recognized from Figures 7 and 9. Among the various electron configurations except ψ_0, the configuration in which an electron is transferred from the SOMO of methyl to the LUMO of ethylene is calculated to be the most dominant, and the one from the HOMO of ethylene to the SOMO of methyl is the next dominant. The present calculation suggests that methyl is positively charged, while ethylene is negatively charged in the interaction. This tendency seems to be in an agreement with the Szwarc's proposition that a methyl radical adds to olefinic double bonds in a nucleophilic fashion.[34]

Conclusion

A configuration interaction treatment of chemical interactions between methyl and methane and between methyl and ethylene revealed interesting features of the unpaired electron of the radical and the electrons of closed-shell systems with opposite spin. The contribution of an unpaired electron to the formation of new bonds through charge-transfer interaction was found to be cancelled either partly or entirely by the exchange interaction. On the contrary, the charge-transfer interaction from a closed-shell molecule to a radical to form an electron pair with the odd electron contributed significantly to bond formation. Such a behavior of the unpaired electron will have a profound importance in understanding the nature of radical reactions, because the SOMO has the greatest amplitude in the neighborhood of the most reactive position of radical, in general. To estimate quantitatively the ratio of the contribitions of the two spins to the formation of new bonds and the weakening of old bonds is hardly possible at the present time because of the crudeness of the calculation. More elaborate calculations will be needed for such a purpose. Nucleophilicity and electrophilicity of radicals will have a concern with this problem.

Acknowledgment. We would like to express our gratitude to the Data Processing Center, Kyoto University, for its generous permission to use the FACOM 230-60 computer.

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The Failure of Some Commonly Accepted Spectroscopic–Enthalpy Correlations for Chloroform Adducts[1a]

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Abstract: In this article we demonstrate that neither the change in the nmr proton chemical shift nor the change in the C–D infrared stretching frequency in chloroform or deuteriochloroform upon complexation with a series of Lewis bases can be used as a reliable estimate of the enthalpy of adduct formation. No linear correlation was found to exist between the enthalpy of adduct formation with the change in infrared stretching frequency although a linear correlation between the enthalpy and the hydrogen bonding chemical shift did exist for a limited number of donors. It is shown that $\Delta\nu_{CD}$ for deuteriochloroform adducts do not fall on a constant base line and a plot of $\Delta\nu_{CD}$ *vs.* $\Delta\nu_{OH}$ (phenol) is not linear. These relationships have been shown to be requirements for a constant acid plot with slope similar to the alcohols. The enthalpies of interaction are nicely correlated by our double scale enthalpy equation. The principal contribution to the interaction of chloroform with the donors studied comes from the "electrostatic" term rather than from the "covalent" interaction term.

In a previous report from this laboratory, a series of Lewis bases were shown to give rise to straight line plots of $-\Delta H$ *vs.* $\Delta\nu_{OH}$, the infrared stretching frequency, when either the hydrogen bonding acid was held constant and the base varied (constant acid plots) or when the base was held constant and the hydroxy acid varied (constant base plots). The correlation encompassed data for phenol,[2] a series of substituted phenols,[3] 1,1,1,3,3,3-hexafluoro-2-propanol,[4] 2-methyl-2-propanol[5] and 2,2,2-trifluoroethanol.[6] By combining equations describing constant acid and constant base plots, we were able to show that any new acid that satisfied both plots would have to give rise to an additional straight line plot with zero intercept when $(\Delta\nu_{O-H})_x$ for a series of bases with this acid were plotted against $\Delta\nu_{OH}$ for any acid (*e.g.*, phenol) already in the correlation[7]

$$\Delta\nu_{OH}(X) = \frac{(n_x - L)\Delta\nu_{OH}(\text{phenol})}{(M_0 - M_x)\Delta\nu_{OH}(\text{phenol}) + (n_0 - L)}$$

where M_0 and M_x are the slopes of the constant acid plots for phenol and the new acid X (these slopes were found to be equal within experimental error for the above acids), n_0 and n_x are the intercepts for the constant acid plots of the reference acid and the new acid

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(1) (a) Abstracted in part from the Ph.D. Thesis of F. L. Slejko, University of Illinois, Urbana, Illinois, 1972. (b) National Science Foundation Predoctoral Fellow 1969–1972.

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X, and L is the intercept for the constant base lines. Thus an enthalpy based constant acid plot can be predicted from infrared shifts measured in CCl_4 for single site donors toward a new hydroxy acid X.

In a subsequent study, it was shown that these considerations could be extended to an N–H hydrogen bonding acid, pyrrole.[7] The bases used in all of these studies are oxygen and nitrogen donors. Recently, we have been able to show that sulfur donors do not obey the constant acid relationships we have been establishing.[8]

At this point, it was of considerable interest to extend these studies to chloroform to see if this acid obeys the reported correlations. Since it is difficult to observe the C–H stretch in chloroform in solution because many of our donor molecules contain C–H bonds, deuteriochloroform was used in these studies and the changes in the C–D stretching frequencies were determined. Very little work involving $CHCl_3$ has been carried out under conditions acceptable to us for inclusion in our correlations (*i.e.*, enthalpies and frequency shifts determined in nonpolar media). Some of the earlier studies attempting to relate enthalpies of interaction to infrared shifts involved chloroform, but shifts in the pure donor as solvent and heats of solution of donor in pure chloroform were often employed.[9-11]

Correlation between $\Delta\omega^0$, the difference in the nmr chemical shift between free and complexed chloroform, and $-\Delta H$ would also be interesting, since these could be compared with similar straight line correlations between $\Delta\omega^0$ and $-\Delta H$ for phenol[12] and fluorinated alcohols[4,6] with various Lewis bases.

In addition, this system provides an opportunity to evaluate an nmr technique for determining enthalpies of interaction between chloroform and various Lewis bases. The $-\Delta H$ values obtained will be used to ascertain if chloroform also fits the double-scale enthalpy equation originally proposed by Drago and Wayland.[13] Presently, this equation accurately correlates over 200 enthalpies of adduct formation between Lewis acids and bases.[14]

Experimental Section

Purification of Materials. Deuteriochloroform was obtained from Diaprep. Inc., and dried with molecular sieves. For the ir frequency shift studies, no special techniques were used to purify the bases except to make sure that they were dry. Solvent purification and the procedure for determining $\Delta\nu_{C-D}$ were carried out as described elsewhere[2] for $\Delta\nu_{OH}$.

Quinuclidine was kindly donated to us by Mallinckrodt Chemical Works, St. Louis, Mo., and was purified by resubliming at ~0.5 Torr and 23° at least three times. 1-Phospha-2,6,7-trioxa-4-ethylbicyclo[2.2.2]octane, $CH_3CH_2C(CH_2O)_3P$ (Arapahoe Chemicals), was purified by resubliming at 0.05 Torr. All handling of this material was done in an N_2-filled dry bag. Trimethyl phosphite, $(CH_3O)_3P$ (Aldrich Chemical Co.), was purified by distillation. All handlings of this compound were made as with the caged phosphite above. γ-Thiobutyrolactone (Aldrich Chemical Co), $OCH_2CH_2CH_2C{=}S$, was purified by distilling twice over CaH_2 The middle fraction was collected and stored in a desiccator. The remainder of the donors used were purified according to previously published procedures.[7]

Chloroform (Baker Spectrograde Analyzed) was washed with H_2O to remove traces of alcohol used as a stabilizer, dried over anhydrous K_2CO_3, and distilled prior to use.

Apparatus. 1. Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer 521 infrared spectrophotometer. For the deuteriochloroform work, it was necessary to use a 0.1-mm cell for approximately 0.1 M $CDCl_3$ and a 0.5-mm cell for concentrations ranging from 0.005 to 0.015 M.

2. Nuclear Magnetic Resonance Spectra. The nuclear magnetic resonance spectra were measured with either a JEOLCO C-60H high-resolution nmr spectrometer, equipped with a JES-VT-2 temperature control unit or a Varian Associates HA-100 high-resolution nmr spectrometer operating in the field sweep mode equipped with a temperature control unit. Chemical shifts of the chloroform peak were measured relative to TMS on the JEOLCO C-60H spectrometer. About 10–15 tracings of the same spectrum were made for each sample and an average was used. On the HA-100, all chloroform chemical shifts were measured relative to the cyclohexane lock signal using a frequency counter. The precision of the chemical shifts is ±0.2 Hz or somewhat better.

The probe temperature was measured immediately after each sample was run with a YSI Model 4256 Tele-Thermometer. The precision of the temperature measurement is ±0.5°.

Solutions. All solutions were made by diluting stock solutions of chloroform (~0.5 M) and the corresponding base (~1.0 M) of known molarity in volumetric flasks which were previously dried in an oven at 120° for several hours.

These solutions were used to fill the nmr tubes in a nitrogen-filled dry bag. Each nmr tube was fitted with a tight-fitting cap and wrapped with Parafilm to prevent evaporation. In all cases, the nmr tubes were filled within 4 hr of the time when the spectra were run to prevent inaccuracies due to evaporation.

Procedure. 1. Infrared Spectra. The deuteriochloroform C–D frequency shift was determined by the same procedure discussed elsewhere[15] for varying concentrations of base. In some cases, two separate peaks were not observed, and the only noticeable effect was enhanced intensity and a very small change in the peak position as more base was added. When the peak position remained stationary upon further addition of base, the distance which the peak maximum moved was taken as $\Delta\nu_{C-D}$. In general, this only occurred for bases giving a shift of $<10\ cm^{-1}$.

2. Nmr Spectra. Enthalpies of adduct formation between chloroform and the Lewis donors were calculated by measuring the equilibrium constant, K, for the equilibrium

$$A + B \rightleftharpoons AB$$

as a function of temperature. Here A is the free proton donor (chloroform) and B the free base, while AB is the hydrogen bonded complex. The equilibrium constant and the hydrogen bonding chemical shift, $\Delta\omega^0$, were determined simultaneously.

The chemical shift observed for A assuming rapid exchange between A and AB is a mole fraction weighted average between the chemical shift of free A, $\omega_A{}^0$, and complexed A, $\omega_{AB}{}^0$.[16] With this fact in mind, the above equilibrium gives

$$K = \frac{\Delta\omega_{obsd}}{(\Delta\omega^0 - \Delta\omega_{obsd})\{[B^0] - (\Delta\omega_{obsd}[A^0]/\Delta\omega^0)\}}$$

where K is the equilibrium constant, $[B^0]$ and $[A^0]$ are the initial concentrations of base and acid, respectively, $\Delta\omega_{obsd}$ is the difference between observed chemical shift and that for the free acid, and $\Delta\omega^0$ is the difference between free and complexed acid, $\omega_{AB}{}^0 - \omega_A{}^0$.[17] By measuring $\Delta\omega_{obsd}$ at n different $[B^0]$ and $[A^0]$, one has n equations and two unknowns, namely K and $\Delta\omega^0$.

A computer program has been described[2,18a] in conjunction with

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(17) A complete derivation of this expression, hydrogen bonding chemical shifts, and Tables III and IV will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-9210. Remit check or mony order for $3.00 for photocopy or $2.00 for microfiche.

Table I. Enthalpies and Infrared and Nmr Shifts for Various Adducts

		Chloroform									Phenol	
No.	Compd	[Acid], *M*	[Base], range, *M*	No. sol	$\Delta\omega^0$, ppm[a]	*K*, l./mol[a,b]	*T*, °C	$-\Delta H_{\text{exptl}}$, kcal/mol	$-\Delta H_{\text{calcd}}$[c,i] kcal/mol	$\Delta\nu_{\text{CD}}$,[d] cm^{-1}	$\Delta\omega^0$, ppm[e]	$\Delta\nu$,[f] cm^{-1}
1	$[(CH_3)_2N]_3P{=}O$	0.02259	0.02837–0.27159	6	1.92 ± 0.04 (0.01)	15.5 ± 1.0 (0.3)	29.0	4.9 ± 0.3	5.15	31		430 ± 10
2	$CH_3CH_2C(CH_2O)_3P$	0.02984	0.1455–0.5577	5	0.19 ± 0.05 (0.01)	2.8 ± 1.5 (0.27)	32.0	2.7 ± 0.3	2.17			
3	$(CH_3O)_3P$	0.0324	0.1916–0.7666	5	0.38 ± 0.02 (0.004)	3.6 ± 0.6 (0.1)	31.0	2.7 ± 0.2				
4	$\overline{OCH_2CH_2CH_2C}{=}S$	0.0398	0.2339–1.0293	5	0.69 ± 0.04 (0.003)	0.59 ± 0.05 (0.004)	31.5	2.8 ± 0.2				
5	$HC(CH_2CH_2)_3N$	0.0395	0.0638–0.3189	6	1.15 ± 0.12 (0.08)	1.21 ± 0.17 (0.11)	37.0	4.1 ± 0.1	4.2		6.10[i]	Obscured
6	$(CH_3CH_2)_3N$	0.300	0.636–2.960	4	1.51 ± 0.04 (0.008)	0.43 ± 0.02 (0.004)	27.3	4.5 ± 0.3	4.76	79	6.90	556 (ref 20)
7	$(CH_2)_4S$	0.300	0.118–2.758	7	0.75 ± 0.03 (0.005)	0.32 ± 0.02 (0.003)	27.3	2.4 ± 0.1	2.3	22		274
8	$(CH_2)_4O$	0.300	0.776–2.716	4	0.84 ± 0.02 (0.003)	0.54 ± 0.02 (0.004)	27.3	3.6 ± 0.5	3.6	5	3.7	285
9	Pyridine	0.0308	0.0593–1.1851	6	1.36 ± 0.07 (0.02)	1.40 ± 0.14 (0.03)	9.5		4.6	33	6.65	500 ± 20
10	2,6-Lutidine	0.2903	0.4017–2.8120	5	1.67 ± 0.03 (0.008)	0.80 ± 0.03 (0.008)	27.3			46		510 (ref 20)
11	$CH_3COOC_2H_5$	0.300	0.374–2.618	6	0.66 ± 0.06 (0.02)	1.0 ± 0.2 (0.06)	27.3		3.2	0	3.6	180 ± 15
12	$(CH_2)_4O$[g]	0.300	0.389–2.725	5	0.59 ± 0.02 (0.003)	0.34 ± 0.02 (0.003)	27.3		3.6	5	3.98	285
13	$(CH_3CH_2)_2S$	0.300	0.619–2.892	5	0.77 ± 0.09 (0.01)	0.28 ± 0.05 (0.007)	27.3		2.2	21	2.61	256
14	$(CH_3C(O)CH_3$	0.300	0.618–2.884	5	0.96 ± 0.01 (0.003)	0.67 ± 0.02 (0.005)	27.3		3.4	0	3.7	240 ± 20
15	Benzene[h]	0.015 (m.f.)	0.10–0.98 (m.f.)	6	−1.58 ± 0.10 (0.07)	1.31 ± 0.07 (0.06) (m.f.)	25.3	2.0 ± 0.1	1.7			50
16	$(CH_3)_2S{=}O$								4.5	13	5.16	366 ± 10
17	$(CH_2)_4S{=}O$								4.7	15		
18	$CH_3C(O)N(CH_3)_2$								4.4	8	5.38	345
19	$(C_2H_5)_2O$								3.4	12	3.35	273
20	$(CH_3)_2NH$								4.7	59		
21	$[(CH_3)_2N]_2C{=}S$									39		
22	$[(CH_3)_2N]_2C{=}O$								4.1	0		338
23	Pyridine *N*-oxide								4.8	19		

[a] Errors given are marginal standard deviation. Those in parentheses are the conditional standard deviation (see text). [b] Equilibrium constant corresponding at the given temperature. [c] Enthalpies calculated using eq 1, uncertainty is approximately ±0.2 kcal/mol. [d] Accuracy is ±5 cm^{-1}. [e] See ref 12. [f] Unless otherwise referenced, see G. C. Vogel, Ph.D. Thesis, University of Illinois, 1970. Also, unless noted differently, accuracy is ±5 cm^{-1}. [g] CCl_4 used as solvent, all others run in cyclohexane. [h] See C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962). $-\Delta H$, $\Delta\omega^0$, and *K* evaluated by our procedure (see text). [i] F. L. Slejko and R. S. Drago, submitted for publication. [j] The C_B and E_B parameters for certain donors have been refined since being published (ref 14). The new parameters for the donors are the following: HMPA ($[(CH_3)_2N]_3PO$) $E_B = 1.518$, $C_B = 3.548$; benzene $E_B = 0.525$, $C_B = 0.681$; $CH_3CH_2C(CH_2O)_3P$ $E_B = 0.548$, $C_B = 6.409$.

calorimetric data[2] to treat this type of equation.[18b] The general program was modified for the nmr data to solve for $\Delta\omega^0$ and K. The procedure utilized for determining the errors in these calculated parameters is similar to one recently published for spectrophotometric data.[18c] In this error analysis, we calculate the marginal and conditional standard deviations in the "best fit" values for $\Delta\omega^0$ and K. Briefly, the conditional standard deviation in one of the above quantities, say ($\Delta\omega^0$), is the error as defined by the CHISQ value used as the criterion for obtaining the "best fit"[2] if the other parameter (K) were known exactly. In our case, since both $\Delta\omega^0$ and K are solved simultaneously, their errors are correlated. The real error in $\Delta\omega^0$ must also include the error in K. This error is defined as the marginal standard deviation.[18c] In some systems, we find that plots of K^{-1} *vs.* $\Delta\omega^0$ for each concentration of base give set lines which are nearly parallel. One can then simultaneously vary the "best fit" values of $\Delta\omega^0$ and K over a large range and still calculate data which fit $\Delta\omega_{\mathrm{obsd}}$ very well. In these systems, we find that the marginal standard deviation is rather large, but the conditional standard deviation is much smaller. The realistic error is given by the magnitude of the marginal standard deviation. Furthermore, we find that whenever the ratio of marginal to 0.05 is greater than approximately 15, one does not really know the values of $\Delta\omega^0$ and K with any degree of precision and we feel that these values should not be published. A copy of the program for determining K and $\Delta\omega^0$ and also the error analysis procedure are available from the authors upon request. A temperature-dependence study of the equilibrium constant allowed us to determine $-\Delta H$. In cyclohexane, the lower temperature at which the equilibrium constant may be studied is $\sim 5°$ and the volatility of $CHCl_3$ sets an upper limit around 50°. With some systems where the $\Delta\omega^0$ values are small and K becomes smaller with increasing temperature, the higher temperature data give ratios of marginal to conditional standard deviations which become greater than about ten and, in some cases, exceed our cutoff value of 15. In these cases, evaluation of the enthalpy becomes somewhat more complicated. We find that for these systems at the lowest temperature K is sufficiently large to allow a precise determination of both $\Delta\omega^0$ and K. Assuming that this $\Delta\omega^0$ does not depend on temperature, for each solution containing a given amount of $[A^0]$ and $[B^0]$, measurement of $\Delta\omega_{\mathrm{obsd}}$ as a function of temperature will give K as a function of temperature and thus determine $-\Delta H$ from a least-squares analysis of this data. In practice, several solutions were studied employing various concentrations of $[A^0]$ and $[B^0]$. The value we report for $-\Delta H$ is, then, the average for these solutions. For those systems where the equilibrium constant was sufficiently large even at high temperatures, an accurate determination could be made of K and $\Delta\omega^0$ simultaneously. In all these cases, the values of $\Delta\omega^0$ at these different temperatures were within the experimental uncertainties. This suggests that our assumption that $\Delta\omega^0$ is independent of temperature is a valid one. However, it may be possible that any temperature dependency on $\Delta\omega^0$ would be masked by its experimental uncertainty. Taking a generous uncertainty in $\Delta\omega^0$ of ± 5 cps and asuming a temperature dependency on $\Delta\omega^0$ of 10 cps over the temperature range studied (about 40°), the uncertainty in the final enthalpy becomes $\sim\pm 0.5$ kcal/mol. This is a maximum limit on the uncertainty, so that it may be safely assumed that the real enthalpy is known somewhat better than this. Since there is no direct evidence in the literature that $\Delta\omega^0$ is indeed temperature dependent, we assume that its behavior is similar to other nonassociated materials. We therefore report the errors on $-\Delta H$ as the standard deviation from the log K *vs.* $1/T$ plots for those systems where both $\Delta\omega^0$ and K are determined simultaneously at each temperature. For those systems where $-\Delta H$ was evaluated by measuring $\Delta\omega_{\mathrm{obsd}}$ as a function of temperature for each solution containing different amounts of A^0 and B^0 and assuming a temperature-independent $\Delta\omega^0$, the error in $-\Delta H$ is the standard deviation in the average value of $-\Delta H$ calculated for these solutions.

In all cases, corrections were made to $[A^0]$ and $[B^0]$ to account for the fact that the volume of the solution changes with temperature.

3. Vibrational Analysis. A detailed description of the method has been published elsewhere [15,19]

Results

Hydrogen Bonding Chemical Shifts. The hydrogen bonding chemical shifts, $\Delta\omega^0$, of chloroform with a series of Lewis bases were determined simultaneously with the equilibrium constants. The original data consisting of acid and base concentration, observed chemical shifts, and temperatures appear immediately following this article in the microfilm edition.[17]

Table I summarizes the results obtained from these determinations. Whenever $\Delta\omega^0$ was evaluated at different temperatures, the value corresponding with the "best fit" is given in Table I together with the corresponding equilibrium constant. The acid concentration, base concentration, and the number of solutions employed are also given. The errors given are both the marginal and conditional standard deviations. The raw data are contained in the microfilm edition.[17]

The shift of the "free" chloroform in cyclohexane relative to an internal standard was not found to change significantly in the range 0.300–0.079 *M;* therefore, it is safe to assume that no self-association of chloroform competes in the studies with the given Lewis bases.

Enthalpies of Interaction. The literature contains very little information concerning the enthalpy of hydrogen bond formation between chloroform and Lewis bases.[20] These are listed in Table II. Several methods have been used to measure these enthalpies, such as direct gas-phase measurements[21] and determination of second virial coefficient in the gas phase.[22] As shall be discussed, most of these values are question-

Table II. Enthalpies of Hydrogen Bond Formation with Lewis Bases

Base	Method[a]	Solvent	$-\Delta H$, kcal/mol	Ref
$CH_3C(O)CH_3$[b]	1	Cyclohexane	3.5 ± 0.2	*c*
$C_6H_5NH_2$[b]	1	Cyclohexane	1.7 ± 0.2	*d*
$C_6H_{11}NH_2$[b]	1	Cyclohexane	3.6 ± 0.3	*d*
$(CH_2)_4O$[b]	2	Cyclohexane	3.6 ± 0.4	*e*
Benzene[b]	2	Cyclohexane	2.01 ± 0.34[j]	*f*
$(CH_3CH_2)_3N$[b]	2	Cyclohexane	4.2 ± 0.2[j]	*f*
$CH_3C(O)N(CH_3)_2$	2	CCl_4	1.1	*g*
$(C_4H_9O)_3PO$[b]	2	Cyclohexane	4.3	*h*
$(C_8H_{17})_3PO$[b]	2	Cyclohexane	5.0	28
$(CH_3)_2NH$	3	Cyclohexane	5.8 ± 1.1	21
$CH_3CH_2NH_2$	4	Cyclohexane	4.19	22
$(CH_3CH_2)_2O$	4	Cyclohexane	6.02	22
$[(CH_3)_2N]_3PO$	5	Cyclohexane	5.11 ± 0.06	*i*

[a] Number describes the method used to measure the enthalpies: (1) infrared intensity changes, (2) nmr, (3) direct gas-phase measurements, (4) second virial coefficients on gas phase, (5) direct calorimetric measurement. [b] Enthalpies considered reliable (see text). [c] R. E. Kagarise, *Spectrochim. Acta*, **19**, 629 (1963). [d] K. B. Whetsel and J. L. Lady, *J. Phys. Chem.*, **68**, 1010 (1964). [e] C. J. Creswell and A. L. Allred, *J. Amer. Chem. Soc.*, **85**, 1723 (1963). [f] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962). [g] W. Masschelein, *Spectrochim. Acta*, **18**, 1557 (1962). [h] S. Nishimura, C. H. Ke, and N. C. Li, *J. Phys. Chem.*, **72**, 1297 (1968). [i] F. L. Slejko and R. S. Drago, to be submitted for publication. [j] Reevaluation of these data using our method of computation gives values of 2.0 ± 0.1 for benzene and 4.0 ± 0.3 kcal/mol for $(CH_3CH_2)_3N$.

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able and cannot be used in our study. For example, the gas-phase enthalpy of 5.8 ± 1.1 kcal/mol[21] for $(CH_3)_2NH-CHCl_3$ has an error limit which is too large for this present work. Also a value of 6.02 kcal/mol for $Et_2O-CHCl_3$[22] seems unreasonable and leads us to question other measurements done by determination of second virial coefficients. Similarly, we are not considering enthalpies which were measured in either pure base or pure $CHCl_3$ as solvent.

Some of the enthalpies measured by the nmr technique given in Table II were carried out in CCl_4 as solvent. As we will show later, the enthalpies measured by an nmr technique in this solvent are also of questionable value. Good agreement exists between our enthalpy for $(CH_2)_4O$ (tetrahydrofuran) and the literature value given in Table II. Similarly, an excellent agreement exists between the enthalpy for HMPA, $[(CH_3)_2N]_3PO$, obtained calorimetrically (Table II) with that obtained by the nmr technique. However, only fair agreement results when our triethylamine enthalpy (4.5 ± 0.3 kcal/mol) is compared with that of Creswell and Allred (Table II).

Hydrogen bonding and other Lewis acid–base enthalpies of adduct formation have been incorporated into the general equation[13]

$$-\Delta H = C_A C_B + E_A E_B \qquad (1)$$

A recent publication summarizes the E and C parameters for a wide range of donors and acceptors.[14] Using the experimental enthalpies in Table I and the ones considered reliable in Table II for those donors for which E_B and C_B parameters are known[14] allows us to incorporate chloroform into the double-scale enthalpy equation (eq 1). The best fit solution to the system of equations produced E_A and C_A values for chloroform of 3.02 and 0.159, respectively. The heats predicted by eq 1 for these donors and the E_A and C_A parameters given above for chloroform are compared with the experimental values in Table I. Based on the results from other hydrogen bonding systems, the calculated values are expected to be accurate to ±0.2 kcal/mol.

With the C_A and E_A parameters available for chloroform, we are able to predict enthalpies of adduct formation for a series of other Lewis bases whose E_B and C_B parameters are known.[14] These results on systems that will be of interest to us are included in Table I also.

Ir Frequency Shifts for Deuteriochloroform. Table I gives $\Delta\nu_{CD} = (\nu_{CD}(\text{free}) - \nu_{C-D}(\text{complexed}))$ for deuteriochloroform with a series of Lewis bases studied in carbon tetrachloride.

For sake of comparison, the corresponding values for $\Delta\nu_{OH}$ of phenol complexing with the same bases are also presented in Table I.

Normal Coordinate Analysis. In order to investigate the possibility of unusual coupling effects influencing the C–D vibration in the complex, a simple normal coordinate analysis was carried out on the system base–$HCCl_3$. The procedure used was similar to that reported for the ethyl acetate system.[15,17]

As a consequence of these calculations, we are confident that the high-frequency mode in the chloroform molecule can be thought of as an isolated C–H stretch with very little contribution from other internal coordinates.

Discussion

E and C Parameters for Chloroform.[22a] Reliable measurements of the solvation-minimized enthalpies of adduct formation with various donors are marked in Table II (footnote *b*). These heats, together with those appearing in Table I, with donors for which E_B and C_B parameters are known, fit the double scale enthalpy equation with a high degree of accuracy as seen in Table I. In principle, two enthalpies are needed to determine E_A and C_A and the remainder constitute checks. In practice, a best fit of the eight enthalpies is employed to obtain $E_{CHCl_3} = 3.02$ and $C_{CHCl_3} = 0.159$. Chloroform is a particularly interesting acid because we have interactions of donors with it in which the enthalpy of interaction is almost completely dominated by the E term. The C term is one of the smallest of any acid presently in our correlation. This gives rise to some interesting "apparent anomalies" for the data in Tables I and II. On the basis of extensive literature material, one is apt to conclude that pyridine is a "weaker" base than triethylamine. However, we find that when chloroform is the acid these bases are equally strong, within experimental uncertainty. This is understandable in terms of our E and C correlation. Most of the common acids studied and reported in the literature have been ones with appreciable C_A parameters. For example, phenol has a C_A equal to 0.442 and E_A is 4.33. However, pyridine has a larger E_B value than triethylamine, 1.17 and 0.991, respectively. However, their C_B parameters differ considerably: $C_{\text{pyridine}} = 6.40$ and $C_{\text{triethylamine}} = 11.09$. Therefore, for an acid with sufficient "C character," one would expect the triethylamine heat to be greater than that of pyridine. With chloroform, on the other hand, the contribution to the enthalpy from the product of the C terms is very small due to the small C term for chloroform. One would then expect that the enthalpies for chloroform would be largely dependent on the E_B term for the bases. In spite of a larger $C_A C_B$, the smaller $E_A E_B$ for triethylamine leads to comparable enthalpies of interaction for triethylamine and pyridine.

It should be emphasized at this point that without prior knowledge of the E and C values for chloroform and the various bases, one might have been tempted to offer an explanation based on steric repulsion to account for the low enthalpy in the triethylamine–chloroform system. As has been previously shown, such an effect causes a discrepancy in the observed heat and that calculated from the E and C correlations.[13] The excellent agreement found here on this system eliminates the possible existence of steric repulsions of the F-strain variety in the formation of the triethylamine–chloroform adduct. The large enthalpy of interaction of the phosphine oxides compared to the amines is indicative of a large E term in the former donors. The quantitative nature of the E and C treatment has again

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[22a] NOTE ADDED IN PROOF. Subsequent to the submission of this article, Wiley and Miller (G. R. Wiley and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 3287 (1972)) reported enthalpies of interaction of chloroform with a series of bases which are only in fair agreement with those reported here. Raw data are not available to permit evaluation by our procedures. These authors made the error of calculating enthalpies with our E and C equation using parameters from two different data fits. Since the standards are different in the two fits, this would be comparable to calculating a potential for a reaction using one half-reaction E^0 based on $H^+ \rightarrow H_2$ as zero and the E^0 for the other half-reaction based on $Cu^{2+} \rightarrow Cu$ as zero.

provided us with insight into intermolecular interactions that were not available to us from earlier qualitative arguments about acid–base interactions. The lack of good intuition was invariably met in earlier work by introducing a new effect. Thus, with this study, we have extended even further the number of donor–acceptor systems that can be correlated with just two effects (E_AE_B plus C_AC_B).

Infrared Frequency Shift Correlations. As mentioned in the introduction, we were very much interested in extending our spectroscopic correlations for O–H and N–H functional groups to chloroform. In view of the above discussion, this can be seen to be very desirable because a reliable quick method for predicting enthalpies toward chloroform would provide us with enthalpies dominated by the E_AE_B term improving the accuracy of our E_B parameters. (To get an accurate E_B, a range of acids of widely differing C/E ratios should be employed.) If one attempts to plot $-\Delta H$ *vs.* $\Delta\nu_{CD}$, one finds that no linear correlation exists. It is expected that the sulfur donors by analogy to their interaction with alcohols[8] would not obey the correlation. However, there are many other problems. Despite comparable infrared shifts, diethyl ether and dimethyl sulfoxide have very different enthalpies. Similar difficulties are encountered with hexamethylphosphoramide (HMPA) and pyridine. Very large values for $\Delta\nu_{C-D}$ are obtained for $(CH_3CH_2)_3N$ and $(CH_3)_2NH$, but the enthalpies of adduct formation are comparable to those predicted for dimethyl sulfoxide. It must be emphasized that those points, where $\Delta\nu_{C-D}$ is less than 10 cm^{-1}, were obtained by adding a large excess of base (*vide supra*). This may give rise to a solvent shift which may be of a "nonspecific" nature. For this reason, the failure of $(CH_3CH_2)_2O$ and $(CH_3)_2SO$ to follow the correlation may not be real, but the correlation is at any rate impractical.

It is of interest to see if the chloroform frequency shifts and enthalpies could be correlated with a series of constant base lines that have been reported to exist for OH and NH compounds. It has been previously reported that when one plots $\Delta\nu$(phenol) *vs.* $\Delta\nu$(2-methyl-2-propanol) or $\Delta\nu$(phenol) *vs.* $\Delta\nu$(pyrrole) linear correlations exist with a zero intercept.[5,7] Acids obeying both these relationships can be expected to give rise to constant acid lines. Consequently, the predictive power of these relationships can be tested by showing chloroform fails this requirement. If one attempts to plot these data on the reported constant base lines in ref 7, one sees that chloroform clearly does not fit the relationships. Furthermore, one does not obtain a linear relationship with a zero intercept when $\Delta\nu_{OH}$(phenol) is plotted against $\Delta\nu_{C-D}$. The failure of deuteriochloroform to satisfy these requirements indicates that relationships similar to those for the alcohols and pyrrole are not to be expected for chloroform.

Part of the reason for this can be seen from the results of the normal-coordinate analysis. If the C–H force constant is not decreased, the C–H frequency in the adduct is expected to increase (Table III microfilm copy). Consequently, for these donors in Table I with $-\Delta H$ of about 3.0 kcal/mol^{-1} and no observed frequency shift, the C–H force constant is apparently decreased just about enough to overcome the predicted increase from forming the adduct bond. Comparing the magnitude of the shift observed with the very strong bases toward $CHCl_3$ ($\sim$50–80 cm^{-1}) and phenol ($\sim$500–600 cm^{-1}) or other alcohols, we see that the C–H frequency shift is much less, *i.e.*, the force constant is decreased much less, in chloroform. This has the net effect of making much of the chloroform data fall on that part of the general type $-\Delta H$ *vs.* $\Delta\nu$ relation which is predicted to curve for most alcohols, *i.e.*, the small frequency shift extreme. The reason for the small change in force constant with $CHCl_3$ is consistent with the weakness of this acid. Compared to phenol, where phenoxide is gradually displaced when this substance behaves as an acid, the much stronger base CCl_3^- must be displaced when chloroform behaves as an acid. In phenol, as the base strength approaches that of phenoxide, the bonding approaches that of a three-center MO (as in $F-H-F^-$) where one pair of electrons in the bonding MO joins the hydrogen to two groups. In this limit, the O–H bond is in effect a half bond and its force constant drastically reduced over that in phenol. The bases used in this study are much weaker than CCl_3^-, so the bonding does not approach this description.

It is ironic that the chloroform system does not fit the attempted enthalpy–infrared shift correlations, for this is one of the first correlations reported[9–11] and has been assumed frequently in subsequent literature. In the initial work, the heat of solution of various bases in chloroform was plotted against the O–H stretching frequency shift of the same base with alcohols. When we plotted the enthalpy of chloroform adduct formation *vs.* $\Delta\nu_{OH}$ of phenol of these adducts, a satisfactory correlation did not result. Thus, one of the most generally accepted spectral–enthalpy correlations is a fortunate accident that resulted from using enthalpies not related to those of adduct formation.

Nmr Chemical Shift Correlation. In view of the rapid exchange between coordinated and free chloroform in solution, the chemical shift of complexed chloroform can only be obtained by simultaneously determining the equilibrium constant and $\Delta\omega^0$. This introduces a certain amount of error into the magnitude of the chemical shift of the complex. Therefore, it is appropriate at this time to point out a number of observations concerning the measurement of these quantities which are summarized in Table I.

First of all, $\Delta\omega^0$, the difference in chemical shift of the adduct ($CHCl_3$–THF) and free chloroform, is different in CCl_4 and in cyclohexane solvent. This effect has also been observed on a whole series of hydrogen bonding acids.[23] The discrepancy between these two experiments could be attributed to a nonspecific solvent effect on the resonance position of the "free" acid in each solvent. However, it could also be due to the hydrogen bonding of the free acids with CCl_4, an effect that would not be compensated for by an internal standard. Although this interaction has been shown[24] to give rise to very small enthalpy effects in the calorimetric experiment, it apparently has a pronounced effect on the chemical shift of chloroform.

The chemical shift of "free" chloroform has been reported to be 0.11 ppm deshielded in CCl_4 relative to cyclohexane.[25] If one takes data for the THF–$CHCl_3$

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(23) T. Gramstad and E. D. Becker, *J. Mol. Struct.*, 5, 253 (1970).
(24) M. S. Nozari and R. S. Drago, to be submitted for publication.
(25) C. F. Jumper, M. T. Emerson, and B. B. Howard, *J. Chem. Phys.*, 35, 1911 (1961).

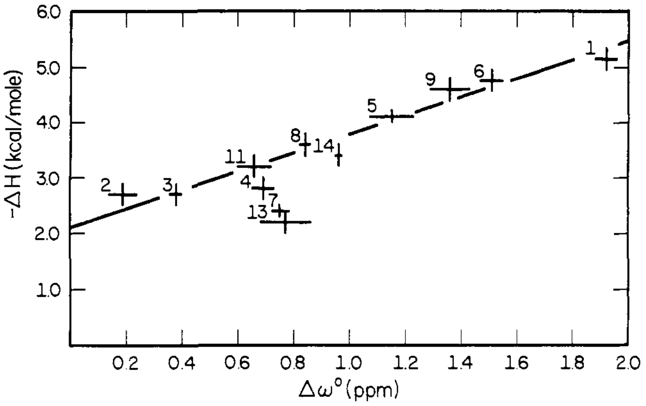

Figure 1. Plot of $-\Delta H$ formation of the chloroform adducts *vs.* $\Delta\omega^0$. Numbers correspond to the donors in Table I.

system in CCl_4 and solves for $\Delta\omega^0$, the shift for the complex can be determined by subtracting that for free $CHCl_3$ in CCl_4. Making this correction, to the difference in the hydrogen bonding chemical shift of chloroform complexed to THF in CCl_4, results in a value of 0.70 ppm for the complex in CCl_4. This is to be compared with a value of 0.84 ppm for the same complex in cyclohexane. The remaining discrepancy is still sufficiently large to cast some doubt on the $\Delta\omega^0$ values obtained in CCl_4 solvent and is probably due to the fact that an apparent K results, which does not properly handle the competing equilibria. The thermodynamic parameters and the shifts obtained by an nmr procedure when the acid is interacting with the solvent could be meaningless. On the basis of these observations, we chose to consider only the values obtained in cyclohexane as solvent.

At this point, it would be worthwhile to treat the same data using the modified Benesi–Hildebrand (B–H) equation.[26,27] The results for some of these systems are shown in Table IV of the microfilm copy.[17] Comparison of the data in this table obtained in cyclohexane with that in Table I illustrates the substantial error in $\Delta\omega^0$ which is introduced by this analysis of the data. Also the THF–$CHCl_3$ data in CCl_4 and cyclohexane give the same value of $\Delta\omega^0$ when treated by the B–H method. In several cases, parallel lines were obtained in a plot of K^{-1} *vs.* $\Delta\omega^0$ when the data were treated by our procedure, but gave a good straight line when treated by the B–H method. Our criterion for a "poor fit" is a ratio of marginal to conditional standard deviation exceeding ~15; however, even in these cases, a good B–H straight line is obtained, giving the false impression that a meaningful $\Delta\omega^0$ may be obtained. Unfortunately, much data in the literature[20] were treated by the B–H method, making many values of $\Delta\omega^0$ reported for weakly interacting systems meaningless.

It has been shown that a straight line correlation exists between $-\Delta H$ and $\Delta\omega^0$ for phenol,[12] 2,2,2-trifluoroethanol,[28] and 1,1,1,3,3,3-hexafluoro-2-propanol[4] when corrections have been made for donor diamagnetic anisotropies. Sulfur donors were found to fall off the nmr constant acid line for 1,1,1,3,3,3-hexafluoro-2-propanol.[4] A similar treatment of the $-\Delta H$ and $\Delta\omega^0$ data for chloroform are shown in Figure 1. No correction was made for the donor anisotropy contributions, as the previously published donor anisotropy contributions are larger than the $\Delta\omega^0$ values obtained for some of these donors with $CHCl_3$, and we do not have accurate base–proton distances to allow us to calculate donor anisotropy corrections for the chloroform adducts. Furthermore, as has been recently pointed out,[29] donor anisotropy effects for donors other than benzene and possibly acetonitrile should be negligible for the chloroform donor systems studied here. As can be seen, a reasonable correlation results except, of course, for the sulfur donors. However, the precision by which enthalpies could be predicted using Figure 1 is not high enough to warrant its use for this purpose. Furthermore, it is almost as much work to measure an accurate value of $\Delta\omega^0$ as it is to determine the enthalpy by the procedure outlined in the Experimental Section.

It is interesting that chloroform does not obey a linear relationship between the enthalpy of adduct formation and $\Delta\nu_{CD}$, but gives a reasonable correlation for $\Delta\omega^0$. It must be emphasized, however, that the $-\Delta H$–$\Delta\nu$ relationships are found for acids which have both significant E and C parameters and similar C/E rations. Chloroform, on the other hand, with a very low C_A/E_A ratio has enthalpies largely dominated by the E_AE_B term. Perhaps the mechanism by which the changes in acid spectroscopic property, $\Delta\nu_{CD}$, occurs are dependent upon fortuitous trends in the magnitudes of the E_AE_B and C_AC_B terms. With chloroform, having a very low C_A/E_A ratio, it is plausible that the relationships between $-\Delta H$ and $\Delta\nu_{C-D}$ assume a different mathematical form than with the other hydrogen bonding acids.[30] All this tends to point toward the lack of a "good" model for hydrogen bonding which will account for all these experimental features. Hopefully, by investigating a wider range of acids and bases having different C/E ratios, more exceptions will be found, for these exceptions have the potential of providing us with a more complete understanding.

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