JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY
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VOLUME 94, NUMBER 10 MAY 17, 1972

Thermodynamic Parameters for Hydrogen Bonding of Chloroform with Lewis Bases in Cyclohexane. A Proton Magnetic Resonance Study[1a]

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Abstract: The pmr technique has been used to obtain precise thermodynamic data for hydrogen bonding of chloroform with 12 proton acceptors in cyclohexane. At 28°, these are (base; K, M^{-1}; $-\Delta H°$, kcal/mol; $-\Delta S°$, eu): $C_2H_5NO_2$, 0.36, 1.5, 7; $(CH_3S)_2$, 0.17, 0.93, 7; $(CH_3)_2CO$, 0.75, 2.3, 8; $CH_3COOC_2H_5$, 0.67, 2.5, 9; 1,4-dioxane, 0.58, 2.6, 10; $(CH_2)_4S$, 0.28, 2.3, 10; $(C_2H_5)_2S$, 0.22, 1.7, 9; *N*-methylpyrrolidone, 3.2, 4.0, 11; cyclohexanone, 1.02, 2.4, 8; $(C_2H_5)_3N$, 0.43; 4.1, 15; $(C_2H_5O)_3PO$, 4.6, 3.8, 10; $(n\text{-}C_4H_9)_2O$, 0.24, 2.4, 5. For the self-association of chloroform, $K = 0.013\ M^{-1}$ at 28°. These figures were obtained by iterative computer fit of pmr dilution shifts to an exact model for 1:1 association. An attempt was made to cover the widest possible range of saturation fraction, s, or degree of association, for optimally defined K values, since this allows one to assess the reliability of association data obtained by spectral methods. A narrow s range immediately implies that the association data, *e.g.*, for dimerization of chloroform, are intrinsically uncertain. When the fit of data for 1:1 association over a broad s range is poor, *e.g.*, for chloroform-nitroethane, then the 1:1 model is suspect. A temperature dependence, averaging ~ -3.6 Hz/60°, was noted in the chemical shift (δ_C) of the complex. From the enthalpy data generated here, we redetermined the Drago acid parameters for chloroform to be $C_A = 0.11$ and $E_A = 3.35$: the electrostatic interactions are more important than the covalent contributions to acid-base association. The advantages of processing dilution shift data in the hyperspace of concentrations and temperature, $\delta = f(A_0, B_0, T)$, are indicated.

The determination of reliable thermodynamic data has often seemed to be a contradiction in terms when applied to weak complexing.[2-4] Here we investigate chloroform as a model proton donor

$$Cl_3CH + B \rightleftharpoons Cl_3CH\cdots B \tag{1}$$

Apart from the intrinsic interest in this simple substrate, we hoped to use it as a probe into various aspects of hydrogen bonding, *e.g.*, theory, pmr methodology, Lewis bases, correlations, carbon acids, etc.

Although chloroform has been employed frequently as a proton donor to bases, simple as chloride[5] or complex as an alkaloid or steroid,[6] and has been studied by a variety of techniques, the number of systems for which thermodynamic data are available is small. Of these, fewer still are fully characterized with K, $\Delta H°$, and $\Delta S°$. Many of these hydrogen-bonding data have been compiled in the thesis;[1b] several surveys are also available.[3,4,7] A selection emphasizing some recent and complete studies is given in Table I. The deficiencies and discrepancies in these data, which are those one often finds for weak complexes, are sufficiently numerous so that one may well ask whether it is even possible to obtain reproducible thermodynamic data for chloroform. In this paper we show that, if the available spectral method is used to full advantage instead of in the inadvertently restrictive manner in

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[1] (a) Research supported in part by Public Health Service Grant No. GM 7021 and by fellowships for G. R. W. from NDEA, the Petroleum Research Fund, administered by the American Chemical Society (No. PRF-GF 769), and the ACS Division of Analytical Chemistry. (b) This work was taken from the Ph.D. thesis of G. R. W., Illinois Institute of Technology, 1971.

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Table I. Selected Hydrogen-Bonding Data for Chloroform as Proton Donor

Base	Solvent	Method	Temp, °C	Δ, Hz	K, M^{-1}	$-\Delta H°$, kcal/mol	$-\Delta S°$, eu	s^a	Ref
$(CH_3)_2SO$	CCl_4	Pmr	30		0.99	1.6		0.02–0.06	*d*
$(C_2H_5)_3N^c$	C_6H_{12}	Pmr	25	88.6	4.2^b	4.15	11.0	0.3–0.8	*e*
			~25	90.6	0.858	4.8		0.3–0.7	*f*
			25	45	4.7^b			0.2–0.8	*g*
$(n\text{-}C_4H_9O)_3PO$	C_6H_{12}	Pmr	21	82	5.2	4.3	11.3	0.78–0.92	*h*
$(CH_3)_2CO^c$	C_6H_{12}	Uv	25		0.8				*i*
	C_6H_{14}	Ir	31		0.9	3.5			*j*
	C_6H_{12}	Pmr	~25	57.8	0.21	3.6		0.1–0.36	*f*
$CH_3COOC_2H_5{}^c$	C_6H_{12}	Pmr	~25	40.7	0.4	3.8		0.12–0.5	*f*
$(CH_2)_4S^c$	C_6H_{12}	Pmr	~25	45.0	0.13	2.4		0.01–0.24	*f*
$(C_2H_5)_2S^c$	C_6H_{12}	Pmr	~25	46.2	0.11	$(2.3)_{\text{calcd}}$		0.06–0.23	*f*
$CH_3CON(CH_3)_2$	CCl_4	Pmr	36	70	0.82	1.1	3.7	0.26–0.57	*k*
C_5H_5N	CCl_4–C_6H_{12}	Pmr	21.7	125.3	1.76^b	2.4		0.15–0.5	*l*
$C_6H_5NH_2$	C_6H_{12}	Ir	25		0.51	1.7	7.1	0.01–0.16	*m*
$((CH_3)_2N)_3PO$	C_6H_{12}	Pmr	20	121.2	13.4			0.24–0.94	*n*
1,4-Dioxane^c		Pmr	28	72	$\sim 1.4^b$	~2.0			*o*
Cyclohexanone^c	C_6H_{12}	Ir	30		1.2				*p*
$(C_4H_9)_2O^c$		Pmr	25		1.33^b	1.9			*q*

[a] Saturation fraction (eq 9). [b] The units are mole fraction^{-1}. [c] For a comparison with our data, see Table III. [d] Y. H. Shaw and N. C. Li, *Can. J. Chem.*, **48**, 2090 (1970). [e] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962). [f] F. L. Slejko, R. S. Drago, and D. G. Brown, private communication. [g] B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectrosc.*, **10**, 117 (1963). [h] S. Nishimura, C. H. Ke, and N. C. Li, *J. Phys. Chem.*, **72**, 1297 (1968). [i] A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.*, **2**, 69 (1968). [j] $CDCl_3$ was used; R. E. Kagarise, *Spectrochim. Acta*, **19**, 629 (1963). [k] F. Takahashi and N. C. Li, *J. Phys. Chem.*, **69**, 2950 (1965). [l] T. J. V. Findlay, J. S. Keniry, A. D. Kidman, and V. A. Pickles, *Trans. Faraday Soc.*, **63**, 846 (1967). [m] K. B. Whetsel and J. H. Lady, *J. Phys. Chem.*, **68**, 1010 (1964). [n] T. Olsen, *Acta Chem. Scand.*, **24**, 3081 (1970). [o] R. Kaiser, *Can. J. Chem.*, **41**, 430 (1963); M. L. McGlashan and R. P. Rastogi, *Trans. Faraday Soc.*, **54**, 496 (1958). [p] K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, **18**, 329 (1962). [q] J. R. Baker, I. D. Watson, and A. G. Williamson, *Aust. J. Chem.*, **24**, 2047 (1971).

which it has often been applied, precise and meaningful measurements can be made.

Experimental Section

Materials. Following a preliminary purification, if needed, liquids were usually treated with Linde 4A and 5A molecular sieves and fractionally distilled. Ir and nmr spectral checks at high gain were made to see that the compounds were anhydrous. The limit of detection of water by ir is ~0.01–0.02%. After this standard treatment of our chloroform (Baker Analyzed reagent) shortly before it was to be used, we could detect no residual water or ethanol by nmr when ten scans coupled to a computer of average transients was employed.

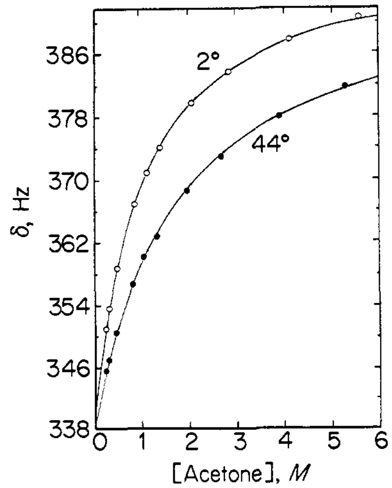

Figure 1. Dilution shifts of chloroform in cyclohexane in the presence of acetone. The solid line is generated by the exact eq 5.

The solvent cyclohexane, of mp 5–6°, was further purified by repeated fractional freezing. Both nmr and vpc indicated <0.25% residual impurity, probably saturated alkane(s), *e.g.*, heptane, but not unsaturates, *e.g.*, cyclohexene, benzene, etc.

Nuclear Magnetic Resonance Spectra. All samples were run on a modified Varian HA 60 IL spectrometer, operating at 60 MHz and equipped with a variable-temperature probe. Chemical shifts (δ) were measured by sweeping through the resonance peak of interest three times in either direction. The peak position was ascertained relative to the solvent cyclohexane lock signal with a Hewlett-Packard 5216A frequency counter. Our typical operating conditions were sweep width 50 Hz, sweep time 1 Hz/sec, and period counts 10^3. We consider our precision in δ to be ±0.2 Hz.

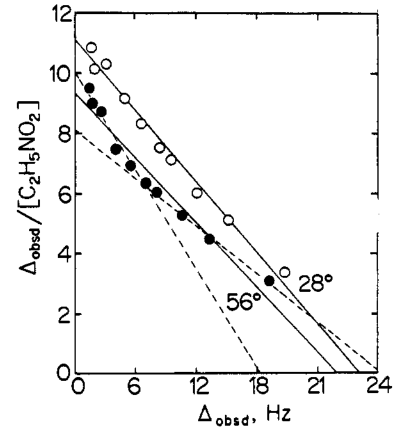

Figure 2. Dilution shifts of chloroform in cyclohexane in the presence of nitroethane. Least-squares plots of eq 6 are shown by the solid lines. (The broken line segments are discussed in the text.)

Temperatures were measured, using sealed samples of methanol or ethylene glycol. For a given temperature, the stability was ±1° and the accuracy probably was ±2°. The ambient probe temperature was essentially constant at 28 ± 0.5°. Periodic checks on samples used to determine the temperature as well as on several solutions were self-consistent and reproducible.

Stock solutions of chloroform were prepared by weighing in a volumetric flask and making up to the mark with cyclohexane. Aliquots of this solution were transferred to volumetric flasks containing weighed quantities of the Lewis base and made up to volume.

Table II. Hydrogen-Bonding Parameters for Triethylamine–Chloroform in Cyclohexane[a]

$\delta(2°)$	$\delta(28°)$[c]	$\delta(41°)$	$\delta(58°)$	$[Et_3N](27°)$[b]
358.08	349.30	346.92	344.10	0.3039
366.76	355.07	351.50″ [d]	347.43	0.4991
370.57	358.01	353.57		0.6143
380.29	365.08	359.47	353.90	0.9324
389.10″ [d]	372.81	366.27	359.29	1.3596
393.90	376.65	369.54		1.6074
399.21	381.43	374.10	365.90	1.9751
403.16	385.51	377.92		2.3397
406.54	388.87	381.22	372.13	2.6790
409.55	392.47	384.75		3.1151
413.65	397.41	389.52	380.17	3.8294
419.22	404.44	397.14	387.60	5.2466
2°	$K = 0.784 \pm 0.012$	$\Delta = 99.20 \pm 0.54$		$\sigma = 0.37$
28°	$K = 0.425 \pm 0.004$	$\Delta = 95.52 \pm 0.40$[c]		$\sigma = 0.15$
41°	$K = 0.324 \pm 0.005$	$\Delta = 93.84 \pm 0.82$		$\sigma = 0.24$
58°	$K = 0.229 \pm 0.002$	$\Delta = 92.14 \pm 0.58$		$\sigma = 0.10$
	$\Delta H° = -4.06 \pm 0.05$	$\Delta S° = -15.2 \pm 0.2$		$\bar{T} = 32°$
2°	$K'' = 0.792 \pm 0.009$	$\Delta'' = 98.98 \pm 0.41$		$\sigma'' = 0.28$
28°	$K = 0.425 \pm 0.004$	$\Delta = 95.52 \pm 0.40$[c]		$\sigma = 0.15$
41°	$K'' = 0.321 \pm 0.004$	$\Delta'' = 94.31 \pm 0.67$		$\sigma'' = 0.19$
58°	$K = 0.229 \pm 0.002$	$\Delta = 92.14 \pm 0.58$		$\sigma = 0.10$
	$\Delta H°'' = -4.05 \pm 0.03$	$\Delta S°'' = -15.2 \pm 0.1$		$\bar{T} = 32°$

[a] Units and definitions: δ, Hz; K, M^{-1}; Δ, Hz; $\sigma \equiv (\text{variance})^{1/2}$, Hz ($\sigma \equiv (\text{variance})^{1/2} \equiv [(\delta - \delta_{\text{calcd}})^2/N]^{1/2}$); $\Delta H°$, kcal/mol; $\Delta S°$, cal/(deg mol); s, saturation fraction; $\bar{T}$, mean temperature, °C; a double prime signifies that this δ was *not* used in calculating K'', Δ'', $\Delta H°''$, and $\Delta S°''$; ± is the standard deviation. [b] $[CHCl_3] = 0.01191$ at 27°; all concentrations were corrected for changes with temperature. [c] $s = 0.11\text{–}0.69$ or 58%. [d] The points omitted deviated from the fit to eq 5 by $\sim 2\sigma$.

Table III. Thermodynamic Parameters for the Association of Chloroform with Various Proton Acceptors[a]

Proton acceptor	$K_{23°}$	$\Delta_{28°}$	σ	s	$\Delta H°$, kcal/mol	$\Delta S°$, eu	$\bar{T}$, °C
$C_2H_5NO_2$[b]	0.358 ± 0.014	29.94 ± 0.59	0.06	0.06–0.69	−1.53 ± 0.03	−7.12 ± 0.10	42
$(CH_3S)_2$[b]	0.170 ± 0.003	34.72 ± 0.33	0.06	0.04–0.53	−0.93 ± 0.27	−6.6 ± 0.9	26
$(CH_3)_2CO$	0.751 ± 0.012	58.31 ± 0.36	0.23	0.15–0.80	−2.34 ± 0.13	−8.37 ± 0.47	25
$CH_3COOC_2H_5$	0.674 ± 0.025	50.51 ± 0.52	0.27	0.05–0.78	−2.51 ± 0.10	−9.03 ± 0.32	23.5
1,4-Dioxane[b]	0.582 ± 0.013	40.53 ± 0.35	0.19	0.17–0.79	−2.56 ± 0.09	−9.64 ± 0.32	21
$(CH_2)_4S$[b]	0.275 ± 0.004	52.39 ± 0.35	0.14	0.02–0.71	−2.28 ± 0.71	−10.2 ± 0.6	23
$(C_2H_5)_2S$[b]	0.219 ± 0.002	55.95 ± 0.30	0.07	~0.01–0.65	−1.70 ± 0.02	−8.65 ± 0.08	23
N-Methylpyrrolidone[b]	3.222 ± 0.085	83.67 ± 0.62	0.42	0.17–0.89	−3.99 ± 0.02	−10.9 ± 0.1	32
$(CH_2)_5CO$	1.023 ± 0.022	59.05 ± 0.59	0.19	0.14–0.70	−2.44 ± 0.10	−8.11 ± 0.35	27
$(C_2H_5)_3N$	0.425 ± 0.004	95.52 ± 0.40	0.15	0.11–0.69	−4.05 ± 0.03	−15.2 ± 0.1	32
$(C_2H_5O)_3PO$[b]	4.637 ± 0.15	80.32 ± 0.57	0.80	0.08–0.97	−3.81 ± 0.04	−9.60 ± 0.12	32
$(n\text{-}C_4H_9)_2O$[b]	0.243 ± 0.015	53.29 ± 2.84	0.03	0.02–0.40	−2.35 ± 0.12	−5.32 ± 0.20	37
$CHCl_3$	0.0126 ± 0.0015[b]	56 ± 5	0.09	~0.01–0.17			

[a] The notation is that of Table II; however, the double prime figures, when available, are used here without identification. The concentrations were corrected for temperature changes, unless otherwise indicated. [b] Concentrations not corrected. This is a self-association K.

All of the volumetric ware was calibrated. The solutions were tightly capped and stored in a refrigerator. The pmr measurements generally began within 24 hr of sample preparation. In the triethylamine-chloroform system, the weight of the cyclohexane was also determined. Here crystalline solid began to separate within several hours after the nmr measurements.

Our corrections of molarity (M) with temperature were applied only to chloroform, cyclohexane, acetone, ethyl acetate, cyclohexanone, and triethylamine.[8,9] (The remaining figures[1b] can be corrected when suitable density data become available.) Assuming ideal solutions, we could obtain these molarities from a relation (eq 2) that was programmed on a Wang calculator, where g = mass in

$$M_{\text{a},T_2} = g_{\text{a}}(\text{MW}_{\text{a}}[g_{\text{a}}d^{-1}{}_{\text{a},T_2} + g_{\text{b}}d^{-1}{}_{\text{b},T_2} + d_{\text{c},T_1}d^{-1}{}_{\text{c},T_2}(V_{\text{soln}} - g_{\text{a}}d^{-1}{}_{\text{a},T_1} - g_{\text{b}}d^{-1}{}_{\text{b},T_1}])^{-1} \quad (2)$$

grams, d is in grams per milliliter, V is in milliliters, MW = molecular weight, T is in degrees Celsius, a (or b) represents acid (or base), and c represents C_6H_{12}. The assumption of ideality was checked for the binary system acetone–chloroform, for which solution densities were available:[10] at a mole ratio of 84.3:15.7, the calculated and observed densities agreed within 1%. The necessity for imposing the temperature correction on M will be shown later—effects on both K and $\Delta H°$ are given in Table IV.

Results and Discussion

At the outset we give an overview of our results, from dilution shift data to the final thermodynamic quantities of interest for process 1 (Figures 1 and 2 and Tables II and III). Later, we take up matters of procedure, errors, interpretation, etc.

Formalism and Preliminaries. If the 1:1 association of eq 1 is fast on the nmr time scale and if chloroform dimers and other complexes are absent, the observed chemical shift (δ) is given by eq 3.[3] δ_{A} is the chemical

$$\delta A_0 = A\delta_{\text{A}} + (A_0 - A)\delta_{\text{C}} \quad (3)$$

shift of chloroform (A), δ_{C} is the chemical shift of the complex (C), and the letters (A, B, C) are the appro-

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priate concentrations. The equilibrium expression for (1) is given by eq 4. An exact working expression,

$$K = C/AB = (A_0 - A)/A(B_0 - A_0 + A) \quad (4)$$

eq 5, can be obtained from eq 2 and 3, if $\Delta \equiv (\delta_C - \delta_A)$.

$$\delta = \delta_A + \Delta[A_0 + B_0 + K^{-1} - \sqrt{(A_0 + B_0 + K^{-1})^2 - 4A_0B_0}]/2A_0 \quad (5)$$

An alternate useful expression, which holds when $B_0 \gg A_0$, is given by eq 6 ($\Delta_{obsd} \equiv \delta - \delta_A$).[11] The best-

$$(\delta - \delta_A)/B_0 = K(\delta_C - \delta) \equiv K(\Delta - \Delta_{obsd}) \quad (6)$$

fit K's at different temperatures were used in the standard expression 7 to obtain the thermodynamic parame-

$$\ln K = -\Delta H°/RT + \Delta S°/R \quad (7)$$

ters collected in Table III.

It should be evident that the preceding analysis would break down if the following "complications" were significant: 1:1 self-association of the donor or of chloroform (eq 8); formation of higher complexes,

$$2Cl_3CH \rightleftharpoons Cl_3CH\cdots Cl_3CH \quad (8)$$

e.g., 1:2, 2:1, etc.; medium dependence of δ_A and δ_C; changes in the activity coefficients of the participants of eq 1. With one possible exception, our systems appeared to be well behaved. Although we shall return to the question of the possible effect of these factors on our 1:1 equilibrium constants, we proceed to treat our thermodynamic data as though they were obtained at the ideal limit of infinite dilution in cyclohexane.

A useful concept in analyzing dilution shift data is to keep track of the fraction associated or the saturation factor, s, which has the limiting values of 0 at $B_0 = 0$

$$s \equiv C/A_0 = (\delta_C - \delta)/\Delta = \Delta_{obsd}/\Delta \quad (9)$$

and 1.0 at complete complexation.[11] Deranleau has pointed out that equilibrium constants are most reliable when they are based on spectral data covering as much as possible of the range s = 0.2–0.8, and become rapidly and increasingly uncertain as $s \rightarrow 0$ or $s \rightarrow 1.0$. His U-shaped plot of the uncertainty $\Delta K/K$ *vs.* s makes this crucial point convincingly.[11] Furthermore, correspondence of the data to eq 5 for at least 75% of the range in s virtually establishes the 1:1 complex as fact and essentially excludes most other possibilities.

In this context, the presentation of data through eq 6, that is, a plot of Δ_{obsd}/B_0 (or $s\Delta/B_0$) *vs.* Δ_{obsd}, as in Figure 2, has the pictorial advantage of encompassing the total range of association. Unlike the plot of Figure 1, the Saunders–Hyne presentation, Benesi–Hildebrand double-reciprocal plots, etc., it is not open ended, and there are no scale expansions or contractions,[3,11] which can be deceptive. The consequences of using a best-fit treatment in restricted regions of s are illustrated by our data for nitroethane–chloroform: the slopes of the broken lines, which equal K, are strikingly different (Figure 2). (Since their fit to eq 6 is least satisfactory among all of our bases, the plots of Figure 2 *are not to be regarded as typical;* this figure was selected because it illustrates the use of eq 6 as well as the hazards of narrow limits on s.) It is not, of course, the manner in which the data are displayed or manipulated to obtain K, but the range and region of s that are important. For this reason, we include s as an essential part of the description of our own results (Table III) and shall use it as a first criterion of the reliability of the results of others (Table I).

A nice example of the use of s in the preliminary appraisal of experimental work follows. In a recent paper, K's were determined by ir and nmr techniques for phenylacetylene–base systems. The effects of self-association, anisotropy, and procedural variants in the nmr approach itself were investigated.[12] Various discrepancies were noted in the resulting K's. Although wide concentration ranges were used and the work appears to be critically and carefully done, the authors had to work with only a few per cent of the low end of the s scale in some systems. Overlooked by these authors, this in itself could account for discrepancies in K.

Broad middle s ranges are often impossible to achieve experimentally.[2,12] This situation would arise in pmr studies if K is small ($<0.1\ M^{-1}$) or large ($>10\ M^{-1}$), and if the accessible concentration range were limited for any reason, *e.g.*, solubility, chemical reactivity, medium dependence, neat base, etc. Work done in our laboratory on the self-association of alkanethiols or their association with electron donors is illustrative of the neat extreme—even at the limit of 100% base, s is still relatively small.[2] For one or other of these reasons, we had problems with the association of chloroform with itself, and we did not proceed beyond preliminary tests in the cases of chloroform with the bases, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, methanol, acetonitrile, nitromethane, and 1,4-diazabicyclo[2.2.2]octane.

Hydrogen Bonding to Chloroform. Chloroform is an uncomplicated proton donor with a single sharp resonance which occurs in a relatively "clean" region of the pmr spectrum. We obtained hydrogen bonding dilution shift data for process 1 for 12 proton acceptors. Table II is representative of similar tables in the thesis.[1b] The self-association of chloroform was also studied and was found to be unimportant (see next section). In general, we have deliberately avoided using bases with aromatic rings;[13] when anisotropy corrections have to be superimposed on dilution shift data of *weak* hydrogen bonding complexes, the resulting equilibrium constants are beset with substantial uncertainty, even when fair corrections are possible.[2] The approximate expression 6 was used to obtain estimates of K and Δ (Figure 2). These quantities were used as initial input for an iterative solution of the exact expression 5 (Figure 1).[14] The final equilibrium data are collected in Table III.

It is well known that several of the important parameters that we evaluate, *i.e.*, K, Δ, and $\Delta H°$, may vary with the concentration scale that is used.[3,15,16] Any controversial aspects of this issue have presumably

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Table IV. The Concentration Scale Dependence of Hydrogen-Bonding Parameters for Triethylamine–Chloroform in Cyclohexane[a]

	Concentration scale		
	M	mF	M_{corr}[b]
$K(2°)$	0.754 ± 0.018	7.28	0.733 ± 0.018
$K(28°)$	0.418 ± 0.007	4.14	0.418 ± 0.007
$K(41°)$	0.330 ± 0.013	3.33	0.336 ± 0.014
$K(58°)$	0.218 ± 0.002	2.35	0.232 ± 0.003
$\Delta(2°)$	100	96.1	100
$\Delta(28°)$	95.3	88.4	95.3
$\Delta(41°)$	91.0	82.8	90.6
$\Delta(58°)$	91.7	79.0	90.5
ΔH, kcal/mol	−3.95 ± 0.21	−3.61 ± 0.11	−3.66 ± 0.15

[a] Six concentrations of Table II were used in this comparison, with $s \simeq 0.28$ to 0.75. The units are those of Table II, except when mole fraction units are indicated for K. [b] The molarity was corrected for temperature changes.

been dispelled by the demonstration that, in contrast to the mole fraction and molal scales, the molar scale is simultaneously compatible with the spectral (pmr) data, the thermodynamic formulation of the 1:1 association and "chemical" interpretations of the results at the molecular level.[16] Although the molar scale was generally used by us, we also obtained mole fraction data for one system, triethylamine–chloroform. Apart from providing an internal comparison, this system has also attracted some interest in the past (see Table I). Our K's and Δ's do differ for both scales, but $-\Delta H°$ is the same within experimental error (Table IV).

Our detailed approach to working up our data deserves comment. To test the 1:1 model for process 1, we used as a criterion the fit to linearity of eq 6 in the range of its applicability ($B_0 \gg A$). On this basis, occasional points, which deviated grossly from the group of four linear plots of eq 6 for each base–chloroform system, were discarded. Secondly, when the fit of δ to the exact eq 5 was such that $\delta \geqslant 1.7\sigma$,[17] the point was dropped. These deletions were made sparingly: only 22 out of a total of 434 points were rejected. Moreover, the changes effected by excision were small, since the average σ for all runs decreased slightly from 0.31 to 0.25 Hz. That the "improvements" are slight can be seen in Table II.

The processing of our data did, however, disclose some puzzling features. In Table III, the σ's for the best fits to eq 5 were not all <0.3 Hz, which we estimated to be our precision in measuring δ. The standard deviations for an occasional Δ, $\Delta H°$, or $\Delta S°$ seem high relative to others in the group. These departures from the norm did not necessarily fit in with our impressions of systems that were less "well-behaved." On the other hand, we believe that one base, nitroethane, whose data clearly gave the least linear version of eq 6 (Figure 2), turns out very respectably in the group of Table III. Certainly, repeated measurements of the utmost precision would pare some of these standard deviations.

Our tests of eq 6 showed good linear fits over broad ranges in s. Accordingly, we interpret these fits as strongly favorable to predominant 1:1 association (eq 1) for 11 bases. But we did not or could not cover the necessary middle 75% of the s range,[11] except for three to four systems. Therefore, we cannot rule out the possibility that other associations may be present and may have skewed the results obtained for the 1:1 model.[18] Under our conditions, we believe that it is improbable that complexes of the type $HCCl_3\cdots HCCl_3$ or base·$2CHCl_3$ are present in significant amounts (see next section), although the latter may well be present in solutions containing high concentrations of chloroform.[4,18a–e] On the other hand, evidence for the formation of base ···base dimers and of $CHCl_3$·2base complexes is sufficiently varied with respect to bases and techniques used that it cannot be ignored, particularly at the higher concentrations of base.[4,18f,g] Thus, dimers of acetone in hexadecane[18f] have been reported and the association of chloroform with certain esters appears to require both 1:1 and 1:2 complexes.[18g] For these reasons we claim only that we have carefully fit our data over a given concentration range, within certain error limits to a specified model.

Nitroethane, the obvious deviant base of our set, can undoubtedly compete with chloroform as a proton donor and may form higher complexes with it.[19]

$$2C_2H_5NO_2 \rightleftharpoons (C_2H_5NO_2)_2$$

$$CHCl_3 + C_2H_5NO_2 \rightleftharpoons C_2H_5NO_2\cdots HCCl_3 \rightleftharpoons CH_3(NO_2)(H)CH\cdots Cl_3CH \quad (10)$$

It is, in fact, not the choice of 1:1 complexes in eq 10, but 1:2 or 2:1 aggregates and/or anisotropy complications that may perturb our model. It may be that such competing equilibriums give rise to the curvature in what was supposed to be a linear plot in Figure 2. An additional problem here was the fact that we were restricted to s = 0.07–0.4 at 12°, because two phases formed above ~2 M nitroethane. In short, despite the acceptable fits of eq 5 at the four temperatures in terms of variance and standard deviation, the 1:1 association model of eq 1 appears to be an oversimplification.

Having dissected our own data, we can now look briefly at the work of others. The chemical shift of chloroform (or any proton donor) at the limit of pure liquid base, $\delta_A(B)$, is sometimes regarded as specially significant. In fact, the practice of characterizing $\delta_A(B)$ as an index of the base strength is fallacious. This shift usually falls somewhere between δ_A and δ_C, unless other complications such as multiple equilib-

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(17) $\sigma \equiv (\text{variance})^{1/2} \equiv [(\delta - \delta_{\text{calcd}})^2/N]^{1/2}$.

(18) (a) R. Kaiser, *Can. J. Chem.*, **41**, 430 (1963); (b) K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, **18**, 329 (1962); (c) E. R. Kearns, *J. Phys. Chem.*, **65**, 314 (1961); (d) M. L. McGlashan and R. P. Rastogi, *Trans. Faraday Soc.*, **54**, 496 (1958); (e) A. L. McClellan, S. W. Nicksic, and J. C. Guffy, *J. Mol. Spectrosc.*, **11**, 340 (1963); (f) T. F. Lin, S. D. Christian, and H. E. Affsprung, *J. Phys. Chem.*, **71**, 968 (1967); (g) J. D. Lambert, J. S. Clarke, J. F. Duke, C. L. Hicks, S. D. Lawrence, D. M. Morris, and M. G. T. Shone, *Proc. Roy. Soc., Ser. A*, **249**, 414 (1959).

(19) I. D. Kuntz, Jr., and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **89**, 6008 (1967).

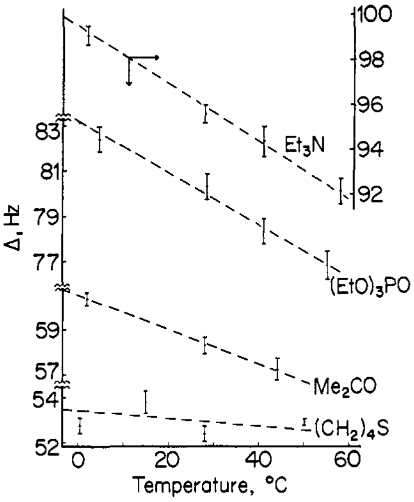

Figure 3. The temperature dependence of Δ for the hydrogen bonding of chloroform with proton acceptors in cyclohexane.

riums, anisotropy effects, etc., intrude, and bears no simple relation to K, which is the proper measure of base strength. In the same vein, we regard binary chloroform-base systems[3,4,18] as intrinsically defective and improper for equilibrium studies. Here the reference state is presumably pure chloroform, itself *ca.* 20% associated (see next section). With the addition of base, this figure for self-association would fall. The changes in δ in the important low base region would thus depend on two processes, eq 1 and 8.

Except for a few systems,[7,13,20,21] the s ranges of Table I are often narrow and unfavorable (<0.2).[7,22-26] According to Deranleau's criterion,[11] K's based on such data must be regarded as uncertain. Five of our systems are identical with those of Drago, *et al.*,[7] but the K's, Δ's, and $\Delta H°$'s are often quite different—compare Tables I and III. This is the sort of divergence which might make one despair of obtaining accurate thermodynamic data for weak associations. But because we took more data for each system, covered a wider range in s, and did not neglect the change in Δ with temperature (see below), we believe that our results are more precise than most of those previously obtained for chloroform by spectral methods analogous to ours.

Chloroform Self-Association and Related Matters. The values of the chemical shift of chloroform (δ_A) infinitely dilute in cyclohexane were required for eq 5 and 6 at several temperatures. First, δ was determined for chloroform at 12 concentrations (0.1176–11.7103 M) and best fit to a polynomial, quadratic in M, with $\sigma < 0.01$ Hz.[14] The values in hertz of δ_A (temperature, °C; number of concentrations) are: 339.10 (6°, 12); 338.92 (7°, 12); 338.69 (14°, 6); 338.66 (28°, 33); 338.41 (42°, 6); 338.42 (46°, 6); and 338.43 (59°, 6). δ_A, downfield from cyclohexane internal lock, varied with temperature (t) to eq 11. That the change is real

$$\delta_A = (339.12 \pm 0.10) - (0.020 \pm 0.007)t + (0.000116 \pm 0.00011)t^2 \quad (11)$$

is supported by the observation that the chemical shift of TMS was essentially constant when referenced to cyclohexane in some of these solutions.

Since a computer program was available,[2] we also evaluated the self-association equilibrium constants of chloroform from the dilution shift data at six concentrations (0.2–10 M). Our values of K, 0.0114 ± 0.003 at 12° and 0.0126 ± 0.0015 M^{-1} at 28°, are in the range of those previously reported, 0.017 M^{-1} and 0.13 or 0.16 mF^{-1} at 25°.[18,25] It should be noted that although we have covered the accessible concentration range—neat chloroform is ~12 M—our saturation factor s = 0.01–0.17. As has been pointed out, such s values are virtually incompatible with the generation of accurate K's and the agreement among all the values to within ~30% must be regarded as satisfactory.

The question of whether the self-association of chloroform competes with the base–chloroform association can now be answered. Since $[B]_0 > [CHCl_3]_0 \simeq 0.1$ M and $K_{AB}/K_{AA} > 25$, chloroform is not diverted into process 8, and self-association introduces no significant errors into the evaluation of K_{AB} for process 1.

The Temperature Dependence of Δ or $\delta_C - \delta_A$. Early in our study, it became apparent that there was a regular fall-off in Δ with increasing temperature. Typical temperature dependencies of Δ are shown in Figure 3; the average slope of such plots for our 12 donors is −0.06 Hz/°C. This phenomenon has been observed for several systems,[2,13,24] but has been missed or ignored in many more.[7,22,23,25] In "strong" hydrogen-bonding systems, *e.g.*, O—H···O or N—H···N, which have received much attention, the most pressing problem is often one of definition: is the complex 1:1, 1:2, etc., or are several complexes present?[3] In "weak" hydrogen-bonding systems, the scatter in the data, anisotropy corrections, or the narrow saturation factor may permit an accommodation in eq 3 of a "constant" Δ and a temperature dependent K.[2] The use of approximations to eq 5 could, of course, obscure any trends, which may in fact be of the same order as the uncertainties in Δ.

A model of 1:1 complexes which has the correct temperature dependence has been given by Muller and Reiter.[27] Consider the stretching vibrational mode of the hydrogen bond. For $Cl_3CH \cdots B$, $\nu_{HB} \simeq 150$ cm^{-1}.[7,28] Using the Maxwell–Boltzman distribution law, one can estimate that *ca.* 65 and 50% of the molecules are in ground state at 200 and 300°K, respectively.[29] Moreover, for hydrogen-bonded complexes whose $-\Delta H° \simeq$ 1–4 kcal/mol, a shallow, anharmonic potential seems appropriate to ν_{HB}. Therefore, relatively large changes in the mean distance r_{HB} with temperature may be expected—see Figure 4. Indeed, at the higher temperatures, the hydrogen bond becomes more elongated and the magnetic environment of the proton approaches that of uncomplexed chloroform; that is, $\delta_C \rightarrow \delta_A$ or Δ decreases as T increases. This is what we found (Figure 4).

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Based on this model and Figure 4, we would expect Δ to increase in a series of complexes, as the anharmonic character of the hydrogen bonding vibration increased, at constant $\Delta H°$ and ν_{HB}. This constraint is essential, for the anharmonicity may very well increase as ΔH or $\nu_{\mathrm{HB}} \rightarrow 0$, but at the limit, there is no complex, $\delta_{\mathrm{C}} \rightarrow \delta_{\mathrm{A}}$, and $\Delta \rightarrow 0$. Given a suitable description of the hydrogen bond, *e.g.*, a Morse potential function which does, in fact, involve $\Delta H°$ and ν_{HB},[29] we could begin to relate Δ to r_{HB}. It does not seem safe, however, to make predictions about Δ based simply on $\Delta H°$ or ν_{HB}.

There is a practical consequence of our knowing the temperature dependence of δ_{C}. Most workers in this field proceed as we have, that is, δ is measured for several concentrations at several temperatures, the *K*'s are evaluated, and then $\Delta H°$ and $\Delta S°$ are found. Assuming δ_{A} and δ_{C} are linear in the temperature *T*, one can combine these with eq 5 and 7 and obtain a master chemical shift relation.

$$\delta = \mathrm{f}(A, B, T) \qquad (12)$$

A computer fit to eq 12 would yield $\Delta H°$ and $\Delta S°$, as well as the slopes and intercepts ($\delta_{\mathrm{A}}°$ and $\delta_{\mathrm{C}}°$) of the equations of δ_{A} and δ_{C}. Sections through this hypersurface at constant concentration lead to simplified relations from which $\Delta H°$ can be estimated rather simply.[3,19]

It is possible, of course, to take δ at any well-spaced instead of fixed temperatures, and in some circumstances this may be more efficient. Now, if one has decided to measure δ of 100 solutions, the strategy of 20 concentrations at 5 temperatures is weaker than 10 concentrations at 10 temperatures, since the errors should be minimized in the latter case. Apart from covering the widest possible range in *T*, there would be no special reason to use or repeat any one *T* value. In this situation, eq 12 would be appropriate for treating such data.

The Drago Relation. A quantitative treatment which is intended to encompass all donor–acceptor interactions in "inert" solvents is given by eq 13.[7,30] Once

$$-\Delta H° = E_{\mathrm{A}}E_{\mathrm{B}} + C_{\mathrm{A}}C_{\mathrm{B}} \qquad (13)$$

the E_{A} and C_{A} parameters are defined for a pair of acids, *e.g.*, iodine and phenol, other *E* and *C* values for bases and then acids are obtained from experimentally observed $\Delta H°$ values. Such a collection of acid and base parameters can be combined to give estimated or predicted values of $\Delta H°$ for any acid–base pair in the set. Clearly, eq 13 merits independent testing.

We have been forcibly impressed with the desirability of a statistical approach to the determination of *E* and *C* parameters. First, there are generally rather large uncertainties or differences in experimentally determined enthalpies. For example, for the dimerization of triethylamine and chloroform in cyclohexane, we observe an enthalpy of -4.05 ± 0.03 kcal/mol; other values of $-\Delta H°$ are 4.15 ± 0.2[13] and 4.8.[7] Similarly, for ethyl acetate–chloroform in cyclohexane, we find $-\Delta H° = 2.51 \pm 0.10$ compared to a reported 3.8 kcal/mol.[7] Certain other systems have far greater scatter.

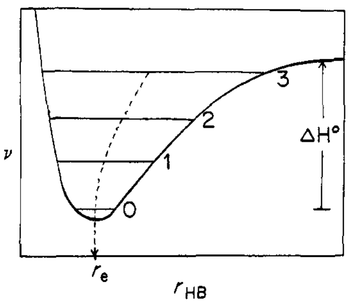
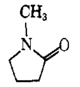


Figure 4. Schematic potential for the stretching vibration $\gamma(\mathrm{B}\cdots\mathrm{HCCl_3})$.

These discrepancies and uncertainties in $\Delta H°$ make for uncertainties in *E* and *C*. For example, early "tentative" values for $\mathrm{CHCl_3}$ were $E_{\mathrm{A}} = 5.11$ and $C_{\mathrm{A}} = 0.10$; for $\mathrm{Et_3N}$, $E_{\mathrm{B}} = 0.65$ and $C_{\mathrm{B}} = 11.35$.[30] The most recent set of $\mathrm{CHCl_3}$ parameters is $E_{\mathrm{A}} = 3.3$ and $C_{\mathrm{A}} = 0.13$,[7] in good agreement with our values. Using the old parameters for $\mathrm{CHCl_3}$ and each of three successive sets of $\mathrm{Et_3N}$ parameters, one calculates $-\Delta H° =$ 4.5, 6.0, or 3.5 kcal/mol; using the new $\mathrm{CHCl_3}$ parameters, 3.6, 4.6, or 3.0 kcal/mol.

To obtain the chloroform parameters we used $\Delta H°$ values for 11 of our bases and their reported E_{B} and C_{B} values (Table V). The weights we assigned to these values reflect our judgment on their reliability and are necessarily subjective. A least-squares treatment of eq 13, both with weighted and unweighted data, yields two straight lines.[1b] Our estimated best values span the region between the lines: $E_{\mathrm{A}} = 3.35 \pm 0.20$; $C_{\mathrm{A}} = 0.11 \pm 0.03$. Drago, *et al.*, give $E_{\mathrm{A}} = 3.24$ or 3.33 and $C_{\mathrm{A}} = 0.145$ or 0.158,[7] values which, in general, derive from bases different from ours.

Table V. Parameters for Determination of Chloroform E_{A} and C_{A} Parameters

Compound	Weight	$-\Delta H_{\mathrm{exptl}}$,[a] kcal/mol	E_{B}[b]	C_{B}[b]
$\mathrm{(CH_2)_4O}$	6.25	3.70[c]	0.973	4.36
$\mathrm{(CH_2)_4S}$	25.0	2.30[c]	0.375	7.96
$\mathrm{(C_2H_5)_2S}$	1.0	1.70	0.380	7.40
Dioxane	1.0	2.50[d]	0.68	2.82
$\mathrm{(C_2H_5)_3N}$	1.0	4.10[c,d]	0.95	11.09
$\mathrm{(CH_3)_2CO}$	0.3	2.50[d]	0.706	0.66
$\mathrm{CH_3CO_2C_2H_5}$	0.05	2.60[d]	0.639	2.42
$(n\text{-}\mathrm{Bu})_2\mathrm{O}$	0.001	2.35[d]	0.7	3.0[f]
$\mathrm{(C_2H_5O)_3}$-	0.005	3.81[e]	1.0	2.0[f]
$\mathrm{(CH_2)_5CO}$	0.01	2.44	0.71	0.66[f]
	0.001	3.99	1.0	3.0[f]

[a] This study, generally, and others as indicated. [b] These parameters have sometimes undergone revision. See ref 30. [c] Reference 13. [d] Table I. [e] See Table I for $(n\text{-}\mathrm{C_4H_9O})_3\mathrm{PO}$. [f] Estimated by analogy with similar compounds, *e.g.*, ether, trimethyl phosphate, acetone, and dimethylformamide, ref 30.

This agreement notwithstanding, we must emphasize two points. Reliable data coupled with a statistical approach are needed to test the scope and limitations of eq 12. To the extent that it does apply, it should be practically useful, *e.g.*, to store and predict $\Delta H°$ values. To the extent that it does or does not apply, it should be theoretically interesting, *e.g.*, in acid–base theory, as a probe for solvation effects, multiple equilibriums, etc.[7,30]

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