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Thermodynamics of Molecular Association. 9. An NMR Study of Hydrogen Bonding of $CHCl_3$ and $CHBr_3$ to Di-*n*-octyl Ether, Di-*n*-octyl Thioether, and Di-*n*-octylmethylamine

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Abstract: Nuclear magnetic resonance studies in the temperature range 10 to 40 °C are reported for the hydrogen bonding between the electron acceptors and donors of the title, all in cyclohexane solution. Data on the variation of the chemical shifts of the haloform C–H proton as a function of donor concentration are treated by the Foster–Fyfe procedure which permits direct determination of the equilibrium constants, K, for 1:1 hydrogen-bonded complex formation. The results are discussed in terms of Deranleau's criteria for reliability of the results and proof of fit of the proposed model. Enthalpies and entropies of hydrogen bonding are determined from the variation of ln K with temperature. The thermodynamic constants so obtained and thermodynamic data previously determined by gas–liquid chromatography are used to evaluate thermodynamic parameters related to halogen/n-donor interaction. Consistent with other evidence and a polarization experiment reported here, the latter interactions are taken to involve negligible complex formation. The enthalpies of halogen/n-donor interaction are found to follow the trends $CHBr_3 > CHCl_3$ and $N > S > O$. The enthalpies of hydrogen bonding, which follow the trends $CHCl_3 > CHBr_3$ and $N > O > S$, are analyzed in terms of the double-scale equation of Drago.

In parts 2[1] and 4[2] of this series we presented thermodynamic data (termed equilibrium constants, enthalpies, and entropies of "complex formation") from gas-liquid chromatography (GLC) for the interaction of $CHCl_3$, $CHBr_3$, and other haloalkane acceptors with four n-electron donors: di-*n*-octyl ether (DOE), di-*n*-octyl thioether (DOTE), di-*n*-octylmethylamine (DOMA), and tri-*n*-hexylamine (THA). Analysis of the results obtained strongly indicated the presence of two types of interactions within these systems: (1) hydrogen bonding of the C–H hydrogen of the haloalkane to the n-donor atom, (2) charge transfer ($n \rightarrow \sigma^*$ type) and/or electrostatic interaction between the n-donor and halogen atoms.

It has been pointed out[1] that thermodynamic measurements *alone* cannot serve to establish the existence of molecular complexes. Moreover, it has been shown recently[3] that the generally accepted GLC methods for obtaining "association constants" yield, in fact, a quantity which is the sum of the equilibrium constant (K_t) for all 1:1 complex formation and a term (α) which reflects any noncomplexing acceptor–donor interactions present in the system, i.e., "K_{GLC}" $= K_t + \alpha$. Hence, given the overwhelming spectroscopic evidence[1] that haloalkanes (such as $CHCl_3$ and $CHBr_3$) do indeed form hydrogen-bonded complexes with n-donors, we were left with two *simple* interpretations of the "K_{GLC}" data: (1) "K_{GLC}" $= (K + K')$, where K and K' are the 1:1 association constants for hydrogen-bonded and halogen-bonded complex formation, respectively, or (2) "K_{GLC}" $= (K + \alpha)$, where α is a measure of noncomplexing halogen/n-donor interaction or contact pairing.[3,4] For lack of any conclusive evidence, one way or the other (see below), we arbitrarily chose the former description. Nevertheless, the qualitative discussion of the "K_{GLC}" and concomitant enthalpy (which reflects a weighted average of all pairwise interactions) presented in parts 2 and 4 turns out to be equally valid for either description.

The nature of halogen/n-donor interactions in these systems, however, is an unsettled matter.[1,2] Charge-transfer bands (attributed to $n \rightarrow \sigma^*$ transitions) have been found in the ultraviolet region for several tetrahalomethane/amine systems,[5,6] but the reliability of the derived K values ($K < 0.1$ l. mol^{-1} for $FCCl_3$, $ClCCl_3$, and $BrCCl_3$ with triethylamine,[5] and $K \approx 0.03$ l. mol^{-1} for CCl_4/*n*-butylamine[6]) is open to question.[6-8] Values this small indicate little or no complex formation and can hardly account for the "K_{GLC}" values and trends observed in parts 2 and 4. Also, no charge-transfer bands have been reported[1] or found in our laboratory for mixtures of CBr_4 or CCl_4 and ether or thioether donors. Hence, while much thermodynamic, spectroscopic, and structural evidence[1] exists for strong halogen/n-donor interactions, it is not clear whether substantial complex formation is involved, or whether charge-transfer interactions play an important role. With respect to the latter point, it should be emphasized that the mere appearance of a charge-transfer band is neither conclusive proof for the existence of complexes, nor proof that charge-transfer interactions (rather than electrostatic interactions) are predominant.[1]

Ideally, then, one would want to conduct studies that would permit partitioning of "K_{GLC}" into its constituent parts, and perhaps shed some light on whether the aforementioned halogen interactions are better described in terms of complex formation or contact pairing. Of the variety of spectroscopic techniques employed in the study of hydrogen bonding, nuclear magnetic resonance (NMR) has proven to be one of the most sensitive and reliable, especially in the study of relatively weakly bonded systems such as those involving the C-H hydrogen. However, only a few of the studies that have been carried out have been quantitative from a thermodynamic point of view,[1] most of them have been on chloroform only,[1,9] and only one of them on any of the n-electron donors studied by GLC.

Accordingly, the proton NMR technique is utilized here to obtain additional thermodynamic data on two of the haloforms previously studied by GLC, viz., chloroform and bromoform, with three n-electron donors: DOE, DOTE, and DOMA. Our expectation is that these data should relate directly to the hydrogen-bonding propensities of the haloforms to the various n-donors and hence (when combined with the GLC data) afford a method of estimating the contribution of halogen/n-donor interactions. This expectation is based on our current view that the latter interactions probably involve negligible complex formation.[3]

Thermodynamic Association Parameters from NMR

The equations presented below have been derived and discussed elsewhere.[3] They are essentially based on an extension to NMR measurements of the Orgel-Mulliken[4] treatment and interpretation of ultraviolet/visible measurements on supposed complexing systems.

Consider a mixture of electron donor (D) and inert solvent (S) of concentration C_D, to which is added a small amount of electron acceptor (A), where the condition $C_D \gg C_A$ obtains. Utilizing the molar concentration scale, an equilibrium or association constant (K) for the reaction $A + D \rightleftarrows AD$ (1:1 complex) may be written

$$K = \frac{C_{AD}}{C_A C_D} \frac{\gamma_{AD}}{\gamma_A \gamma_D} \tag{1}$$

where C_i and γ_i represent respectively the equilibrium concentration and activity coefficient of component i, and where $\gamma_i \rightarrow 1$ as $C_i \rightarrow 0$. Given the dilute solution condition of A, and lacking any other information, it is assumed that $\gamma_{AD}/\gamma_A \approx 1$. Also, while recognizing that, in general, it is often not valid to neglect donor nonideality,[3,10] it is assumed (and later justified) that $\gamma_D \approx 1$. Hence, the equilibrium constant is taken to be approximately equal to the equilibrium quotient $C_{AD}/C_A C_D$. Finally, it is assumed that all acceptor-donor reactions or interactions are rapid compared with the NMR time scale.

For the systems considered here, we shall allow for two possible, simple interpretations of the observed proton chemical shift of A (δ) at concentration C_D.

(1) δ is the concentration-weighted average of the chemical shifts corresponding to: (a) free A molecules, as in pure S (δ_A); (b) A molecules perturbed by 1:1 hydrogen-bonded complex formation with D (δ_{AD}); (c) A molecules perturbed by 1:1 halogen-bonded complex formation with D (δ_{AD}'). The resulting equations are[3]

$$\frac{\Delta}{C_D} = -(K + K')\Delta + (K + K')\Delta_C \tag{2}$$

$$\Delta_C = \frac{K\Delta_{AD} + K'\Delta_{AD}'}{K + K'} \tag{3}$$

where $\Delta = (\delta - \delta_A)$, $\Delta_{AD} = (\delta_{AD} - \delta_A)$, $\Delta_{AD}' = (\delta_{AD}' - \delta_A)$, and where K and K' are the equilibrium constants for hydrogen and halogen bonding, respectively.

(2) δ is the weighted average of the proton chemical shifts corresponding to: (a) free and unperturbed A molecules, as in pure S(δ_A); (b) A molecules perturbed by 1:1 hydrogen-bonded complex formation with D (δ_{AD}); (c) A molecules perturbed by noncomplexing interactions or contact pairing between the halogen atoms of A and D ($\delta_{A\text{-}D}$). The resulting equations are then:[3]

$$\Delta/C_D = -K\Delta + K\Delta_C \tag{4}$$

$$\Delta_C = (K\Delta_{AD} + \alpha\Delta_{A\text{-}D})/K \tag{5}$$

where Δ, Δ_{AD}, and K are as defined above, $\Delta_{A\text{-}D} = (\delta_{A\text{-}D} - \delta_A)$, and where the thermodynamic parameter α (the nature of which is described elsewhere[3]) has been defined previously.

Equations 2 and 4 are in the preferable[8] Foster-Fyfe[11] form. Thus, for a series of solutions in which C_D is varied, a plot of Δ/C_D against Δ should be linear with $(K + K')$ (eq 2) or K (eq 4) being obtained directly as the negative gradient without recourse to an extrapolation. The value of Δ_C, which is concentration independent, may be obtained from the intercept with the ordinate which involves extrapolation to an infinitely dilute solution.

The "K_{GLC}" represent values corrected for minor donor nonideality.[1,2] Thus, if the model leading to eq 2 is applicable, one should find that "K_{GLC}" = $(K + K')$, i.e., that the negative gradient should be equal to the GLC "association constant". Furthermore, if the temperature dependence of K is sufficiently different from that of K', then, according to eq 3, one should find Δ_C to have a significant temperature dependence,[3] even if $\Delta_{AD}' \approx 0$. On the other hand, if eq 4 is applicable, the negative gradient should be less than "K_{GLC}", i.e., "K_{GLC}" > K and "K_{GLC}" = $(K + \alpha)$. Also, from eq 5, if the temperature dependence of K is sufficiently different from that of α, then Δ_C should, in general, have a significant temperature dependence. However, for the case $\Delta_{A\text{-}D} \approx 0$, Δ_C should be virtually temperature independent, assuming, of course, that Δ_{AD} is relatively temperature independent.

Experimental Section

Materials. Reagent grade chloroform was washed with concentrated sulfuric acid, dilute sodium hydroxide, and water, until the washing was neutral. The chloroform was then dried over anhydrous potassium carbonate and distilled immediately before use (bp 61.0 °C). Bromoform (bp 149.5 °C) was purified by the same procedure used for chloroform. The purification procedure for carbon tetrabromide (used in a polarization experiment; see later) is described elsewhere.[12] Cyclohexane (the inert solvent) was Fisher Spectroanalyzed reagent liquid and was used without further purification. The purification of the n-electron donors, di-*n*-octyl ether, di-*n*-octyl thioether, and di-*n*-octylmethylamine, is described elsewhere.[1,2] The concentrations of the *pure* donors at 30 °C are: 3.299 (DOE), 3.238 (DOTE), and 3.096 (DOMA), all in mol $l.^{-1}$ (M).

Preparation of Samples. In our experiments the haloform concentration was kept constant at 0.05 M, while the concentrations of the electron donors were kept in large excess and were varied from about 0.5 to 2.1 M in five well-spaced concentrations. Solutions were made up at room temperature by weighing the requisite amount of electron donor in 10-ml volumetric flasks, adding 1 ml of a freshly prepared haloform stock solution (0.5 M in cyclohexane), and enough cyclohexane to reach the 10 ml mark. Samples were transferred to 5-mm o.d. precision NMR tubes. For all samples, the tubes were filled to a height of at least 7 cm, sealed, and kept in the dark. The molarity of the solutions, at temperatures other than room temperature, was calculated from the change in density with temperature of cyclohexane and the respective electron donors.[1,2]

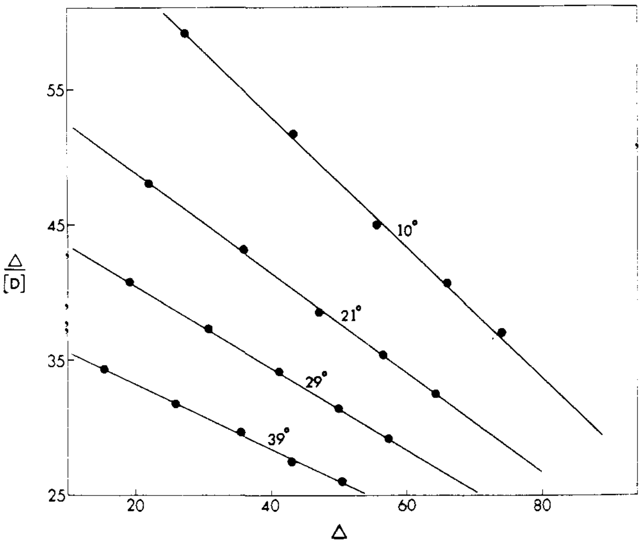

Figure 1. $CHCl_3$/DOMA: Linear plots of $\Delta/[D]$ vs. Δ at four temperatures, where $[D] = C_D$. Negative of the slope equals K (see eq 4).

NMR Measurements. Proton NMR spectra were obtained at four temperatures with a Bruker HFX-90 high-resolution spectrometer operating at 90 MHz, in conjunction with a Bruker B-ST 100/700 variable temperature probe. Temperature measurements were carried out using a calibration curve involving the temperature dependence of the separation of the hydroxyl and methyl peaks of methanol.[13] This method, which permits measurements to tenths of a degree, was employed several times during a set of runs. The temperature was observed to vary not more than ±0.5 °C, although it is possible that there may have existed a constant difference between the temperature observed with methanol and that existing in a given type of sample. Thermal equilibrium was attained by allowing 15 min before making measurements after insertion of a sample tube into the probe.

Chemical shifts of the C–H signal in the haloform were measured by carrying out a frequency sweep with respect to cyclohexane used as an internal lock and are quoted as Hertz (Hz). The spectra were recorded at a sweep rate of 0.12 Hz/s. All signals are downfield from the cyclohexane reference. The precise frequencies were measured by means of a Hewlett-Packard HP 5216A 12.5 MHz electronic counter. Frequency sweeps were carried out in triplicate on all samples, and, in general, the results indicated that the precision of the measurements was about ±0.1 Hz.

Results

In order to apply either eq 2 or 4 the concentration of one component of the complex must be small compared with the second component. In this respect a concentration of 0.05 M was chosen for both chloroform and bromoform, which is adequate to ensure a good signal-to-noise ratio while being low enough to satisfy eq 2 or 4 and also to ensure that no significant dimerization of the haloform occurs.[9] In the absence of donor, the chemical shifts of chloroform and bromoform (with respect to cyclohexane) were found to be constant at 508.4 and 473.0 Hz, respectively, over the temperature range 10–40 °C. These frequencies were therefore taken to be δ_A, the chemical shifts of the free and unperturbed monomer.

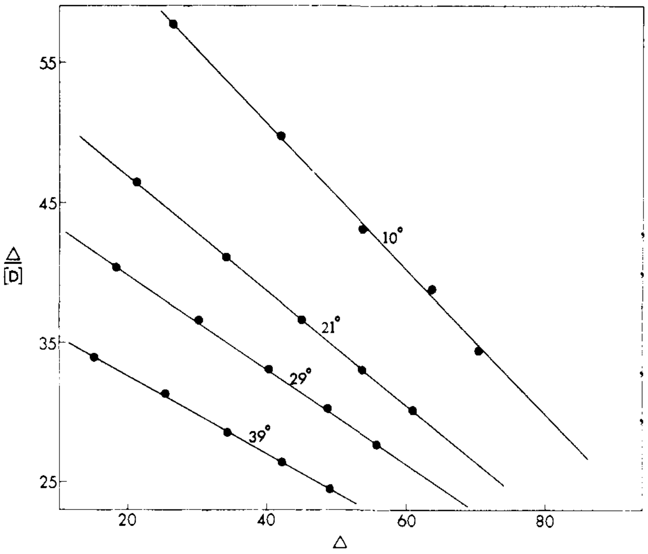

Figure 2. $CHBr_3$/DOMA: Linear plots of $\Delta/[D]$ vs. Δ at four temperatures, where $[D] = C_D$. Negative of the slope equals K (see eq 4).

Table I. Equilibrium Constants K (l. mol^{-1}) of Hydrogen Bonding

System	10 °C	21 °C	28 °C	39 °C
$CHCl_3$/DOE	0.398	0.321	0.285	0.226
$CHBr_3$/DOE	0.324	0.279	0.253	0.212
$CHCl_3$/DOTE	0.358	0.321	0.285	0.252
$CHBr_3$/DOTE	0.381	0.326	0.309	0.282
			29 °C	
$CHCl_3$/DOMA	0.478	0.371	0.301	0.242
$CHBr_3$/DOMA	0.523	0.412	0.339	0.282

Table II. Enthalpies (kcal mol^{-1}) and Entropies (cal mol^{-1} deg^{-1}) of Hydrogen Bonding

System	$-\Delta H$	$-\Delta S$	Δ_C, Hz
$CHCl_3$/DOE	3.40 ± 0.09	13.8 ± 0.3	83 ± 2
$CHBr_3$/DOE	2.56 ± 0.10	11.2 ± 0.3	81 ± 1
$CHCl_3$/DOTE	2.17 ± 0.12	9.7 ± 0.4	77 ± 1
$CHBr_3$/DOTE	1.80 ± 0.12	8.3 ± 0.4	65 ± 1
$CHCl_3$/DOMA	4.16 ± 0.07	16.1 ± 0.2	153 ± 2
$CHBr_3$/DOMA	3.77 ± 0.07	14.6 ± 0.2	136 ± 2

System	$-\Delta H$	System	$-\Delta H$
$CHCl_3$/n-$(C_4H_9)_2O$[a]	2.35 ± 0.12	$CHCl_3$/$(C_2H_5)_2S$[c]	2.2 ± 0.3
$CHCl_3$/tetrahydrofuran[b]	3.6 ± 0.4	$CHCl_3$/$(C_2H_5)_3N$[a]	4.05 ± 0.03
$CHBr_3$/tetrahydrofuran[b]	2.6 ± 0.2	$CHCl_3$/$(C_2H_5)_3N$[d]	4.2 ± 0.2
$CHCl_3$/$(C_2H_5)_2S$[a]	1.70 ± 0.02		

[a] Reference 9. [b] C. J. Creswell and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1723 (1963). [c] K. W. Jolley, L. M. Hughes, and I. D. Watson, *Aust. J. Chem.*, **27**, 287 (1974). [d] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).

Typical plots of Δ/C_D against Δ for the complexes of DOMA with chloroform and bromoform are shown in Figures 1 and 2. Values for the negative gradient were determined by means of linear least-squares analysis and are summarized for all systems at four temperatures in Table I. Since these values are clearly smaller than the corresponding "K_{GLC}"[1,2] (see later), we shall commence to assume that they correspond to K values for 1:1 hydrogen-bonded complex formation, i.e., that eq 4 and 5 apply. The standard deviations in K range from 0.002 to 0.009, with a typical value being 0.005. Values of the enthalpy (ΔH) and entropy (ΔS) of hydrogen-bond formation were obtained by linear least-squares analysis of ln K as a function of T^{-1} according to the usual expression

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

The values of ΔH and ΔS and the corresponding standard deviations are listed in Table II, along with enthalpy data determined by others for similar systems using NMR. With two

Table III. Saturation Fraction Range[a,b]

System	10 °C	39 °C
$CHCl_3$/DOE	0.17-0.46 (0.57)	0.10-0.32 (0.42)
$CHBr_3$/DOE	0.17-0.41 (0.52)	0.12-0.31 (0.41)
$CHCl_3$/DOTE	0.15-0.43 (0.54)	0.11-0.34 (0.45)
$CHBr_3$/DOTE	0.16-0.45 (0.56)	0.12-0.37 (0.48)
$CHCl_3$/DOMA	0.18-0.49 (0.60)	0.10-0.32 (0.43)
$CHBr_3$/DOMA	0.19-0.52 (0.62)	0.11-0.36 (0.46)

[a] See eq 7. [b] Values in parentheses are the maximum attainable saturation fractions, i.e., pure donor values. (Pure donor concentrations are listed in ref 1 and 2.)

exceptions, the agreement is reasonably good. Included in Table II are the mean values of Δ_C calculated at each temperature from the intercept with the ordinate of eq 4. No systematic variation of Δ_C with temperature was observed.

Discussion

Deranleau[8] has shown that equilibrium constants are most reliable when they are based on spectral data covering as much as possible of the saturation fraction range $s = 0.2$-0.8, where

$$s \equiv \frac{\Delta}{\Delta_C} = \frac{KC_D}{1 + KC_D} \tag{7}$$

s being the saturation fraction of the dilute component (A). Moreover, high uncertainty and little information result when $s < 0.1$. Summarized in Table III are the saturation fraction ranges at the lowest and highest temperature studied, where the values in parentheses represent the *maximum* attainable saturation fractions, i.e., the values corresponding to the use of pure donor. While $s \geq 0.1$ for all measurements, it is apparent that we did not and could not cover the recommended middle range. However, spot checks using 0.05 M solutions of $CHCl_3$ in pure donor revealed excellent accord with eq 4 and the results in Tables I (K), II (Δ_C) and III (maximum s).

The relatively small attainable saturation fraction range presents another potential problem apart from experimental error. Deranleau suggests[8] that roughly 75% of the saturation fraction range be covered for adequate proof of fit of a given stoichiometric model, the primary concern here being the possibility of AD_2 termolecular complexes, the substantial presence of which would produce curvature in the Δ/C_D vs. Δ plot over a wide enough C_D range. Although we have assumed that eq 4 rather than eq 2 applies, let us consider the possibility of AD_2 complexes involving simultaneous hydrogen bonding and halogen bonding to the same acceptor. It appears improbable that, once a 1:1 hydrogen-bonded complex has formed, a second donor molecule would be able to interact readily with the halogen atoms in view of the bulkiness of the alkyl side chains of the donors. Second, for the systems studied, over the concentration range studied, linear correlation coefficients in excess of 0.999 were found. Finally, in relation to the GLC experimental data, the question of AD_2 complexes has been dealt with in considerable detail.[3,14] Suffice it to state here that current evidence[14,15] (see later) points to the unlikelihood of AD_2 complexes for our six systems. Thus, we have carefully fit our NMR data over a reasonable concentration range to a specified model (i.e., allowing 1:1 complexes only), which we regard to be the most realistic model.

The validity of our assumption of donor ideality (i.e., $\gamma_D \approx 1$) merits discussion. In the GLC experiment *n*-octadecane (OD) was used as the inert solvent.[1,2,14] Experimental evidence[14,15] in the form of linearity of solute (A) partition coefficient vs. C_D plots over a very wide concentration range (including pure D) fully supports our previous estimates[1,2] that $\gamma_D \approx 1$ with OD as the solvent and DOE, DOTE, and DOMA as the electron donors. (It also supports our assumption that the concentration of AD_2 complexes is negligibly small.[3,14]) It might seem then, as it once did to us, that OD rather than cyclohexane should have been the inert solvent of choice for the NMR experiment. However, considerable line broadening (especially at low C_D) was found with OD (mp 28 °C), even for the strong singlet absorption of the haloforms. This may have been due to the relatively high viscosity of OD, compared to that of cyclohexane. Nevertheless, one set of experiments was conducted, with difficulty, on the system $CHCl_3$/DOE/OD at 30 °C. A K value of 0.27 ± 0.02 was obtained, in excellent agreement with the cyclohexane value of 0.285 ± 0.003 at 28 °C (Table I) and an interpolated value of 0.269 at 30 °C (Table IV), and in good agreement with 0.305 at 30 °C, the value determined for the system $CHCl_3$/DOE/*n*-heptadecane.[15] Thus, the evidence points to a rather small correction, if any, for donor nonideality when cyclohexane is used as the inert solvent.[3,10]

We have made and must examine the critical assumption that the NMR and GLC data are consistent with the model leading to eq 4 and 5, i.e., that "K_{GLC}" $= K + \alpha$, where K is the 1:1 equilibrium constant for hydrogen bonding and α is a measure of *noncomplexing* halogen/n-donor interactions. Listed in Table IV are the values for K and α at 10 °C intervals from 10 to 60 °C. They were calculated as follows. The "K_{GLC}"[1,2] (measured at 30, 40, 50, and 60 °C) were extrapolated to 10 and 20 °C by utilizing the linear least-squares fit of $\ln K_{GLC}$ as a function of T^{-1}. Similarly, the K values from NMR were interpolated or extrapolated through eq 6, utilizing the least-squares values of ΔH and ΔS (Table II). From the difference, α was calculated. Also, the values listed in Table V were determined from

$$\ln \alpha = \frac{-\Delta H_\alpha}{RT} + \frac{\Delta S_\alpha}{R} \tag{8}$$

where ΔH_α may be regarded as a measure of the strength of halogen/n-donor interactions.[11] (For a discussion of the physical significance of α-related quantities and an example of their theoretical interpretation, the reader is referred elsewhere.[3,4,11])

We note first that many of the α values are substantial and that, at a given temperature and for a given donor, the α values for $CHCl_3$ and $CHBr_3$ are clearly different. Thus, consistent with the experimental evidence cited previously, α can hardly be attributed to the use of different inert solvents in the NMR and GLC experiments, i.e., to the nonideality of donor/cyclohexane mixtures in the NMR experiment.[3,10] In relation to the observed temperature independence of Δ_C, given that the temperature dependencies of K (Table II) and α (Table V) are significantly different, we are lead by eq 5 to conclude that $\Delta_{A\text{-}D} \approx 0$, i.e., $\Delta_C \approx \Delta_{AD}$. This implies that the proton supposedly "perturbed" by halogen/n-donor interaction is magnetically equivalent to a "free" haloform proton, a not unreasonable implication considering the separation of the former proton from the interacting centers. It should also be noted that eq 3 cannot account for the observed temperature independence of Δ_C.

Additional corroborative evidence can be offered in defense of the aforementioned critical assumption that halogen/n-donor interactions result in negligible complex formation. First, spectrophotometric studies on tetrahalomethane/amine systems[5,6] indicate that, if complexes do indeed exist, the K values must be quite small (<0.1 l. mol^{-1}). Second, a polarization study conducted on the system CBr_4/DOMA at 20 °C revealed no evidence of significant complex formation. Dielectric constants and refractive indices were measured and analyzed using the Guggenheim-Smith[16,17] method as applied to the investigation of tetracyanoethylene/aromatic complexes[18] and CBr_4/aromatic interactions.[12] The apparatus and procedure used are described elsewhere.[12] The dipole moment of DOMA

Table IV. Values of K and α (l. mol^{-1}) from 10 to 60 °C

System	10 °C		20 °C		30 °C		40 °C		50 °C		60 °C	
	K	α	K	α	K	α	K	α	K	α	K	α
$CHCl_3$/DOE	0.398	0.136	0.327	0.131	0.269	0.127	0.225	0.123	0.190	0.119	0.162	0.116
$CHBr_3$/DOE	0.324	0.207	0.280	0.187	0.243	0.170	0.212	0.156	0.187	0.143	0.166	0.133
$CHCl_3$/DOTE	0.358	0.167	0.317	0.152	0.280	0.139	0.250	0.129	0.224	0.119	0.203	0.111
$CHBr_3$/DOTE	0.381	0.574	0.337	0.493	0.304	0.427	0.276	0.373	0.253	0.329	0.232	0.292
$CHCl_3$/DOMA	0.478	0.230	0.374	0.199	0.296	0.174	0.237	0.153	0.193	0.136	0.159	0.122
$CHBr_3$/DOMA	0.523	0.419	0.417	0.356	0.337	0.306	0.276	0.266	0.229	0.233	0.193	0.206

Table V. Enthalpies (kcal mol^{-1}) and Entropies (cal mol^{-1} deg^{-1}) of Halogen Interaction

System	$-\Delta H_\alpha$	$-\Delta S_\alpha$
$CHCl_3$/DOE	0.62	6.2
$CHBr_3$/DOE	1.68	9.1
$CHCl_3$/DOTE	1.53	9.0
$CHBr_3$/DOTE	2.53	10.0
$CHCl_3$/DOMA	2.39	11.3
$CHBr_3$/DOMA	2.67	11.2

in *n*-heptane (1.58 ± 0.03 D) was found to be essentially the same as that in a 0.3 M solution of CBr_4 in *n*-heptane (1.60 ± 0.02 D).

Examining the α values and the results in Table V in more detail, we note that the α and ΔH_α values are surprisingly large overall, especially in those systems involving the ether or thioether where there is no direct evidence of charge-transfer interaction. However, as discussed previously,[1] electrostatic interactions are probably an important contributive factor. It is evident that both enthalpic and entropic terms are affecting the magnitude of and trends in α. For example, the system $CHBr_3$/DOTE has a somewhat smaller ΔH_α than $CHBr_3$/DOMA, but has larger α values. Clearly, the smaller ΔS_α value for $CHBr_3$/DOTE (perhaps due to the greater accessibility of the sulfur atom) governs the trend in α. Given the combined experimental errors involved in their evaluation, the absolute values of ΔH_α cannot be regarded as accurate quantities. Nevertheless, the *trends* in ΔH_α are clear: $CHBr_3 > CHCl_3$ and DOMA > DOTE > DOE. This is significant and supportive of our model, in that thermodynamic, spectroscopic, and structural studies on haloalkane/n-donor systems[1] also indicate interaction strengths following the trends Br > Cl and N > S > O.

An implication of our model is that the lifetime of halogen/n-donor interactions is of the order of the duration of a molecular collision, i.e., that the A-D "contact pair" has no extended lifetime as a separate entity.[4] One might wonder, then, why it is that hydrogen-end collisions of the haloform with the n-donor lead to long-lived complexes, while halogen-end collisions apparently do not. This is particularly pertinent in view of the relative heats involved, the ranges being not terribly different: 1.8-4.2 kcal mol^{-1} for hydrogen bonding (Table II) and 0.6-2.7 kcal mol^{-1} for halogen interaction (Table V). In interpreting dielectric absorption measurements on CCl_4/aromatic systems, North and Parker[19] suggested that it is the slope of the repulsive part of the pair interaction potential that governs the lifetime of the encounter rather than the "strength" (ΔH) of the interaction, viz., the greater the slope, the more "elastic" the collision, and the shorter the lifetime. They also suggested that charge-transfer interaction should lower the slope. Rationalizing our model in these terms then, the (angle-dependent) pair potential for halogen-end/n-donor interaction should exhibit a steep repulsive slope, a not unreasonable possibility, considering the relative electronegativities of the halogen and n-donor atoms and the lack of any direct evidence for charge-transfer interaction with two of the donors. To shed additional light on the lifetimes of these collisions, dielectric absorption measurements[19] on A/D systems with A = $CHCl_3$, $CHBr_3$, CCl_4, and CBr_4 and D = ether, thioether, and tertiary amine would be of great use.

Turning to the hydrogen bonding data and regarding ΔH as the only meaningful measure of hydrogen bonding "strength",[20] we see from Table II that the donor strength follows the sequence N > O > S, while the acceptor strength is always in the order $CHCl_3 > CHBr_3$. These are the classical trends.[1] Thus, while it was difficult to discern definite trends in the weighted-average GLC enthalpies,[1,2] the "separated" enthalpies (ΔH and ΔH_α) show very clear and reasonable trends indeed. The above donor strength sequence was also found in a study of 18 aliphatic alcohol/n-donor systems,[21] where the enthalpies were correlated with some success through the single-scale expression

$$|\Delta H_{ij}| = Q_i^{a} Q_j^{b} \tag{9}$$

where Q_i^{a} is the enthalpy parameter for acid i and Q_j^{b} is the enthalpy parameter for base j, both referred to an assigned Q^b value of 1.00 for DOTE. Q^b values of 2.01 and 1.48 were found for DOMA and DOE, respectively.[21] Analyzing the data in Table II, we obtain acid parameters of 2.17 and 1.80 for $CHCl_3$ and $CHBr_3$, respectively, and base parameters of 2.00 and 1.50 for DOMA and DOE, respectively.

A more quantitative correlation of the enthalpy of hydrogen bonding is attainable through Drago's double-scale equation[21-23]

$$-\Delta H = E_A E_B + C_A C_B \tag{10}$$

where E_A and E_B were interpreted as the susceptibility of the acid and base, respectively, to undergo electrostatic interactions, and C_A and C_B as the susceptibility to undergo covalent interactions. Using the recommended procedure[23] and taking our previously estimated E_B and C_B values for DOE, DOTE, and DOMA[21] as initial trial values, a set of acid and base parameters was found which minimized the differences between the retrieved (through eq 10) and experimental (Table II here and Table V of ref 21) ΔH values. In all, 24 points were used to determine the 22 acid and base parameters listed in Table VI. With this set of parameters the retrieved and experimental values differed by an average of ±0.07 kcal mol^{-1} for all systems and ±0.09 kcal mol^{-1} for the haloform systems, of the order of experimental error. The parameters are in good agreement with those given for the bases di-*n*-butyl ether (C_B = 3.40, E_B = 1.06), diethyl thioether (C_B = 7.40, E_B = 0.34), and triethylamine (C_B = 11.09, E_B = 0.99), and the acid $CHCl_3$ (C_A = 0.159, E_A = 3.02).[23] It is particularly encouraging (and supportive of our model) that enthalpies of hydrogen bonding for aliphatic alcohol/n-donor systems from GLC[21] are compatible with NMR values for haloform/n-donor hydrogen bonding, and that both sets of data are compatible with the results of others.

We see from Table VI that, in terms of its hydrogen-bonding characteristics, chloroform is quite similar to isopropyl alcohol and is a "harder" acid than bromoform. The sequence of effective base "hardness", as measured by E_B/C_B,[22,23] is DOE

Table VI. Acid and Base Parameters for Double-Scale Equation of Enthalpy of Hydrogen Bonding[a]

	C_A	E_A
Acids[b]		
n-Propyl alcohol	0.183	2.96
Isopropyl alcohol	0.156	2.59
n-Butyl alcohol	0.234	2.72
Isobutyl alcohol	0.259	2.72
sec-Butyl alcohol	0.184	2.58
tert-Butyl alcohol	0.150	2.39
Chloroform	0.159	2.54
Bromoform	0.155	1.95
Bases[b]		
DOE	3.01	1.11
DOTE	7.71	0.34
DOMA	11.50	0.97

[a] See eq 10. [b] Alcohol and base values are revised values; see ref 21.

> DOMA > DOTE. Taken at face value, the results indicate that, for the two haloforms, electrostatic forces account for roughly 85% of the total hydrogen bonding energy with DOE, about 55% with DOMA, and about 40% with DOTE, in accordance with the above sequence. Also, although the absolute electrostatic contribution (E_AE_B) to $-\Delta H$ is greater for the DOE systems, the net $-\Delta H$ is greater for the DOMA systems, due to the substantial covalent parameter of the amine.

In summary, the simple model leading to eq 4 and 5, the NMR results for hydrogen bonding, auxiliary experimental information, and some useful concepts[3,4,19,22] have permitted us to further resolve and understand thermodynamic data previously determined by GLC for haloform/n-donor systems.[1,2] While the evidence at hand indicates that halogen/n-donor interactions do not result in significant complex formation, additional studies are needed to fully clarify the situation.

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^{13}C–^{1}H Coupling Constants in Carbocations. II.[1] Angular Dependence of $^{1}J_{CH}$ in Groups Adjacent to Cationic Carbons. A New Criterion for Interpreting NMR Spectra of Carbocations

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Abstract: The values of $^{1}J_{CH}$ in groups adjacent to cationic carbons in classical, static, carbenium ions are dependent upon the dihedral angle between the C–H bond and the unoccupied p orbital of the cationic carbon. This dependence is given by $\Delta J = A - B\cos^2\theta$, where ΔJ is the difference in J_{CH} between that in the cation and that in a neutral model compound (ketone), A is the maximum inductive enhancement of J_{CH} (22.5 Hz), and B is the maximum hyperconjugative diminution of J_{CH} (33.1 Hz). The equation provides another criterion by which chemical shift assignments may be made. In the case of the 2-methylnorbornyl cation, some discrepancies in the previous assignments have been corrected. Comparison of the shift of the methyl carbon of this cation with that in the corresponding alcohol shows that this carbon experiences *no deshielding* upon ion formation. The significance of this finding is discussed. The equation is applicable to some equilibrating classical cations, and can be used to determine conformations in cations, for example, the *tert*-amyl cation.

In our investigation of the applicability of J_{CH} as a criterion for the presence of σ bridging in cyclopropylcarbinyl cations,[1] it was necessary to determine the effect of the adjacent positive charge on the apical, methine coupling constant in classical (non-σ bridged) cyclopropylcarbinyl cations. Thus the $^{1}J_{CH}$ values increase in the tertiary cations **1** and **2**[3] from those in the neutral model compounds **4** and **5** by 25 and 22 Hz, respectively (ΔJ). The ketones are considered to be appropriate model compounds since they contain a trigonal carbon and are therefore more appropriate models than the corresponding hydrocarbons or carbinols.[1] A similar, large increase occurs for J_{C_1H} in the 2-methylnorbornyl cation **3**[4] from that in 2-