelectronic neutral complexes, $\mathrm{Be(acac)_2}$ and $\mathrm{Al(acac)_3}$, at a concentration of 10 g/100 ml of solvent in dichloromethane, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane, as well as in deuteriochloroform. The methyl group $\Delta\sigma$ values (defined here as the difference between the chemical shift for a charged complex and the corresponding isoelectronic neutral complex) are the same (± 0.01 ppm) in all four solvents. The ring proton $\Delta\sigma$ values are the same in dichloromethane, dichloroethane, and tetrachloroethane but are larger by *ca.* -0.1 ppm in deuteriochloroform. Similar results were obtained for $[\mathrm{B(acac)_2}][\mathrm{HCl_2}]$, $[\mathrm{Si(acac)_3}]\mathrm{Cl}$, and $[\mathrm{Si(acac)_3}]\mathrm{Br}$. The slightly larger CH proton $\Delta\sigma$ values in deuteriochloroform could be due to hydrogen bonding. However, variations in $\Delta\sigma$ attributable to hydrogen bonding are small compared with the total, observed $\Delta\sigma$ values (*cf.* Table III).

The Linear ΔH–$\Delta\bar{\nu}_{\mathrm{C=O}}$ Relation for Ethyl Acetate Adducts and Its Significance for Donor–Acceptor Interactions

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Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois. *Received February 21, 1968*

Abstract: A linear correlation has been found between the ethyl acetate carbonyl frequency shift upon complexation and the enthalpy of adduct formation for a series of Lewis acids. This phenomenon is discussed with respect to the energetics of adduct formation. A modified idea of the traditional reorganization energy is necessary to explain the correlation. An alternative way to look at the energetics of adduct formation is introduced using the concepts of unit basicity and unit acidity.

We have been interested in establishing quantitative correlations between changes in the spectroscopic properties of a donor or acceptor upon coordination and the gas-phase (or equivalent) enthalpy of adduct formation, ΔH_f. Successful correlations have been reported between the change in the O–H stretching frequency of phenol upon complexation, $\Delta\bar{\nu}_{\mathrm{OH}}$, and ΔH_f for 1:1 adducts with a whole series of donors,[2,3] and another between the change in the tin–proton coupling constant of $\mathrm{(CH_3)_3SnCl}$ upon adduct formation and ΔH_f.[4] A theoretical rationalization for the phenol correlation has been presented.[5] It is of interest to extend these correlations to a donor molecule which undergoes a pronounced spectral change on complexation.

In a series of recent articles, Lappert[6] has used the shift in the carbonyl stretching frequency of ethyl acetate to investigate the acceptor properties of various Lewis acids. By making the assumption that the stronger Lewis acid will shift the carbonyl infrared stretch more upon complexation, he found the same qualitative trends in acidity along a series of Lewis

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(1) National Science Foundation Predoctoral Fellow, abstracted in part from the Ph.D. thesis of D. G. Brown.

(2) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2037, 2696, 3817 (1962).

(3) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967).

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

(5) K. F. Purcell and R. S. Drago, *ibid.*, **89**, 2874 (1967).

(6) (a) M. F. Lappert, *J. Chem. Soc.*, 542 (1962); (b) M. F. Lappert and J. K. Smith, *ibid.*, 5826 (1965).

acids from this spectroscopic method as those indicated from measurements of condensed-phase heats of formation. However, no quantitative relationship appears to exist between the condensed-phase heats and the carbonyl frequency shift. In view of the complexity of enthalpies of formation obtained on condensed-phase systems, one can question whether or not these results provide reliable information concerning even qualitative trends in Lewis acid strength. The acidity order which Lappert observed was a reasonable one, so we decided to determine if a quantitative correlation exists between the carbonyl frequency shift and the enthalpy of adduct formation of 1:1 adducts with various acids. We have measured, calorimetrically, the enthalpies of formation of a number of adducts of ethyl acetate with various Lewis acids in CCl_4 as solvent. Little or no interaction of the reactants or products with this solvent is expected.

There are several factors which would lead one to expect no simple relationship between the enthalpy of adduct formation and $\Delta\bar{\nu}_{C=O}$. Kinematic coupling in the adduct between the adduct bond $(C{=}O\cdots B)$ and the carbonyl vibration could lead to difficulties. Secondly, the varying contributions to the measured enthalpy from reorganization energies could complicate a simple ΔH_f–$\Delta\bar{\nu}_{C=O}$ relationship. Reorganization energy is defined[7] as an energy term associated with rehybridization and rearrangement of the donor or acceptor to produce a geometry similar to that which it has in the adduct. Figure 1 shows a conventional[7a] thermochemical cycle for describing various contributions to the acceptor (A)–donor (D) interaction, *i.e.*, $A + D \rightleftarrows AD$. The gas-phase enthalpy change, $\Delta H_{(g)}$, is seen to be the sum of several factors. Step I is the energy required to transform the acid into the same configuration that it has in the adduct, and step II is a similar term for the donor, D. Step III is the energy released when A* and D* are brought together. One might expect that the carbonyl shift would be more closely related to step III because it is this step in which electron density is transferred from the carbonyl bond to the acid. Varying contributions to $\Delta H_{(g)}$ from step I should destroy a linear ΔH_f–$\Delta\bar{\nu}_{C=O}$ relationship. For example, the enthalpies of formation of adducts with C_6H_5OH, I_2, BF_3, and $SbCl_5$ would all be expected to have different contributions to $\Delta H_{(g)}$ from the rearrangement that occurs upon adduct formation (step I). This rearrangement energy may not be reflected in $\Delta\bar{\nu}_{C=O}$ but would be in $\Delta H_{(g)}$.

We present evidence from normal coordinate analysis and molecular orbital calculations on this system which sheds some light on the problems mentioned above. The relationship found between the enthalpy of adduct formation and the carbonyl frequency shift of ethyl acetate suggests that the traditional concept of reorganization energy results from an artificial factoring of the energetics producing terms that are interrelated. A different model for considering the energetics associated with geometrical rearrangements of the donor and acceptor molecules that occur upon adduct formation is proposed. An explanation for the relative acidities of BF_3 and BCl_3 is offered which is consistent with the linear ΔH_f–$\Delta\bar{\nu}_{C=O}$ relationship and the model we propose.

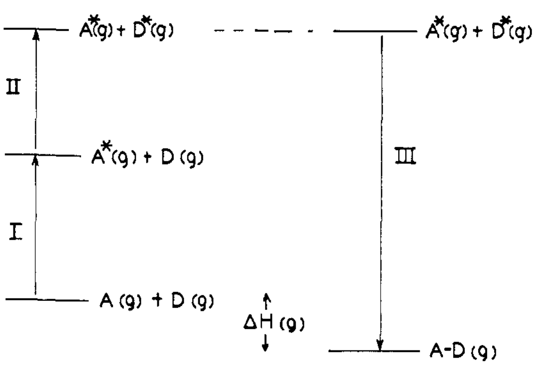

Figure 1. Thermochemical cycle describing adduct formation.

Experimental Section

A. Purification of Chemicals. Fisher Spectranalyzed carbon tetrachloride, dried over Linde 4A Molecular Sieves, was used in the infrared and calorimeter work. Spectrograde cyclohexane was similarly treated. Eastman iodine monochloride (practical) was purified by repeated crystallization (mp 27.2°) and stored until use in sealed vials. Phenol was purified by the method previously described.[3] Ethyl acetate was refluxed for 4 hr with acetic anhydride and sulfuric acid in the following proportions: ethyl acetate, 900 ml; acetic anhydride, 100 ml; sulfuric acid, 10 drops. The mixture was then fractionated, stored over Linde 4A molecular sieves for several days, and refractionated after refluxing over anhydrous potassium carbonate.

B. Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer. The infrared spectra of solutions of ethyl acetate with Lewis acids were recorded in the region 1850–1500 cm^{-1}. The carbonyl frequency shifts were obtained by measuring the difference in the wavelength of the peak maxima for the free and complexed carbonyl bands. These bands were almost always symmetric and the location of the peak maxima was straightforward. In cases where the Lewis acid absorbed in this region, an acid solution of the same concentration as the sample was prepared for the reference solution. When very small frequency shifts were observed, a solution of ethyl acetate of the same concentration as the sample was prepared for the reference solution. In most cases, the values of $\Delta\bar{\nu}_{C=O}$ were reproducible to $\pm 2\ cm^{-1}$.

C. Preparation of Solutions. Solutions of hydroscopic materials were prepared in a drybox in standardized volumetric flasks which had been rinsed with acetone, heated at 120° for several hours, and flushed with dry nitrogen prior to use.

D. Calorimetric Measurements. The calorimetric measurements were performed as previously described.[8]

Results

A. Thermodynamic Measurements. The equilibrium constants and the enthalpies of formation of the ethyl acetate adduct with iodine monochloride were calculated using eq 1,[8] where A^0 and B^0 represent the

$$K^{-1} = \frac{1000H'}{V\Delta H_f} + \frac{A^0B^0V\Delta H_f}{1000H_1} - (A^0 + B^0) \qquad (1)$$

initial concentrations of the acid and base, V represents the total volume of the solution in milliliters, H' is the experimentally measured enthalpy of reaction, and ΔH_f is the calculated molar enthalpy of formation of the complex. The experimental data along with the calculated K^{-1} and ΔH_f values are given in Table I. Usually more than one experiment was performed at the same approximate concentrations, and the average values of A^0, B^0, and H' were used for the calculation of

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(7) (a) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958); (b) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959); (c) S. H. Bauer, G. R. Finlay, and A. W. Laubengayer, *J. Am. Chem. Soc.*, **65**, 889 (1943); (d) D. D. Eley and H. Watts, *J. Chem. Soc.*, 1319 (1954).

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

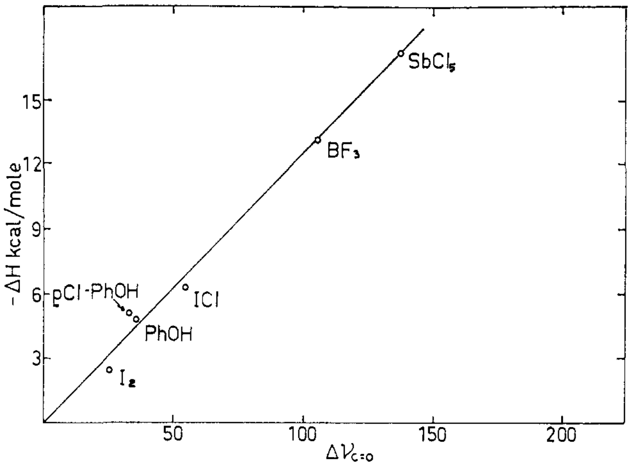

Figure 2. $\Delta\bar{\nu}_{C=O}$ plotted *vs.* $-\Delta H_f$.

ΔH_f. The sharpness of fit procedure previously discussed[8,9] was used to estimate error limits.

Attempts were also made to measure the enthalpy of formation of an adduct with tin tetrachloride using the same procedure. However, inconsistent data were obtained probably owing to partial hydrolysis of $SnCl_4$ or to formation of a 2:1 adduct molecule even though the experiments were carried out with excess $SnCl_4$.[9a]

Table I. ΔH_f and Equilibrium Constant Determination by Calorimetry at 26° for Ethyl Acetate–ICl (CCl_4)

A^0, mole $l.^{-1}$	B^0, mole $l.^{-1}$	V, ml	$-H'$, cal	K^{-1}, mole $l.^{-1}$
0.03197	0.9007	100.0	16.44	0.16
0.02930	0.7113	100.0	14.09	0.19
0.03161	0.4902	100.0	14.16	0.17
0.02957	0.3006	100.0	11.40	0.16
0.02763	0.1073	100.0	5.94	0.18
0.03252	0.1190	100.0	7.67	0.17

$K^{-1} = 0.17 \pm 0.02$ mole l^{-1}

$\Delta H_f = -6.1 \pm 0.3$ kcal mole^{-1} at sharpness ≥ 20

The enthalpy of formation of the iodine adduct with ethyl acetate of -2.5 kcal mole^{-1} has been measured previously.[10] The enthalpy of formation and equilibrium constant for the adduct of ethyl acetate and phenol was measured in exactly the same manner as that mentioned above for ICl. The values are K^{-1} = 0.14 ± 0.02 mole $l.^{-1}$ and $\Delta H_f = -4.8 \pm 0.1$ kcal mole^{-1} at sharpness $\geqslant 20$.[3] The enthalpy of formation of the BF_3 adduct in the gas phase[11] is -13.0 ± 0.7 kcal mole^{-1} at a confidence level of 90%. Olafsson, Lindquist, and Summer[12] have measured the enthalpy of formation of the antimony pentachloride adduct with ethyl acetate in the solvent 1,2-dichloroethane. This is apparently a sufficiently inert solvent because these workers have determined the interaction of carbonyl donors with it to be on the order of 0.1–0.4 kcal mole^{-1}. It was found that at 25° the heat of formation of the $SbCl_5$ adduct with ethyl acetate was $\Delta H° = -17.1 \pm 0.1$ kcal/mole. An enthalpy of formation for the adduct of ethyl acetate with *p*-chlorophenol has been reported as -5.0 kcal mole^{-1} by Epley and Drago.[13] The procedure was essentially the same as that described above for phenol and iodine monochloride. The enthalpy data are summarized in Table II.

Table II. Enthalpies of Formation of Various Ethyl Acetate Adducts

Acid	$-\Delta H_f$, kcal mole^{-1}	Acid	$-\Delta H_f$, kcal mole^{-1}
I_2	2.5	ICl	6.1
C_6H_5OH	4.8	BF_3	13.0
p-ClC_6H_4OH	5.0	$SbCl_5$	17.1

B. Infrared Measurements. Infrared measurements on the various adducts in carbon tetrachloride indicated in all cases a complexed carbonyl band shifted to lower energy. Table III contains the values of $\Delta\bar{\nu}_{C=O}$ for several Lewis acids [$\Delta\bar{\nu}_{C=O} = \bar{\nu}_{C=O}$(free) $- \bar{\nu}_{C=O}$(complexed) where $\bar{\nu}_{C=O}$(free) = 1740 cm^{-1}].

Table III. Infrared Frequency Shift Measurements for Ethyl Acetate Adducts in CCl_4 Solution

Acid	$\Delta\nu_{C=O}$, cm^{-1}	Acid	$\Delta\nu_{C=O}$, cm^{-1}
I_2	26	*n*-$C_4H_9SnCl_3$	43
$(CF_3)_2CHOH$	33	$C_6H_5SnCl_3$	47, 90
p-ClC_6H_4OH	33	ICl	55
m-$CF_3C_6H_4OH$	33	$SnCl_4$	90
HF	35	BF_3	107
$(CH_3)_3SiCl$	35	$SbCl_5$	138
C_6H_5OH	36	BCl_3	153
$GeCl_4$	36	BBr_3	169
$SiCl_4$	42		

Using those acids for which both ΔH_f and $\Delta\bar{\nu}_{C=O}$ were known, a plot of $-\Delta H_f$ *vs.* $\Delta\bar{\nu}_{C=O}$ was made. The results are shown on the graph in Figure 2. It appears that a simple linear relationship exists between $-\Delta H_f$ and $\Delta\bar{\nu}_{C=O}$.

C. Normal Coordinate Analysis. In order to gain insight into the nature of the vibrations in ethyl acetate, a normal coordinate analysis was attempted on methyl acetate, a similar molecule for which the vibrational assignments have been made in the gas phase and to some extent in carbon tetrachloride solution.[14,15] Methyl acetate has symmetry Cs and therefore all the vibrational modes have either A or A′ symmetry. Only the in-plane A vibrations were treated because these include all the skeletal vibrations of interest.

The *G* matrix was calculated using a program written by Schachtschneider.[16] The symmetry force constants were evaluated using a perturbation (refinement)

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(9) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Amer. Chem. Soc.*, **86**, 388 (1964).

(9a) Note Added in Proof. Recently A. Kemula and R. T. Iwanoto [*J. Phys. Chem.*, **72**, 1334 (1968)] reported the enthalpy of -10.1 ± 1.0 kcal mole^{-1} for this adduct. Employing our measured value of $\Delta\nu_{C=O}$ and this enthalpy, this system fits nicely into the correlation to be discussed below.

(10) R. L. Middaugh, R. S. Drago, and R. J. Niedzielski, *ibid.*, **86**, 388 (1964).

(11) R. S. Drago, L. J. Sacks, and D. P. Eyman, submitted for publication.

(12) G. Olafsson, J. Lindquist, and S. Summer, *Acta Chem. Scand.*, **17**, 259 (1963).

(13) T. D. Epley and R. S. Drago, submitted for publication.

(14) J. K. Wilmshurst, *J. Mol. Spectry*, **1**, 201 (1957).

(15) B. Nolin and R. N. Jones, *Can. J. Chem.*, 34, 1382 (1956).

(16) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules III," Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.

program also written originally by Schachtschneider. The use of these programs has been described elsewhere.[17-20]

The initial attempt was to fit the observed frequencies using a simple force field; however, it was found impossible to obtain a satisfactory set of force constants using this approximation. Therefore the calculation was done using only a few selected interaction constants. The results are given in Table IV. The units for the stretching force constants are in millidynes/ångström. With these force constants the actual frequencies may be calculated to within experimental error. However, this set of force constants is only a crude approximation to those one would obtain from a rigorous analysis. Despite numerous attempts, we were unable to simultaneously fit the protonated and fully deuterated molecules with a limited number of interaction constants. This failure to fit both molecules is undoubtedly due to our limited and arbitrary choice of interaction constants when there is considerable coupling between the skeletal and C–H stretching and bending modes.

Table IV. Symmetry Force Constants for *A* Vibrations of CH_3COOCH_3

$F_{11} = 4.61$	Sym C–H stretch acetyl methyl
$F_{22} = 4.60$	Asym C–H stretch acetyl methyl
$F_{33} = 4.66$	Sym C–H stretch methoxy methyl
$F_{44} = 4.64$	Asym C–H stretch methoxy methyl
$F_{55} = 9.48$	C═O stretch
$F_{66} = 4.23$	H_3C–C stretch
$F_{77} = 5.78$	C–O stretch
$F_{88} = 9.25$	O–CH_3 stretch
$F_{99} = 0.40$	Sym acetyl methyl deformation
$F_{10,10} = 0.44$	Asym acetyl methyl deformation
$F_{11,11} = 0.38$	Acetyl methyl rock
$F_{12,12} = 0.44$	Sym methoxy methyl deformation
$F_{13,13} = 0.46$	Asym methoxy methyl deformation
$F_{14,14} = 0.53$	Methoxy methyl rock
$F_{15,15} = 1.81$	O–C–O bend
$F_{16,16} = 1.52$	C–O–C bend
$F_{17,17} = 0.52$	C–C–O bend
$F_{6,9} = -0.26$	CH_3–C stretch, sym methyl deformation interaction
$F_{8,12} = -0.26$	O–CH_3 stretch sym methyl deformation interaction
$F_{5,7} = 0.30$	C═O stretch, C–O stretch interaction
$F_{5,17} = -0.85$	C═O stretch, C–C–O bend interaction
$F_{6,7} = 0.30$	CH_3–C stretch, C–O stretch interaction
$F_{7,8} = 1.50$	C–O stretch, O–CH_3 stretch interaction
$F_{7,15} = 1.00$	C–O stretch, O–C–O bend interaction
$F_{8,16} = 0.48$	O–CH_3 stretch, C–O–C bend interaction

However, we are only interested in comparing changes which occur in ethyl acetate upon adduct formation, a system in which there is only a small change in certain force constants. Furthermore, we are interested only in skeletal vibrations for which our force constants are reasonably good. As a result, we feel the force constants in Table IV describe this system adequately for our purposes.

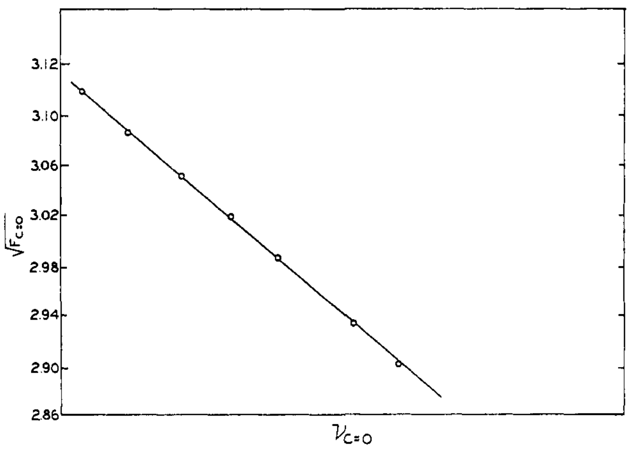

Figure 3. $\tilde{\nu}_{C=O}$ as a function of the square root of the carbonyl force constant.

Using these force constants for methyl acetate, a calculation was carried out in which several different masses were placed 2 Å from the carbonyl oxygen and a small force constant was assigned to the bond between this mass and the oxygen atom. This arrangement should approximate an adduct molecule. The purpose of this calculation was to investigate in what manner the frequencies of the methyl acetate (in particular the C═O stretch) would be perturbed upon complexation. The results shown in Table V are insensitive to the magnitude of the mass over a large range. As can be seen from the small change in frequency of the C═O vibration when one simulates an adduct bond, the effect of kinematic coupling is negligible.

Table V. Effect on the Carbonyl Stretch Due to Complexation

O···mass force constant, mdyn/Å	$\tilde{\nu}_{C=O}$, cm^{-1}	$\tilde{\nu}_{O\cdots mass}$, cm^{-1}
0	1740	0
0.5	1744	203
1.0	1746	254

From this information it appears that one can assess the change in the vibrational energies of the methyl acetate molecule which occur upon coordination by simply repeating the previous calculation using a lower value for the carbonyl force constant. The lower the value for the force constant, the stronger the acceptor one is simulating. In order to find how the carbonyl force constant and the corresponding stretching frequency are related, we performed a series of calculations changing only the C═O force constant and calculating the resulting carbonyl vibrational frequencies. The result, shown in Figure 3, indicates that the frequency is proportional to the square root of the force constant as one would expect from a simple harmonic oscillator.

None of the other vibrations in the molecule seem to change very significantly when the C═O force constant is lowered. This indicates that the C═O vibration is a highly localized one and acts much like an isolated diatomic molecule. This conclusion is substantiated by the fact that the potential energy matrix indicated that the C═O vibration is highly localized. Therefore, one might expect a quantitative relationship (not necessarily linear) to exist between the amount of electron density drained from the C═O bond (determined by the strength of adduct bond formed) and the stretching frequency.

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(17) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85, 117 (1963).

(18) J. Aldous and I. M. Mills, *ibid.*, **19**, 1567 (1963).

(19) J. Overend and J. R. Scherer, *J. Chem. Phys.*, 32, 1289, 1296, 1720 (1960).

(20) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966).

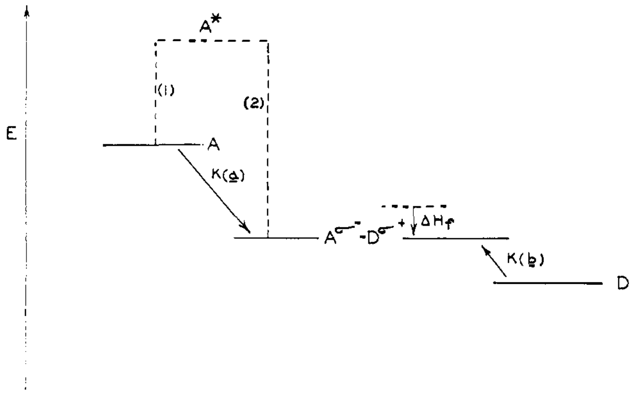

Figure 4. Thermodynamic cycle for adduct formation.

Discussion

In view of the results obtained from vibrational analysis, it appears that there are no vibrational interactions in methyl acetate which complicate the interpretation of the frequency shift in the adducts. However, the question of reorganization energies cannot be as easily dismissed. Traditionally, the reorganization energy is viewed as a lump sum of energy to be expended in order to prepare the molecule for adduct formation.[7] In the traditional view, the reorganization energy is not necessarily related to the strength of the adduct bond formed. If this viewpoint were correct, one might expect a large C=O frequency shift and a small ΔH_f when the complexing acid has a large reorganization energy. For example, breaking the B–F π bonds in BF_3 would require energy so the net ΔH_f would be small, but the C=O frequency shift might still be expected to be large. Our ΔH_f-$\Delta\bar{\nu}_{C=O}$ correlation includes such varied acids as phenol, iodine, boron trifluoride, and antimony pentachloride, clearly violating the above conclusion. These molecules obviously do not have the same reorganization energy. We propose that the present concept of reorganization energy is misleading in that it is not an independent factor in the formation of an adduct molecule.

If one were to add a pair of electrons to BF_3, the resulting species would be predicted to be pyramidal. Similarly, the electron density added to the BF_3 upon formation of a BF_3 donor bond would produce a more stable adduct when the arrangement of fluorines about the boron is nonplanar. This is equivalent to saying that step III of Figure 1 includes an energy contribution associated with stabilizing the B–F bonds over what they are in BF_3*. (Recall BF_3* refers to a geometry for this species just like it has in the adduct.) Thus part of the energy associated with step III arises from putting electron density on the Lewis acid.

An alternative way of looking at this interaction is illustrated in Figure 4. Here, A represents the free Lewis acid, D the free Lewis base, and $A^{\delta-}$–$B^{\delta+}$ the adduct. The quantity *a* represents the *unit acidity* for A. If the energy of A could be determined as a function of electron density transferred to it, the unit acidity would be the magnitude of the slope of a plot of energy *vs.* transferred charge. Thus *a* is a quantity which describes the response of the energy of A to added electron density. If *a* is large, A is stabilized a great deal for a relatively small amount of charge transferred; thus a large unit acidity makes a large contribution to the energy of the adduct. The unit basicity is inversely related to the magnitude of *b* which is defined as the slope of a similar plot of energy for D *vs.* fraction of electron density removed. The unit basicity is inversely related to the ionization potential of the base. For a large unit basicity not very much energy is expended in removing electron density from the base. Thus a small *b* helps contribute to a large unit basicity and energy of adduct formation. The magnitudes of the unit acidity and unit basicity are related to the polarizability of the molecules, ionization potentials, electron affinities, lone-pair dipole moments, etc. The quantity *K* in Figure 4 reflects the amount of electron density transferred during formation of the adduct. The magnitude of *K* is related to the strength of both the acid and base, the overlap properties of the filled and empty orbitals, and other mechanisms for transferring electron density from D to A.

In this model, the concept of reorganization energy is not required. The geometry of the acid changes on forming the adduct in direct proportion to the amount of charge transferred. If the acid is difficult to polarize or rearrange geometrically, the unit acidity is low and the acid is weak, *i.e.*, for this type of acid a small slope is obtained as one plots the energy of A *vs.* electron density added. There is no energy term which is independent of the acceptor properties of a molecule associated with formation of an adduct. The energies required to change geometries and rehybridize atoms are simply factors which contribute to the unit acidity or acceptor properties of various Lewis acid molecules. Furthermore, for a given Lewis acid the extent of distortion is not constant but is dependent on the strength of the Lewis base. The distortion is determined in part by the overlap properties and energy match of the donor–acceptor bond which in turn affect the amount of charge transferred, and thus the extent of geometrical rearrangement for the acid and base. If one wants to look at this interaction in the traditional manner (see dotted line in Figure 4), he must realize that the energy difference in going from A to A* is dependent upon the properties of the base through both the ease with which electron density can be removed from it and overlap properties. Steps 1 and 2 are intimately related to each other. Returning to Figure 1, it must be that both steps I and II are proportional to step III. This is apparently due to the fact that the effective overlap and energy match of the acid and base is the driving force in adduct formation and thus determines the magnitude of the various energy terms. With this model the linear correlation of $-\Delta H_f$ with $\Delta\bar{\nu}_{C=O}$ and the established correlations with phenol adducts and $(CH_3)_3SnCl$ adducts are reasonable. Experimental evidence exists for the proposal that the extent of distortion of the acid is a function of the donor strength of the base. In trimethyltin chloride adducts, the value of J_{SnCH} is directly proportional to $-\Delta H_f$.[4] On forming the adduct, $(CH_3)_3SnCl$ undergoes a change in geometry from C_{3v} to a trigonal bipyramid with three methyls in equatorial positions. The change in J_{SnCH} is interpreted to indicate variable distortion of the methyls toward planarity in proportion to the donor strength.

Using our carbonyl frequency shift correlation, a number of interesting problems can be investigated.

Ethyl acetate represents the first Lewis base that has been successfully incorporated into a quantitative enthalpy spectral correlation. As in the phenol and trimethyltin chloride systems,[2,4] one of the principal values of the correlation is that it permits one to predict the enthalpy of formation of ethyl acetate adducts without recourse to the more time-consuming traditional measurements. For instance, we can predict the enthalpy of formation of ethyl acetate adducts with BCl_3 and BBr_3, systems which are extremely difficult to measure directly and for which most reported data have been measured in interacting solvents and are therefore of questionable value for our application. From Figure 2, we obtain enthalpies of -18.9 and -20.8 kcal mole^{-1}, respectively, for the heats of formation of the BCl_3 and BBr_3 adducts. The measured value for BF_3 is -13.0 kcal mole^{-1}.

From this information and the condensed-phase thermodynamic data of Lappert and Smith,[6b] we can evaluate the heat of sublimation, ΔH_{subl}, of the various BX_3 adducts using the following cycle, where ΔH_{cp} is

$$\begin{tikzcd}
\mathrm{BX_3(standard\ state)} \arrow[d, "\Delta H_{\mathrm{v}}"] & + & \mathrm{EtOAc(l)} \arrow[r, "\Delta H_{\mathrm{cp}}"] \arrow[d, "\Delta H_{\mathrm{v}}'"] & \mathrm{BX_3{:}EtOAc(S)} \arrow[d, "\Delta H_{\mathrm{subl}}"] \\
\mathrm{BX_3(g)} & + & \mathrm{EtOAc(g)} \arrow[r, "\Delta H_{\mathrm{f}}"] & \mathrm{BX_3{:}EtOAc(g)}
\end{tikzcd}$$

the condensed-phase heat of formation, ΔH_{v} the heat associated with taking BX_3 from its standard state to the gas phase, $\Delta H_{\mathrm{v}}'$ the heat of vaporization of ethyl acetate, ΔH_{f} the gas-phase enthalpy of adduct formation, and ΔH_{subl} the heat of sublimation for the various adducts.

The values for the first four of these quantities are listed in Table VI. Since from the above cycle, $\Delta H_{\mathrm{subl}} = \Delta H_{\mathrm{f}} + \Delta H_{\mathrm{v}} + \Delta H_{\mathrm{v}}' - \Delta H_{\mathrm{cp}}$, we can easily calculate ΔH_{subl}, the heat of sublimation for the various adducts.

Table VI. Thermodynamic Quantities (kcal/mole) for the BX_3 Molecules

	ΔH_{cp}[6]	ΔH_{v}[6]	$\Delta H_{\mathrm{v}}'$[6]	ΔH_{f}	ΔH_{subl}
BF_3	-24.2	0	8.7	-13.0	19.9
BCl_3	-32.4	5.5	8.7	-18.9	27.5
BBr_3	-36.9	8.2	8.7	-20.8	33.0

In the past it has been assumed that the heats of sublimation for a related series of compounds D–BX_3 (where X is a halogen and D a Lewis base) are very close to one another,[21] and that this term may be ignored. However, as can be seen from Table VI, this is a very poor approximation. Differences in lattice energy are much larger than differences in the gas-phase enthalpy of adduct formation. Fortunately, in this series, the trend in lattice energies is in the same direction as the trends in acceptor strengths so the correct ordering results from data on the condensed phases.

It is of interest to look more closely at the Lewis acids BF_3 and BCl_3. We will consider factors affecting the acidity of these molecules to see why BCl_3 is in fact a better Lewis acid than BF_3 in terms of our ideas concerning unit acidity and basicity. In order to gain some insight as to the nature of the actual geometrical rearrangement in a molecule, we performed a few extended Hückel molecular orbital calculations. The details of this type of calculation have been discussed previously.[22] The usual idea of the reorganization energy for these molecules is that breaking the π bonds in going from a planar molecule to one with approximately tetrahedral angles is almost completely responsible for the reorganization energy. We therefore performed molecular orbital calculations for planar and pyramidal (tetrahedral X–B–X angles) BF_3 and BCl_3 using known bond lengths in the free acid and the adducts. In other calculations, the bond lengths were kept the same for the planar and pyramidal molecules. We then calculated all the overlap energies between a boron and halogen. The overlap energy has been defined by Mulliken[23] as $\Omega_{ij} = \rho_{ij}\beta_{ij}/S_{ij}$, where $\beta_{ij} = H_{ij} - {}^1/_2 S_{ij}(H_{ii} + H_{jj})$. The results are shown in Table VII. The differences in the overlap energies for the planar and pyramidal molecules are really quite small. These differences reflect the destabilization due to bending the molecules from planar to pyramidal. Furthermore, the total energies calculated for the planar and pyramidal molecules are essentially unchanged for both geometries. This type of calculation appears to be quite good for considering changes in total energy due to changes in bond angles.[24] These data show there is a fairly small energy term associated with bending these molecules from planar to a geometry with approximately tetrahedral angles. The results

Table VII. Overlap Energies for B–X Bond in Planar and Pyramidal BF_3 and BCl_3

BF_3	Planar Ω, eV	Pyramidal Ω, eV
$B_{2p_z}F_{2p_z}$	-1.69	-1.15
$B_{2s}F_{2s}$	-2.36	-2.16
$B_{2s}F_{2p}$	-1.76	-1.76
$B_{2p}F_{2s}$	-3.40	-3.54
$B_{2p_\sigma}F_{2p_\sigma}$	-2.43	-2.66
Total	-11.64	-11.27
BCl_3		
$B_{2p_z}Cl_{3p_z}$	-0.93	-0.58
$B_{2s}Cl_{3s}$	-1.07	-0.98
$B_{2s}Cl_{3p}$	-1.84	-1.81
$B_{2p}Cl_{3s}$	-1.79	-1.90
$B_{2p_\sigma}Cl_{3p_\sigma}$	-2.21	-2.46
Total	-7.84	-7.73

Pyramidal Molecules with Lengthened Bonds			
BF_3	Ω, eV	BCl_3	Ω, eV
$B_{2p_z}F_{2p_z}$	-0.97	$B_{2p_z}Cl_{3p_z}$	-0.47
$B_{2s}F_{2s}$	-1.68	$B_{2s}Cl_{3s}$	-0.66
$B_{2s}F_{2p}$	-1.88	$B_{2s}Cl_{3p}$	-1.78
$B_{2p}F_{2s}$	-2.96	$B_{2p}Cl_{3s}$	-1.57
$B_{2p_\sigma}F_{2p_\sigma}$	-2.73	$B_{2p_\sigma}Cl_{3p_\sigma}$	-2.35
Total	-10.22		-6.83

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also show that if one wants to consider reorganization energies, bond lengthening is a much more substantial energy requirement. Usually, the reorganization energy is viewed as an intrinsic property of a molecule and, for a Lewis acid, not related to the strength of the adduct bond formed with some base. For example, in BF_3 there is much more π bonding than in BCl_3. At a first glance, one might look at the reorganization energy in these molecules as a lump-sum energy required to break the π bonding when going from BX_3 (planar) to BX_3 (pyramidal). Thus one might expect the observed order of acidity $BF_3 \ll BCl_3 < BBr_3$ to reflect only the energy required to break the π bonds; that is, even though the $D \cdots BX_3$ bond may be stronger in the order $BF_3 > BCl_3 > BBr_3$, the difference in π bond strengths are of sufficient magnitude to reverse this order when one measures the enthalpies of adduct formation. If this were the case, one would expect the carbonyl frequency shift to be greater for BF_3. However, the carbonyl shift decreases as $BBr_3 > BCl_3 \gg BF_3$. Thus the observed acidity orders are in fact due to the strength of the $D \cdots BX_3$ bond. The reason for this can be explained as follows. The π bonding in these molecules is not destroyed on going from planar to pyramidal geometry. This can be seen in Table VII by noting that the p_π–p_π overlap energy only decreases 0.54 eV for BF_3 and 0.35 for BCl_3. That is, much of the π bonding is still present in the pyramidal molecules. The critical factor seems to be the residual π bonding. This residual π bonding ties up the B_{2p_z} orbital so that it will not accept electron density readily. In order to become a good electron acceptor, the boron atom must rehybridize in such a way to make the p_z orbital available to accept electron density, thus diminishing the amount of π bonding. It is interesting to notice that the amount of π bonding destroyed upon adduct formation is not a constant quantity but is determined by the strength of the donor. Therefore, in the pyramidal geometry BF_3 has much stronger π bonds remaining than BCl_3 and the p_z orbital is made available for accepting electrons to a lesser extent in BF_3. Furthermore, since there is a competition between the base lone-pair electrons and the fluorine electrons for the B_{2p_z} orbital, there can still be appreciable B–F π bonding in the adduct molecule. Consequently, the residual π bonding determines the response of the energy of BF_3 to added electron density; *i.e.*, the unit acidity of BF_3 is less than that of BCl_3. For this reason, BF_3 is the weakest Lewis acid in the BX_3 series and not because stronger π bonds are broken.

Cotton and Leto[7b] have concerned themselves with the acidities of the boron halides and attempted to calculate reorganization energies. They used a rather simplified molecular orbital calculation and estimated bonding energies from the corresponding overlap. The calculated values for reorganization energies were the sums of the π-bond energies and the energy change in the σ bonds as the molecules go from planar to pyramidal. The changes in energy in the σ framework were estimated to be extremely small and thus their calculated reorganization energies were virtually identical with the calculated π bond energies. Our results are in disagreement with these conclusions. When one examines Table VII of this paper, substantial changes in σ bond strengths are observed. It is also interesting to note that Cotton and Leto allow for the possibility that in some instances not all π bonding need be lost upon adduct formation in which case their calculated values are only upper limits. We claim that the loss in π-bond energy is in direct proportion to the amount of electron density transferred in the acceptor orbital. Consequently the reorganization energy is not an independent energy term and it is misleading to break up the energy as in Figure 1. Since BF_3 is the most extensively π bonded of the boron halides, its unit acidity is less because the added electron density must compete more with the π bonds for the acceptor orbital.

We do not consider this discussion as a theoretical proof of the relationship between the heat of adduct formation and the carbonyl stretching frequency. However, it is intended to give some insight into the phenomenon we have observed. We feel that our interpretation of the energetics associated with adduct formation is a workable model capable of explaining more data than the traditional explanation.

More thermodynamic data would certainly be useful to test the reliability of the ΔH_f–$\Delta\tilde{\nu}_{C=O}$ relationship. These data are very difficult to obtain, especially for strong acids, owing to solubility problems in inert solvents. In the absence of such data, we feel that the infrared frequency shift can give a good indication of the heat of reaction of an acid with ethyl acetate.

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