Anion–Molecule Complexes in Solution. I. Nuclear Magnetic Resonance and Infrared Studies of Halide Ion–Trihalomethane Association

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Abstract: In weakly solvating media, the trihalomethanes associate specifically with the anions of tetraalkylammonium salts. The concentration and temperature dependence of the trihalomethane proton shielding has been analyzed to yield shieldings in the complex, equilibrium constants, and thermodynamic parameters. The values of ΔH suggest that complex formation is a process of differential solvation. CHF_3, $CHCl_3$, and $CHBr_3$ are deshielded by 1–3 ppm in the complex; this and the infrared evidence indicate primarily hydrogen bonding to the ion. CHI_3, on the other hand, shows increased shielding in the complex, and infrared spectra suggest a polarization or charge-transfer interaction *via* the iodine atoms. Since the field strength of a monopolar ion is known, the value of the coefficient *a*, in the Buckingham–Musher equation, $\delta\sigma_E = a \times 10^{-12}E_z - b \times 10^{-18}E^2$, may be evaluated from the complex shifts; the commonly used value of $a = 3$ esu^{-1} appears to be a lower limit. Interpretation of the stabilities of the complexes in terms of an electrostatic model indicates that both hydrogen- and halogen-bond energies are dominated by the polarizability of the carbon–halogen bond in the molecule.

The usefulness of nmr and infrared spectroscopy in the detection of hydrogen bonding of trihalomethanes (haloforms) to various nitrogen and oxygen bases is well established.[1-6] H-Bond formation characteristically produces a decrease in shielding of the hydrogen nucleus[1] and in the C–H stretching frequency.[2] The hydrogen deshielding has been interpreted in terms of the interaction of the electrostatic field of the dipolar base with electrons in the vicinity of the hydrogen nucleus.

There is evidence that anions act as Lewis bases toward hydrogen-bonding molecules;[3] indeed, this interaction is considered to be dominant in the solvation of small anions[7] in protic solvents. This work was inspired by the discovery,[4] by nmr, of specific anion complexes to certain β-D-glucopyranose derivatives. We have observed deshielding of trihalomethane protons of magnitude up to 3 ppm, on addition of tetraalkylammonium halide salt to a dilute solution of the trihalomethane in an aprotic or weakly H-bonding solvent. In strongly H-bonding solvents, such as ethanol, no significant shifts are observed. In such solvents, the weakly H-bonding trihalomethanes fail to compete with the more strongly interacting solvent molecules.

We interpret the salt-concentration-dependent shifts as arising from specific interaction of the trihalomethane with the anion.[8] This is consistent with our observation that tetraalkylammonium salts of perchlorate ion, which has a low surface potential, *e*/*r*, and added neutral solutes of comparable molar volume, such as cyclohexane, have no significant effect on the trihalomethane spectrum.

The trihalomethane–halide interaction has been studied in two solvents, acetonitrile and tetrachloromethane. These were chosen for the following reasons: they afford adequate solubility; they do not hydrogen-bond significantly; acetonitrile is a representative highly polar solvent, whereas tetrachloromethane is nonpolar but highly polarizable.[9] To facilitate interpretation of the chemical shifts, conditions were chosen to favor 1:1 complex formation: the concentration of trihalomethane was kept as low as possible (*ca.* 0.1 *M*), and the proton shielding was observed as a function of halide ion concentration.

Experimental Section

Materials. Baker reagent grade acetonitrile was distilled two to five times under nitrogen, from P_2O_5 and Na_2CO_3 initially, and straight the final time. The middle cut collected had a boiling range of less than 1°. This material was stored in a drybox.

Shawinigan reagent grade tetrachloromethane was passed through a column of alumina (Activity Grade 1), made up to 2–10% in tetramethylsilane, and stored in a refrigerator. A separate check confirmed that results were unaffected by the exact concentration of tetramethylsilane in this solvent.

Tetramethylsilane from N.M.R. Specialties was refrigerated over 4A molecular sieves before using.

Shawinigan reagent grade trichloromethane was washed with distilled water to extract the ethanol preservative. The water and residual ethanol were then removed on an alumina column in the drybox. The effluent was stored in an opaque bottle.

Matheson Coleman and Bell tribromomethane as received was stabilized with diphenylamine. It was shaken with acetic acid and washed with distilled water; it was then put through a column of activated charcoal and into an opaque bottle, which was kept in the drybox. There, it was passed through an alumina column and stored in an opaque bottle.

British Drug House reagent grade triiodomethane was dissolved in acetone; the solution was mixed with activated charcoal and then filtered. Distilled water was added to precipitate the triiodomethane. The precipitate was filtered off and dried under vacuum in a desiccator over P_2O_5.

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[1] A. L. McClellan, S. W. Nicksic, and J. C. Guffy, *J. Mol. Spectrosc.*, **11**, 340 (1963).

[2] A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 1715 (1963).

[3] A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 1233 (1963).

[4] R. U. Lemieux, J. S. Martin, and J. I. Hayami, Preliminary Report, International Symposium on NMR, Tokyo, Sept 1965, No. M-2-17.

[5] B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectrosc.*, 10, 117 (1963); I. D. Kuntz Jr., and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **89**, 6008 (1967).

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[7] R. Alexander and A. J. Parker, *J. Amer. Chem. Soc.*, 89, 5549 (1967).

[8] J. B. Hyne, *ibid.*, **85**, 304 (1963).

[9] Landolt-Börnstein, "Zahlenwerten und Funktionen," Band I, Teil 3, Springer-Verlag, Berlin, 1951, pp 509–517.

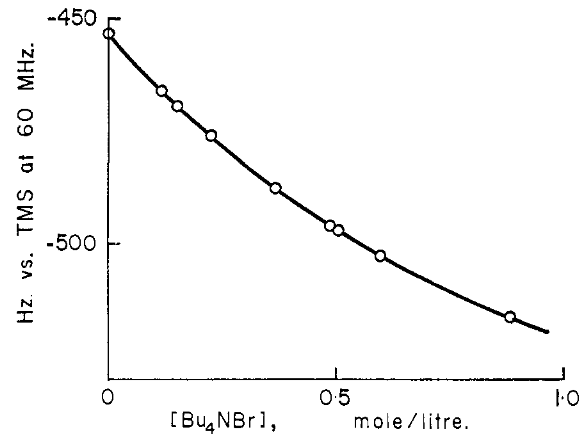

Figure 1. Proton shielding of 0.1 M trichloromethane in acetonitrile as a function of tetrabutylammonium bromide concentration.

Tetraalkylammonium Halide Salts. Tetraethylammonium chloride and bromide, tetrabutylammonium chloride, bromide, and iodide, and tetraheptylammonium bromide and iodide, all Eastman White Label material, were dried by pumping in a vacuum desiccator over P_2O_5 for several weeks.

Procedures. All samples were prepared inside a sealed drybox which was kept under a slight positive pressure of dry nitrogen. Volumetric tubes (2 ml) were weighed before and after solid materials (*e.g.*, salts and triiodomethane) were placed in them. Enough solvent was added to dissolve the solids; then the liquids were added using a 50-μl syringe (typical quantities were 17-20 μl). The solutions were then made up to the mark with solvent, thoroughly mixed, and *ca.* 0.5 ml transferred to nmr sample tubes fitted with auxiliary stopcocks to exclude air, connected to a vacuum rack, degassed by freezing and pumping, and sealed.

The concentrations of the solid materials were calculated from their weights and the volumes of the volumetric tubes. The concentrations of a number of trihalomethane samples were checked by integration *vs.* solvent ^{13}C satellite peaks and *vs.* salt peaks. The concentration was found to be reproducible, for $CHCl_3$ and $CHBr_3$, at 0.09 ± 0.01 M. This concentration is not critical.

The nmr spectra were obtained, for the most part, on a Varian HA-60 spectrometer, with a few on a Varian HA-100. The internal reference used for the lock signal was either tetramethylsilane (TMS) or solvent, although all measurements are ultimately referred to internal TMS; the line positions were measured by setting the sweep oscillator at the resonance and measuring the difference between its frequency and that of the lock-in oscillator.

Samples for infrared spectra were prepared as above, in a drybox, and transferred to matched infrared cells, of path length 0.5-1 mm. Cells were of NaCl, KBr, and CsCl.

Preliminary spectra were obtained on a Perkin-Elmer Model 337 spectrometer; some further spectra were run on a Perkin-Elmer Model 421, particularly in the range 625-200 cm^{-1}.

Analysis of Nmr Shielding *vs.* Concentration. Assuming only 1:1 complexes of donor (ion) and acceptor (trihalomethane) and ideal equilibrium behavior

$$D + A \rightleftarrows C \tag{1}$$

$$\frac{[C]}{[D][A]} = K \tag{2}$$

Nmr spectra of all systems studied showed only one sharp proton signal, whose position varied monotonically with the halide ion concentration (Figure 1). This indicates that the equilibrium is extremely rapid;[10] the observed shielding, σ, is a concentration-weighted average of its value in the free acceptor, σ_A, and in the complex, σ_C

$$\frac{(\sigma - \sigma_A)}{(\sigma_C - \sigma_A)} = \frac{\Delta}{\Delta_c} = \frac{[C]}{([C] + [A])} \tag{3}$$

Since these complexes are relatively weak, K being in the range 0.5-4 M^{-1}, it is impossible to obtain pure complex and thus to observed Δ_c directly. To deduce values of K and Δ_c, Scott's modification[11a] of the Benesi-Hildebrand method[11b] was used. Equations 2 and 3 may be readily combined to yield Scott's equation

$$\frac{[D]}{\Delta} = \frac{1}{K\Delta_c} + \frac{[D]}{\Delta_c} \tag{4}$$

A least-squares fit

$$y = b_1 + b_2 x \tag{5}$$

where $y = [D]/\Delta$, and $x = [D]$ yields

$$\Delta_c = 1/b_2 \tag{6}$$

$$K = b_2/b_1 \tag{7}$$

with standard deviations

$$(\delta\Delta_c)^2 = (\delta b_2)^2/b_2{}^4 \tag{8}$$

$$(\delta K)^2 = (\delta b_2)^2/b_1{}^2 + b_2{}^2(\delta b_1)^2/b_1{}^4 \tag{9}$$

δb_1 and δb_2 include an evaluation of contributions from the experimental uncertainty in Δ and [D]. This evaluation is described in the Appendix.

In practice, the free donor concentration, [D], is unknown; it differs from the total ion concentration by the complex concentration. Since the acceptor concentration has been kept small, the total initial salt concentration is a good first approximation to [D]. At each concentration, the derived values of Δ_c and K may be used to compute [C], and thus a better value of [D]. This may be used for a second Scott analysis, yielding better values of Δ_c and K, and so on to self-consistency. A FORTRAN IV computer program, SHEBA,[12] was written to do this.

Results

In Table I are the ambient-temperature (*ca.* 27°) values of Δ_c and K deduced for complexes of the four trihalomethanes with three halide ions (Cl^-, Br^-, and

Table I. Experimentally Determined Quantities for Trihalomethane-Base Complexes[a]

Acceptor (trihalomethane)	Donor (base)	Solvent	K, l. mole,$^{-1}$	Limiting shift, Δ_c, ppm
CHF_3	Cl^-	CCl_4	2.43 ± 0.13	−2.15 ± 0.06
	Br^-		1.38 ± 0.16	−2.17 ± 0.21
	I^- [b]		0.55 ± 0.30	−3.1 ± 1.7
$CHCl_3$	Cl^-	CCl_4	2.51 ± 0.17	−2.92 ± 0.12
	Br^-		1.78 ± 0.08	−2.51 ± 0.08
	I^- [b]		1.07 ± 0.43	−2.30 ± 0.90
$CHCl_3$	Cl^-	CH_3CN	1.18 ± 0.05	−3.08 ± 0.11
	Br^-		0.73 ± 0.09	−2.76 ± 0.33
	I^-		0.48 ± 0.05	−2.18 ± 0.22
$CHBr_3$	Cl^-	CCl_4	2.45 ± 0.16	−2.29 ± 0.10
	Br^-		1.86 ± 0.09	−1.82 ± 0.04
	I^- [b]		1.95 ± 0.45	−1.06 ± 0.22
$CHBr_3$	Cl^-	CH_3CN	1.10 ± 0.06	−2.34 ± 0.11
	Br^-		1.11 ± 0.20	−1.57 ± 0.24
	I^-		1.17 ± 0.09	−0.83 ± 0.05
CHI_3	Cl^-	CH_3CN	3.30 ± 0.25	+0.31 ± 0.01
	Br^-		3.76 ± 0.22	+0.32 ± 0.01
	I^-		3.56 ± 0.18	+0.36 ± 0.01
$CHCl_3$	Pyridine	CCl_4	0.38 ± 0.07	−1.07 ± 0.19
$CHBr_3$	Pyridine		0.34 ± 0.05	−1.16 ± 0.17
CHI_3	Pyridine		0.39 ± 0.07	−0.38 ± 0.06

[a] Salts were tetra(n-butyl)ammonium salts, except as noted. [b] Donor anion provided by tetra(n-heptyl)ammonium iodide.

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(10) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 12.

(11) (a) R. L. Scott, *Rec. Trav. Chim. Pays-Bas*, **75**, 787 (1956); (b) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

(12) SHEBA = $P_{34} \cdot P_{13} \cdot$ BHSEA (Benesi-Hildebrand-Scott equilibrium analysis). Listings of this program may be obtained from J. S. M.

I$^-$) in the solvents acetonitrile and tetrachloromethane. There are no entries in the table for triiodomethane in CCl_4, since it is sparingly soluble in this solvent. While complexes of trifluoromethane form in acetonitrile, the variation of shift with ion concentration in these systems was so slight that a meaningful analysis of the data was not possible. It appears likely that the complex shifts are about the same as in tetrachloromethane, but that the equilibrium constants are extremely small. Except where otherwise noted, tetrabutylammonium halide salts were used. Table I also contains data for complexes of a nitrogen base, pyridine, with the trihalomethanes.

Our analysis was verified by observation of the infrared spectra of deuterated trihalomethanes in the same solvents. On addition of a tetraalkylammonium halide to a $CDCl_3$ or $CDBr_3$ solution, the characteristic "C–D H-bonded stretch band"[2,13] appeared at about 2170–2200 cm^{-1}. In every case, the intensity of this band was proportional to the concentration of complex as computed using the equilibrium constant deduced from nmr measurements. Figure 2 is a plot of some H-bond band intensities (ir) against computed complex concentration (nmr).

CDI_3, at concentrations comparable to those for the nmr work, showed no evidence in the infrared of H-bond formation. Inspection of Table I reveals that the nmr parameters for ionic complexes of this compound are anomalous. This behavior is discussed in a later section.

Effect of Temperature and Solvent. Table II shows Δ_c and K as a function of temperature for complexes of trichloromethane and tribromomethane with the three halide ions studied. Note that the complex shifts are independent of temperature, to within experimental error, in all cases.

Table II. Temperature Dependence of K and Δ_c for Trihalomethane-Halide Ion Complexes[a]

Acceptor	Donor (base)	Temp, °K	K, l. mole^{-1}	Limiting shift, Δ_c, ppm
$CHCl_3$	Cl$^-$	248	1.98 ± 0.09	−2.91 ± 0.08
		268	1.61 ± 0.07	−2.99 ± 0.09
		288	1.34 ± 0.06	−3.04 ± 0.10
		313	1.08 ± 0.06	−3.12 ± 0.13
		333	0.98 ± 0.07	−3.08 ± 0.19
$CHCl_3$	Br$^-$	248	0.99 ± 0.10	−2.92 ± 0.28
		273	0.83 ± 0.09	−2.92 ± 0.31
		298	0.74 ± 0.09	−2.81 ± 0.33
		318	0.65 ± 0.10	−2.81 ± 0.44
		338	0.60 ± 0.10	−2.72 ± 0.43
$CHCl_3$	I$^-$	248	0.64 ± 0.05	−2.32 ± 0.18
		273	0.55 ± 0.05	−2.34 ± 0.20
		323	0.43 ± 0.06	−2.19 ± 0.31
$CHBr_3$	Cl$^-$	248	1.64 ± 0.11	−2.27 ± 0.11
		273	1.32 ± 0.08	−2.34 ± 0.11
		298	1.09 ± 0.06	−2.38 ± 0.11
		323	0.99 ± 0.05	−2.34 ± 0.11
		348	0.85 ± 0.09	−2.38 ± 0.22
$CHBr_3$	Br$^-$	248	1.63 ± 0.16	−1.58 ± 0.12
		273	1.27 ± 0.15	−1.63 ± 0.16
		298	1.10 ± 0.14	−1.62 ± 0.18
		323	0.95 ± 0.12	−1.63 ± 0.19
		348	0.87 ± 0.12	−1.56 ± 0.19
$CHBr_3$	I$^-$	248	1.58 ± 0.11	−0.89 ± 0.05
		273	1.29 ± 0.10	−0.92 ± 0.06
		298	1.06 ± 0.09	−0.93 ± 0.07
		323	1.13 ± 0.09	−0.80 ± 0.06
		348	1.01 ± 0.09	−0.76 ± 0.06

[a] Solvent: acetonitrile.

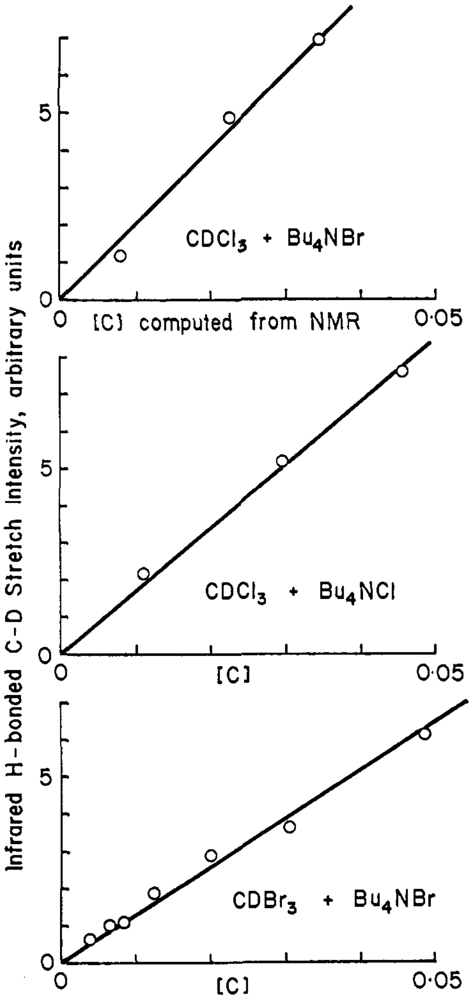

Figure 2. Intensity (absorbance) of infrared C–D "hydrogen-bond" stretch band as a function of complex concentration computed from the nmr analysis (solvent, tetrachloromethane).

A least-squares fit of log K to $1/T$ yields the enthalpy and entropy changes on complex formation; these are given in Table III. As one might expect, ΔH becomes increasingly negative with decreasing ionic radius. No trend in ΔS relative to ionic radius is apparent beyond the limits of experimental error.

Table III. Thermodynamic Quantities for Trihalomethane–Halide Ion Complexes[a]

Complex	ΔH, kcal mole^{-1}	ΔS, eu
$CHCl_3$ + Cl$^-$	−1.38 ± 0.04	−4.2 ± 0.1
$CHCl_3$ + Br$^-$	−0.93 ± 0.04	−3.7 ± 0.1
$CHCl_3$ + I$^-$	−0.84 ± 0.01	−4.3 ± 0.1
$CHBr_3$ + Cl$^-$	−1.10 ± 0.04	−3.5 ± 0.2
$CHBr_3$ + Br$^-$	−1.07 ± 0.05	−3.4 ± 0.2
$CHBr_3$ + I$^-$	−0.71 ± 0.09	−2.0 ± 0.3

[a] Solvent: acetonitrile.

Muller and Reiter[14] have estimated the temperature dependence of the chemical shift of H-bonded com-

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(13) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp 197–199.

(14) N. Muller and R. C. Reiter, *J. Chem. Phys.*, 42, 3265 (1965).

plexes *via* excitation of the H-bonded stretch vibrational mode, for various assumed potential-well depths, and corresponding enthalpies of H-bond formation. They predict that for weak H bonds, and thus shallow wells, many excited vibrational states are thermally accessible and $\delta\Delta/\delta T$ is large.

Fitting the values of Δ_c over a range of temperatures for each complex (see Table II), a least-squares straight line was obtained and its slope taken as a measure of $\delta\Delta_c/\delta T$; the standard errors for these lines are in general larger than the slopes themselves, indicating that the uncertainties in the values of Δ_c are of at least the same magnitude as any systematic variation could possibly be. Furthermore, four of the six lines so obtained give a slope in the wrong sense to fit the analysis of Muller and Reiter. We conclude that it is reasonable to say that $\delta\Delta/\delta T$ is no greater than 0.25×10^{-2} ppm deg^{-1}, and thus the complex represents the minimum of a potential well of depth $\gg RT$. Comparison of this to the values given in lines 6, 7, and 8 of Table I in ref 14 indicates an H-bond energy of perhaps 10 kcal/mole.

Such a value would be more consistent with the observed enthalpies of formation of $X—H\cdots D$ bonds in the gas phase, where D is a dipolar base. These are generally in the range -3 to -8 kcal mole^{-1}.[15] It seems reasonable to expect that the enthalpies of H bonds to monopolar bases (anions) would be at least as large. For example, the enthalpy of hydration of chloride ion is -80.3 kcal mole^{-1};[16] dividing this among eight or nine solvating water molecules yields an $O—H\cdots Cl^-$ energy of 8-10 kcal mole^{-1}. This may be regarded as establishing a range for enthalpies of formation of hydrogen bonds to anions from *isolated* constituents.

Table IV. Temperature Variation of Limiting Shifts, by Least Squares

Complex	Δ_c/T, ppm deg^{-1}
$CHCl_3 + Cl^-$	$(+0.24 \pm 0.23) \times 10^{-2}$
$CHCl_3 + Br^-$	$(-0.22 \pm 0.64) \times 10^{-2}$
$CHCl_3 + I^-$	$(-0.18 \pm 0.78) \times 10^{-2}$
$CHBr_3 + Cl^-$	$(+0.09 \pm 0.23) \times 10^{-2}$
$CHBr_3 + Br^-$	$(-0.01 \pm 0.27) \times 10^{-2}$
$CHBr_3 + I^-$	$(-0.15 \pm 0.11) \times 10^{-2}$

The discrepancy between these values and the observed enthalpy changes of *ca.* 1 kcal/mole is removed if the process of complex formation is regarded as differential solvation of the ion, where the trihalomethane molecule displaces *n* solvent molecules.

$$XS_m^- + CHY_3 \rightleftharpoons CHY_3XS_{m-n} + nS \qquad (10)$$

If the trihalomethane molecule displaces a single solvent molecule, the observed value of ΔH is the difference between the solvation energies of the two molecules for the ion. If we regard the difference of 9.23 in pK_{SP} values of thallous chloride in water and acetonitrile[17] as arising entirely from the difference in solvation enthalpy of chloride ion between the two solvents, then the solvation enthalpy of Cl^- in acetonitrile is $-80 + RT \ln 9.23$, or -66 kcal. This implies a single-molecule solvation enthalpy of -7 to -9 kcal.

Discussion

Buckingham, Schaefer, and Schneider[18] have divided the extramolecular effects on the shielding in solution of a proton into four terms: a bulk susceptibility term, which in this case will be constant since all chemical shifts are referred to an internal reference signal (TMS); a solvent anisotropy term, which for this system turns out to be small even in acetonitrile, the shift of $CHCl_3$ being 7.22 ppm below TMS in CCl_4 and 7.57 ppm in acetonitrile; a van der Waals term and an electrostatic field term, both of which will be discussed in greater detail below.

Chemical Shift in the Complex. Models of C–H proton shifts by electrostatic fields predict field dependence of the form[19–21]

$$\delta\sigma_E = a \times 10^{-12}E_z - b \times 10^{-18}E^2 \qquad (11)$$

The *z* axis is directed from C to H. The parameter *a*, which may be related to the bond polarizability, has been evaluated theoretically[19–21] and experimentally,[19,22,23] for sp^2 and sp^3 C–H bonds as about 3 esu^{-1}. The coefficient of E^2, *b*, is usually assumed to have the hydrogen-atom value,[24] 0.738 esu^{-2}.

If we postulate a symmetric complex, as in Figure 3a, the electrostatic field may be regarded as originating in a point charge at the center of the ion. If the distance from the ion center to the hydrogen nucleus is ρ ångströms, and the angle between the C–H and H–ion vectors is θ, the complex shift, in parts per million, is predicted to be

$$\delta\sigma_E = -4.803a\left(\frac{1}{\rho^2}\right)\cos\theta - 23.07b\left(\frac{1}{\rho^4}\right) \qquad (12)$$

Our analysis of the shieldings, and related infrared evidence, suggests that trifluoromethane and trichloromethane interact with halide anions by hydrogen bonding, while triiodomethane interacts by an entirely different, charge-transfer or polarization, mechanism. Tribromomethane appears to be an intermediate case. The four molecules will be discussed below in an order which emphasizes this interpretation.

1. Trichloromethane. If the anion is assumed to be collinear with the C–H bond, eq 12 expresses the complex shift as a quadratic in $1/\rho^2$. The internuclear distance observed in many H-bonded complexes is typically 0.3 to 0.6 Å less than the sum of the appropriate van der Waals radii.[25] For this analysis, we have chosen to represent ρ as

$$\rho = r_- + r_H - 0.5 \qquad (13)$$

where r_H is the hydrogen van der Waals radius, 1.2 Å, and r_- is the crystal radius of the ion.

At these distances, the term in b/ρ^4 in eq 12 will contribute only about 15% of the observed shielding. We

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[15] Reference 13, p 212.

[16] R. M. Noyes, *J. Amer. Chem. Soc.*, **84**, 513 (1962).

[17] J. F. Coetzee and J. J. Campion, *ibid.*, **89**, 2517 (1967).

[18] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[19] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[20] J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962); P. J. Berkeley and M. W. Hanna, *J. Amer. Chem. Soc.*, **86**, 2990 (1964).

[21] T. Yonemoto, *Can. J. Chem.*, **44**, 223 (1966).

[22] P. Diehl and R. Freeman, *Mol. Phys.*, **4**, 39 (1961).

[23] C. MacLean and E. L. Mackor, *ibid.*, **4**, 241 (1961).

[24] T. W. Marshall and J. A. Pople, *ibid.*, **1**, 199 (1958).

[25] D. J. Sutor, *J. Chem. Soc.*, 1105 (1963).

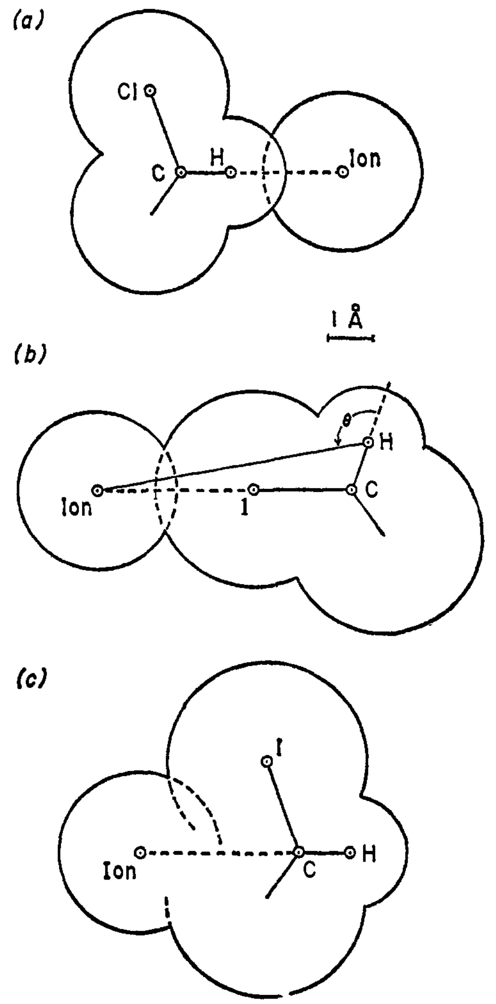

Figure 3. Postulated structures of complexes: (a) hydrogen-bonded, (b) asymmetric halogen-bonded, (c) symmetric halogen-bonded.

have assumed that b has the value 0.738 esu^{-2}, and evaluated a by plotting $(\Delta_c + 23.07b/\rho^4)$ *vs.* $1/\rho^2$ (Figure 4).

The trichloromethane data are best fitted by a line through the origin, of slope -16.0, which yields a value of $a = 3.3$ esu^{-1}. The line on the figure corresponds to $a = 3.0$.[20] Note that the observed values show a consistent deviation of about -0.2 ppm from this line.

Yonemoto[21] predicts a van der Waals deshielding of a hydrogen nucleus at distance ρ from an ion given by

$$\delta\sigma_w = 1.8 \times 10^{-53} \frac{\langle \sum_i x_i^2 \rangle}{a_0^2} \rho^{-6} \tag{14}$$

Using Yonemoto's values for $[\langle \Sigma x_i^2 \rangle / a_0^2]$, $Cl^- = 12.5$, and $Br^- = 18$, and, estimating $I^- = 30$, we find that the van der Waals shift is the same for all halide ions, -0.9 ppm. The liquid-phase van der Waals shifts for hydrocarbons are typically about -0.5 ppm,[26] so it is not unreasonable to expect an increase of deshielding by a few tenths of a part per million on formation of the complex.

Several reservations are necessary with regard to the validity of the a coefficient as determined from these experiments. First, the effect of the counterion will be such as to reduce the field at the hydrogen below the value which we have assigned to it, namely Ze/ρ^2, and to give a value of a which is too low. Preliminary results in this laboratory indicate that the counterion effect in tetrabutylammonium salts is no greater than 50% of the primary ion effect, depending on the size of the halide ion. Second, we have assumed a shortening of the van der Waals radius of hydrogen from 1.2 to 0.7 Å; in fact, the shortening is probably less than 0.5 Å rather than more; if the H bond is longer than we have assumed, we must postulate either a larger value of a or a larger van der Waals term to account for the observed shifts. Third, we have assumed no dielectric properties of the space intervening between the anion and the proton (*i.e.*, $\epsilon = 1$); this is not necessarily so, and a value of ϵ greater than 1 would decrease the field at the proton, making our estimate of a too low. Hence, it would appear that we are justified in accepting $a = 3$ as merely a lower limit, and not necessarily a definitive value of the coefficient.

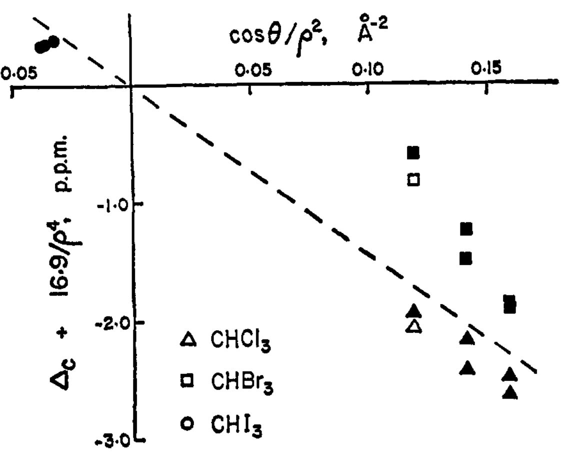

Figure 4. Evaluation of electrostatic shielding mechanism: open symbols, tetraheptylammonium salts.

2. Trifluoromethane. The complex shifts of this molecule are imprecisely determined, and their variation is not significant. They appear to be of about the same magnitude as those in trichloromethane.

3. Triiodomethane. The apparent paradox of positive complex shifts is resolved if one postulates a complex involving the anion and the *iodine atoms*, rather than the hydrogen. E_z now is directed in the reverse sense, and $\delta\sigma_E$ is positive.

To test this postulate, the entire infrared spectrum, from 4000 to 200 cm^{-1}, was examined for each trihalomethane alone in solution and in the presence of tetraalkylammonium salts at concentrations comparable to those used in the nmr study (0.1–1 *M*). As described previously, C–D H-bonded absorptions at 2170–2200 cm^{-1} were observed for CHF_3, $CHCl_3$, and $CHBr_3$ in the presence of any of the halide ions studied.

C–D H-bond absorptions have been reported for complexes of triiodomethane with several strong dipolar bases.[2] We observed the H-bond band of CDI_3 in CCl_4 solution in the presence of excess dimethyl sulfoxide or pyridine, but not in the presence of tetraalkylammonium halide salts up to about 1 *M*. (A weak H-bond band was observable in a Nujol mull of equimolar CDI_3 and any tetrabutylammonium halide.)

The triiodomethane spectrum does, however, show evidence of perturbation in the low-frequency region on

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(26) (a) S. Gordon and B. P. Dailey, *J. Chem. Phys.*, **34**, 1084 (1961); (b) B .B. Howard, B. Linder, and M. T. Emerson, *ibid.*, **36**, 485 (1962).

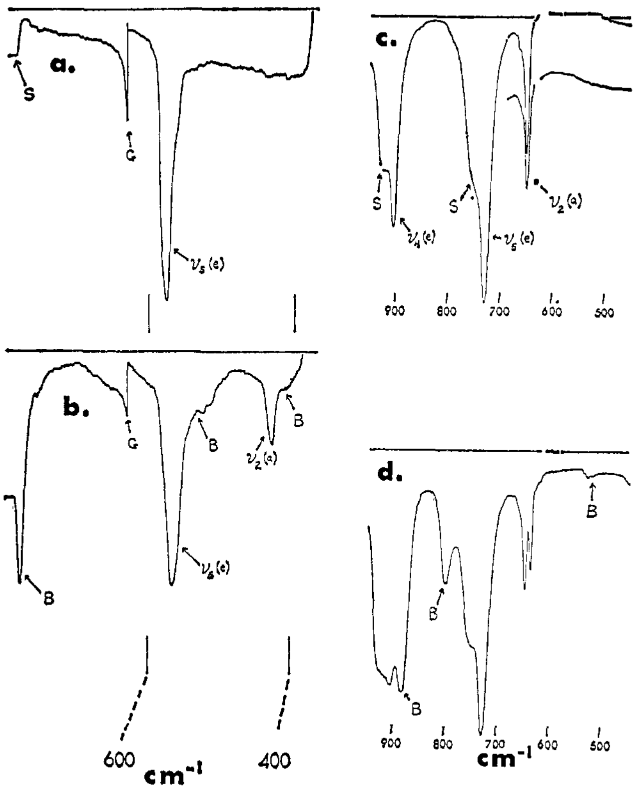

Figure 5. Infrared spectra in the carbon-halogen region: (a) CHI_3, 0.1 *M*, in acetonitrile; (b) CHI_3, 0.1 *M*, and Bu_4NBr, 0.34 *M*, in acetonitrile; (c) $CDCl_3$, 0.1 *M*, in acetonitrile; (d) $CDCl_3$, 0.1 *M*, and Bu_4NCl, 0.14 *M*, in acetonitrile. Identification of features: S = solvent absorption; B = tetra(*n*-butyl)ammonium cation absorption, G = grating change.

addition of anions. The absorption at 420 cm⁻¹, a symmetric C–I stretch designated ν_2 in Herzberg's notation,[27] is extremely weak in acetonitrile solution. On addition of a halide ion at concentrations in the range 0.1–1 *M*, the intensity of this band was enhanced by a factor of the order of 100 (Figure 5a,b) and became comparable to that of the e-stretch, ν_5, at 580 cm⁻¹.

This enhancement may be taken as evidence for polarization of the C–I valence electrons by a nearby ion, which causes enhancement of the bond dipole derivative and thus of the electric dipole transition moment. No such enhancement is observed for the corresponding absorptions in the other trihalomethanes on addition of salts. In $CHCl_3$ and $CHBr_3$, a satellite of ν_2 appears and grows in intensity as the proportion of complex increases, with the new peak 5–10 cm⁻¹ to low frequency of, of width comparable to, and growing at the expense of, the parent (Figure 5c,d). This presumably reflects a slight change in carbon–halogen force constant on formation of the complex.

The C–H and C–D bend absorptions, at *ca.* 1065 and 790 cm⁻¹, respectively, are masked by solvent absorption in solution. However, these regions are transparent in Nujol, and in several cases the complexes are sufficiently soluble to show an infrared spectrum in the mull. A normal[13] H-bond shift of 25 cm⁻¹ to high frequency was observed for the $CHCl_3$–Br^- complex; however, the complex band of CHI_3–Br^- in this region is 22 cm⁻¹ lower than the parent CHI_3 bend at 1065 cm⁻¹. A similar shift was observed for the CDI_3–Br^- complex. This is further evidence that the interaction of triiodomethane with anions is substantially different from the "normal" hydrogen bonding of trichloromethane.

We consider this evidence to be adequate to justify our postulate that the triiodomethane complex involves interaction of the iodine, rather than the hydrogen, with the anion.[28]

Two configurations of such complexes suggest themselves: (a) an asymmetric structure, the ion collinear with the C–I bond; (b) a trigonally symmetric complex, the ion collinear with the C–H bond, equidistant from the iodine atoms. The asymmetric structure involves strong interaction with a single iodine atom and is analogous to that of the linear I_3^- ion, whereas the symmetric structure preserves the symmetry of the molecule and involves weak interactions with all three iodine atoms. The latter model would be more consistent with the observation that the only significant change of the infrared spectrum on complex formation is the enhancement, without frequency shift, of a symmetric C–I stretch mode absorption.

Nmr complex shifts, $\delta\sigma_E$, computed using eq 11, are +0.11 ppm in the unsymmetric model and +0.54 ppm in the symmetric one. The observed values are all in the range +0.30 +0.36 ppm. They are included in Figure 4, at the values of $\cos\theta/\rho^2$ appropriate to the symmetric model. It is not easy to rationalize the observed values' being more positive than the predicted ones in the unsymmetric complex. However, three mechanisms could reduce the shielding from +0.5 to +0.3 ppm in the symmetric complex. (a) A small fraction, f_H, of the triiodomethane complex may be hydrogen bonded. This would decrease the shift by *ca.* $2.5f_H$ ppm. Thus, less than 10% of hydrogen bonding, which would be undetectable by other means, would account for the discrepancy. (b) The field at the proton is transmitted from the ion primarily through space occupied by highly polarizable iodine atoms. Using an estimated molar polarization of iodine of 14.5 cm³ mole⁻¹,[29] we compute an effective dielectric constant of E = 3.4 for space filled by covalent iodine. This is in excess of the value of 2–2.5 for hydrocarbon structures, which is contained implicity in the coefficients of eq 11. It is reasonable to expect that the field at the proton, arising from an ion beyond the CI_3 structure, would be reduced by about 40%. (c) The pyridine shifts suggest that *a* may be smaller in CHI_3 than in $CHCl_3$.

A semiclassical calculation of ion–molecule interaction energies, discussed in the next section, predicts a lower energy for the symmetric complex. The nmr and infrared spectra of solutions of 2-iodopropane and halide salts showed no evidence of complexing with a single iodine.[30]

4. Tribromomethane Complex Shifts. These are intermediate between those of $CHCl_3$ and CHI_3. This compound probably interacts with halide anions *via* hydrogen bonding and *via* its halogen atoms in roughly equal proportions. The infrared evidence is inconclu-

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(27) G. Herzberg, "Infrared and Raman Spectroscopy," D. Van Nostrand Co., Toronto, Canada, 1945, pp 312–322; R. M. Hexter and H. Cheung, *J. Chem. Phys.*, 24, 1186 (1956).

(28) See T. Bjorvatten, *Acta Chem. Scand.*, 17, 2292 (1963); O. Hassel, *ibid.*, 19, 2259 (1965).

(29) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(30) An attempt to form complexes of iodomethane and chloride ion resulted in the authors' rediscovery of the SN2 displacement.

sive: a ν_2 satellite appears as in $CHCl_3$. Since ν_2 is fairly intense in uncomplexed $CHBr_3$, enhancement is not easy to detect. As mentioned above, normal H-bond absorption is observed. It may be significant that the constant of proportionality between H-bond absorption intensity and complex concentration computed from nmr data is smaller for $CHBr_3$ than for $CHCl_3$ (see Figure 2). This suggests that only a constant fraction of the $CHBr_3$ complex involves H bonding.

Equilibrium Constants. The significant trends of the equilibrium constants in Table I may be summarized as follows.

(a) In a given solvent, for a given trihalomethane, the equilibrium constant increases in the order $I^- < Br^- < Cl^-$ as the anion radius decreases. This is the order expected if the complex energy is controlled by the electrostatic field of the anion.

(b) In a given solvent, with a given anion base, the equilibrium constants increase in the order $CHF_3 < CHCl_3 < CHBr_3 < CHI_3$. This is the opposite order to that of the molecular dipole moments, which presumably determine the electrophilicity of the hydrogen. The values of ΔH and ΔS in Table III suggest that the difference between $CHCl_3$ and $CHBr_3$ is determined as much by entropy as by enthalpy. This is difficult to interpret and may have to do with the difference in molecular size.

(c) For a given complex, the equilibrium constant in tetrachloromethane is about twice that in acetonitrile at ambient temperature. The rapid decrease in solubility of salts in CCl_4 with decreasing temperature precludes evaluation of ΔH and ΔS in that solvent. If the enthalpies of formation are interpreted as differences between solvent- and trihalomethane-complex energies, they appear to be characteristically $RT \ln 2 = 0.4$ kcal/mole larger in CCl_4. This might be interpreted as indicating that the enthalpy of solvation of anions is approximately 0.4 kcal/mole more negative in acetonitrile than in CCl_4, per solvent molecule in the solvation shell.

(d) The equilibrium constants for association of pyridine with $CHCl_3$, $CHBr_3$, and CHI_3 are essentially equal, in contrast to the large variation relative to any anion base. The interaction of the dipolar base, pyridine, appears to differ essentially from that of the monopolar anions with trihalomethane molecules.

In view of the difficulty of obtaining precise values of ΔH and ΔS for all of the complexes studied (those given in Table III are experimentally the most favorable cases), we shall assume that the ambient-temperature equilibrium constants generally reflect enthalpy changes of -1 or -2 kcal/mole, and that the relative magnitudes of the equilibrium constants reflect corresponding changes in $-\Delta H$, except as noted above. This requires that ΔS either be substantially constant, or at least vary in the same way as ΔH.[31]

An Electrostatic Model of Anion–Molecule Interaction. The complexes studied are of two distinct types: H-bonded (CHF_3, $CHCl_3$, $CHBr_3$) and halogen-bonded or charge-transfer ($CHBr_3$, CHI_3). All pyridine complexes appear to be H bonded. Both H-bonding and charge-transfer bonding have been evaluated by quantum-mechanical models.[32,33] Quantitative application of such models is restricted by the need for such parameters as intermolecular overlap integrals and excited-state configuration data.

Simple electrostatic models, involving parameters such as dipole moments and polarizabilities which are accessible to independent determination, have been used successfully to evaluate H-bond energies.[33,34] We shall adapt for our purposes a model of this sort which has been useful in predicting ion hydration energies.[35,36]

We compute the electrostatic potential energy of interaction of the ion, regarded as a point charge Ze, with the permanent and induced dipole moments of the molecule. Since the field of the ion is far from uniform across the molecule, and it is known that both permanent dipole moments and polarizabilities may reasonably be divided into bond contributions,[37,38] we evaluate this interaction for each bond, and sum as follows.

$$U_e = \sum_i \left(\frac{A_i}{r_i^{12}} - \frac{B_i}{r_i^{6}}\right) - \sum_{i<j} \eta_{ij}(\mu_{ij}\mathbf{E}_{ij} + \frac{1}{2}\mathbf{E}_{ij}\alpha_{ij}\mathbf{E}_{ij}) \quad (15)$$

The first sum is over atoms and contains the van der Waals repulsive and attractive terms. The second sum is over pairs of atoms: $\eta_{ij} = 1$ if atoms i and j are bonded; otherwise $\eta_{ij} = 0$. μ_{ij} and α_{ij} are respectively the bond dipole moment vector and polarizability tensor. $\mathbf{E}_{ij}$ is the field of the ion at the i–j bond.

Since we are primarily interested in the effects of the ionic monopole, we shall assume that the envelope of the atomic van der Waals spheres defines an equipotential surface with respect to the first sum in eq 15. We may now disregard its contribution as constant provided that we evaluate ion–molecule energies with the ion always just touching the van der Waals surface so defined. Such a procedure is not unprecedented: it is simply an extension of the "hard-sphere" model.[39]

The permanent dipole is represented by a set of point charges at the atomic nuclei, made up of bond-dipole contributions. The charges due to a bond dipole μ are equal and opposite and of magnitude μ/l, where l is the bond length. The total charge on atom i is therefore

$$q_i = \sum_j \eta_{ij}\mu_{ij}/l_{ij} \quad (16)$$

A positive value of μ_{ij} implies polarity $i+, j-$.

We make the usual assumption that the bond polarizability tensor is diagonal and symmetric with respect to the bond axis; its principal components are $\alpha_\parallel$ along the axis and $\alpha_\perp$ in any direction normal to the axis. We are compelled to choose a location on the bond for the effective polarization dipole $\alpha_{ij}\mathbf{E}_{ij}$; a reasonable location is the polarizability centroid of the

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[31] Reference 13, pp 220–222.

[32] R. S. Mulliken, *J. Chim. Phys.*, 61, 20 (1964); P. J. Berkeley and M. W. Hanna, *J. Chem. Phys.*, 41, 2530 (1964).

[33] Reference 13, pp 226–241.

[34] E. S. Campbell, G. Gelernter, H. Heinen, and V. R. G. Moorti, *J. Chem. Phys.*, 46, 2690 (1967).

[35] J. D. Bernal and R. H. Fowler, *ibid.*, 1, 515 (1933).

[36] G. Sposito and K. L. Babcock, *ibid.*, 47, 153 (1967).

[37] R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, *J. Amer. Chem. Soc.*, 73, 2263 (1951).

[38] K. Pitzer, *Advan. Chem. Phys.*, 2, 79 (1949).

[39] A. D. Buckingham, *Discussions Faraday Soc.*, 24, 151 (1957).

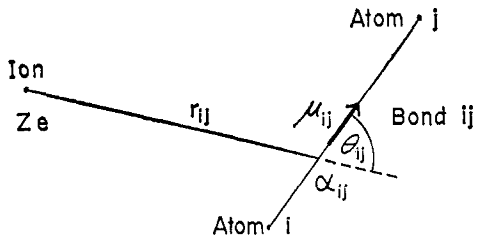

Figure 6. Interaction of anion, charge *Ze*, with bond dipole μ_{ij} and polarizability α_{ij}.

bond, r_{ij}

$$\mathrm{r}_{ij} = (\bar{\alpha}_i\mathrm{r}_i + \bar{\alpha}_j\mathrm{r}_j)/(\bar{\alpha}_i + \bar{\alpha}_j) \tag{17}$$

α_i and α_j are the mean atomic polarizabilities of atoms *i* and *j*, respectively; r_i and r_j are the vectors locating atoms *i* and *j* relative to the ion.

Subject to the above approximations, if distances are in cm × 10^{-8}, charges in esu × 10^{-10}, dipole moments in Debyes and polarizabilities in $\mathrm{cm}^3 \times 10^{-24}$, the ion dipole electrostatic potential energy U_e, in kcal mole^{-1}, is given by

$$U_\mathrm{e} = 69.13Z\sum_i q_i/r_i - 332.1Z^2\sum_{i<j}\eta_{ij}(\alpha_{\perp ij}\sin^2\theta_{ij} + \alpha_{\parallel ij}\cos^2\theta_{ij})/2r_{ij}^4 \tag{18}$$

The various radii, etc., are specified in Figure 6.

Among the more important terms left out of this computation are the dipole–dipole repulsion of the molecules solvating the ion and the molecular dipole–ion polarizability interaction. Both of these can be estimated: they are of the order of 1 kcal/mole of molecules, that is, roughly an order of magnitude less than the primary interaction energies. They will also tend to cancel out in the complex *vs.* the purely solvated ion.

Values of U_e computed using this unscaled, conceptually simple model should reflect the large-scale trends in ΔH and thus, inversely, the equilibrium constants. It is probably not reasonable to expect valid comparison of the energies of structurally different complexes; such cases, in addition to being exceptionally severe tests of the consistency of the two terms in the energy, are also those in which there may be significant differences in the entropy contribution to *K*. Nevertheless, if the model is reasonable, it should predict energies of the same order for complexes of comparable stability.

Parameters used in the computation are given in Table V. Bond polarizabilities are from Denbigh;[29] bond moments are assigned to match the experimental dipole moments,[40] assuming tetrahedral geometry and that $\mu_\mathrm{CH} = 0$.[37]

Mean atomic polarizabilities are taken from Groves and Sugden[41] or estimated from X–C and X–H bond moments. Their values are not critical. Bond lengths, ionic radii, and van der Waals radii are taken from standard sources.[42] The computations were programmed in FORTRAN IV for the IBM 360-65/67 computer, which produced the values of U_e in Table VI.

Table V. Parameters Used in the Electrostatic Energy Computations

a. Bond Polarizabilities, $\mathrm{cm}^3 \times 10^{24}$

Bond	$\alpha_\parallel$	$\alpha_\perp$
C—H	0.79	0.58
C—F	0.96[a]	0.55[a]
C—Cl	3.67	2.08
C—Br	5.04	2.88
C—I	8.09[a]	4.61[a]
C≡N	3.1	1.4

b. Atom Polarizabilities, $\mathrm{cm}^3 \times 10^{24}$		c. Bond Moments, D	
H	0.4	C—H	0.0
C	1.0	C—F	1.64
F	0.7[b]	C—Cl	1.1
Cl	2.8[b]	C—Br	1.0
Br	4.0[b]	C—I	0.8
I	6.5[b]	C≡N	3.96
N	0.8[b]		

[a] Estimated from mean polarizability, assuming $\alpha_\perp/\alpha_\parallel = 0.57$ (see ref 37). [b] Estimated from bond polarizabilities.

Table VI. Computed Ion-Molecule Electrostatic Potential Energy (kcal mole^{-1})

	Ion		
Molecule[a]	Cl^-	Br^-	I^-
$\mathrm{CHF_3}$ (h)	−9.8	−8.9	−7.9
$\mathrm{CHCl_3}$ (h)	−9.0	−8.2	−7.0
$\mathrm{CHBr_3}$ (h)	−9.1	−8.2	−7.1
$\mathrm{CHI_3}$ (h)	−9.5	−8.6	−7.4
$\mathrm{CHF_3}$ (s)	+1.3	+1.6	+2.0
$\mathrm{CHCl_3}$ (s)	−3.8	−3.0	−2.7
$\mathrm{CHBr_3}$ (s)	−6.7	−5.4	−3.9
$\mathrm{CHI_3}$ (s)	−9.4	−7.8	−6.0
$\mathrm{CHCl_3}$ (a)	−1.2	−1.0	−0.7
$\mathrm{CHBr_3}$ (a)	−2.1	−1.8	−1.3
$\mathrm{CHI_3}$ (a)	−3.9	−3.4	−2.7
$\mathrm{CCl_4}$ (f)	−9.1	−7.7	−6.0
$\mathrm{CH_3CN}$ (f)	−13.4	−12.4	−10.9

[a] (h) hydrogen-bonded complex; (s) symmetric halogen-bonded complex, (a) asymmetric halogen-bonded complex, (f) most favorable (lowest energy) configuration.

As might be expected, for a particular complex, U_e is computed to be more negative as the ionic radius decreases: this simply reflects the increase in electrostatic field strength.

If the variation of equilibrium constants in the trihalomethane series is determined by electrostatic energy, then the monotonic increase in energy from $\mathrm{CHF_3}$ to $\mathrm{CHI_3}$ indicates that the induced, rather than the permanent, dipole of the molecule dominates its interaction with anions. The computed energies are in accord with this, since for the series $\mathrm{CHCl_3}$, $\mathrm{CHBr_3}$, $\mathrm{CHI_3}$ they become increasingly more negative as the polarizability of the halogen increases. Any increase in the estimate of the polarization energy in the model would tend to put $\mathrm{CHF_3}$ into the observed sequence.

One might expect this model to underestimate somewhat the polarization energy, since, for any reasonable charge distribution in a bond, the expectation value $\langle\alpha/r^4\rangle$ should be larger than the value of α/r^4 at the centroid. Considering this and the fact that the interpretation of the experimental *K*'s as reflecting energy differences alone is least certain in this case, the failure of the model to predict a monotonic increase in stability of the complexes in all series $\mathrm{CHF_3}$ to $\mathrm{CHI_3}$ is not serious.

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(40) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, pp 37–39.

(41) L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937).

(42) "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Co., Cleveland, Ohio, 1963.

One of the most striking features of the computed set of U_e's is the rapid decrease in energy in all series of symmetric halogen-bonded complexes, in the order $CHF_3 > CHCl_3 > CHBr_3 > CHI_3$. As the polarizability increases, such structures become increasingly stable. Our model predicts that CHI_3 halogen-bonded complexes will have stability comparable to that of the corresponding hydrogen-bonded complexes. The experimental evidence suggests that the two complexes are of comparable stability in the case of $CHBr_3$, and that, in the case of CHI_3 the halogen-bonded complex is significantly more stable. Again, the model would appear to be underestimating slightly the polarization contribution to the energy.

In the absence of reliable values of the carbon–hydrogen bond moments,[37] we have assigned to μ_{CH} the value zero in all cases. Denariez and Lecayer[43] have estimated, from absolute infrared intensities, that the value of μ_{CH} in $CHCl_3$ is 0.69 D, hydrogen positive. It is reasonable to suppose, then, that μ_{CH} increases in the series CHI_3, $CHBr_3$, $CHCl_3$. Such a trend strengthens our argument that the complex type changes between $CHCl_3$ and CHI_3.

Our model predicts unambiguously that the symmetric halogen-bonded complex will in every case be of lower energy than the asymmetric complex containing a linear $C—X\cdots Y^-$ structure. Computation of U_e at various points on the halogen van der Waals surface reveals a strong potential minimum in the region of symmetric interaction with all three halogens.

Consistent with our concept of complex formation as differential solvation, the model predicts solvation energies of tetrachloromethane which are slightly smaller, on the average, than the energies of those trihalomethane complexes which are observed to be stable. It correctly predicts a more negative solvation energy for acetonitrile, indeed, one much larger than those of the trihalomethanes. It is very likely that the model is too simpleminded an approximation to the structure of acetonitrile, since it treats the very large molecular dipole as arising entirely from two charged atoms, as $C^+–N^-$.

Interaction energies were also computed at distances of approach 0.5 Å closer than the sum of radii, consistent with the shielding computations and with many observed H-bond and charge-transfer bond lengths. These energies were consistently about 30% greater in magnitude but showed exactly the same trends as the values in Table VI.

The failure of the dipolar base, pyridine, to form halogen bonds to triiodomethane could be explained, within the charge-transfer formalism, as a consequence of its very high ionization energy, 213 kcal mole^{-1}, relative to those of the halide anions, 74–96 kcal mole^{-1}. Our electrostatic model also affords an explanation for this, provided that the stable complex is the symmetric one. A monopolar ion has a spherically symmetric potential and can interact strongly with three polarizable halogens simultaneously. Dipolar pyridine, on the other hand, can interact strongly only in one specific direction, as in hydrogen bonding; its interaction over a large solid angle, as in the halogen polarization complex, will be relatively weaker than that of a monopole.

Conclusions

The interaction of a halide anion with a trihalomethane molecule, at low concentration in a weakly interacting solvent, appears to be adequately interpreted in terms of a 1:1 complex equilibrium, in which the trihalomethane molecule displaces (presumably) one solvent molecule from the primary solvation shell of the ion. The proton nuclear shielding change on formation of the complex reveals the position of the ion relative to the C–H bond. Its insensitivity to temperature change indicates that the complex formed is strongly bound; that is, $-\Delta H \gg RT$ for the complex in the absence of competing solvent molecules.

Both nmr and infrared evidence suggests that the smaller trihalomethanes interact primarily *via* the hydrogen, whereas the larger ones, especially triiodomethane, bond *via* the halogen atoms. The complex stability constants show the expected increase with decreasing ionic radius. There is evidence that the association energy of these complexes (with the possible exception of those with trifluoromethane) is dominated by the polarization of the carbon–halogen structure of the molecule, rather than by the electrophilicity of the C–H fragment. Since the evidence for C–H hydrogen bonding, except in crystals,[25] is confined to cases where the carbon also bears one or more highly polarizable groups,[2] it may well be that such interaction is not properly described as hydrogen bonding.[14]

A simple monopole–dipole electrostatic model, using only independently determined parameters, appears to account adequately for all of the established energetic data, in particular the dependence on ionic size, structure, and molecular polarizability.

It appears to be feasible to evaluate the counterion effect on the proton shieldings, and thus evaluate more accurately the coefficient of E_z in the Buckingham–Musher equation for various bonds to hydrogen, since the field at the hydrogen would then be known. Our data are consistent with a lower bound of 3.0×10^{-12} esu^{-1}, which is in accordance with previous estimates.

Since our experiment yields the proton shielding of a single molecule in the primary solvation shell of an ion, it appears feasible to use it to study the structure of solvation complexes involving such fundamentally interesting molecules as water. Work in our laboratory is proceeding in this direction. It should be possible to determine unambiguously the polarization contribution to the shift of water shielding arising from anion solvation; the molar ionic shift could then be resolved into polarization and steric or structure-breaking contributions[44] without introducing arbitrary assumptions.

Acknowledgments. We wish to express our gratitude to Dr. John Bertie, Dr. Paul Kebarle, Dr. B. Kratochvil, and Dr. R. U. Lemieux for valuable criticism and suggestions. Our debt to Terry W. Fenton, our undergraduate summer research assistant, should be evident from the fact that each entry in Table I required his preparation of six or more samples. R. D. G. holds a studentship from the National Research Council of Canada. This research was supported in part by NRC Grant No. A-2051.

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[43] M.-M. Denariez and A. Lecayer, *J. Chim. Phys.*, **60**, 421 (1963).

[44] M. S. Bergqvist and E. Forslind, *Acta Chem. Scand.*, **16**, 2069 (1962).

Appendix. Experimental Error Estimates in Linear Regression Analysis

All of the least-squares fits to straight lines in the Benesi-Hildebrand-Scott analyses (Tables I and II) and the evaluation of ΔH and ΔS (Table III) and of $\delta\Delta/\delta T$ (Table IV) were done using a weighted polynomial regression subroutine, LSE.[45] In the case of first-order polynomials (linear regression), this is identical with the method described by Worthing and Geffner.[46]

In this study, where four to eight points were fitted to a best straight line, we occasionally observed fortuitous coincidence of the points to the best line so derived. In such cases, the resulting extremely small standard deviations of intercept, δb_1, and of slope, δb_2, were not representative of the experiments which yielded the points.

We have, therefore, included in the standard deviations reported in this paper estimates of the error contributions arising from evaluable error ranges in the observed quantities, as follows. To each value y_i fitted to an equation such as (5) we assigned an error range δy_i.[47] Now the standard deviations δb_1 and δb_2 are both proportional to the square root of the sum of squares of residuals

$$\sum_i w_i r_i^2 = \sum_i w_i(y_i - b_1 - b_2 x_i)^2 \qquad (19)$$

As a measure of the possible deviation of y_i from the line, we augmented the square of the residual, r_i^2, by the square of the error, $(\delta y_i)^2$. The calculation of standard deviations was then carried out in the usual way, with the sum of squares of residuals replaced by the quantity

$$\sum_i w_i[r_i^2 + (\delta y_i)^2]$$

To allow for skewed error distributions (for example, in the Benesi-Hildebrand-Scott analysis, the errors in the y_i's became larger at lower concentrations[47]), the points were assigned weights, w_i, inversely proportional to δy_i. All experimental quantities for which error estimates are given are reported as best value plus or minus the standard deviation computed by this method.

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[45] LSE uses subroutines for which we are indebted to Dr. J. A. Plambeck and the University of Illinois Computing Center.

[46] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

[47] In the case of the Benesi-Hildebrand-Scott analysis, where y_i is defined in eq 5, the error range of y_i is given by

$$(\delta y_i)^2 = (\delta d)^2/(\sigma - \sigma_A)^2 + [(\delta\sigma)^2 + (\delta\sigma_A)^2]d^2/(\sigma - \sigma_A)^4$$

where d is the donor concentration, δd is its estimated error (usually 0.005 M), and $\delta\sigma$ is the estimated error in shielding (usually 0.0017 ppm, *i.e.*, 0.1 Hz at 60 MHz).

Rates of Ozone-Olefin Reactions in Carbon Tetrachloride Solutions[1]

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Abstract: The values of the second-order rate constants (k_1) for the reactions of ozone with a number of simple alkenes have been determined at room temperature. The rates vary with olefin structure in a manner very similar to that found previously in this laboratory for the vapor-phase reactions of ozone with olefins. The results, therefore, confirm the vastly different behavior from the one observed in air-pollution studies at very low reactant concentrations. The reason for the difference is not clear.

Ozonation of olefins in solution at low temperatures has been the subject of many investigations.[3] Most of these studies have dealt primarily with product analysis and not with reaction rates. More kinetic work has been done with the aromatic compounds, which react with ozone considerably more slowly than do olefins. Nakagawa, Andrews, and Keefer[4] have determined ozonation rates of alkyl-substituted benzenes in carbon tetrachloride and acetic acid solutions and found excellent correlations of reaction rates with the number of alkyl substituents. The results show that ozone exhibits an electrophilic tendency in its attack on simple aromatic systems responding to the increased electron density in the aromatic ring at greater alkyl substitution.

Although no systematic determinations have been made of the rates of ozone attack on simple olefins in solution, a number of gas-phase investigations have been carried out. Ozone is a constituent of earth's atmosphere and also plays an important role in air-pollution phenomena. Most of the gas-phase work has been done from the point of view of ozone's implication in air pollution, and the concentrations of the reactants used have been intentionally kept very low (in the part per million range) to simulate the conditions in polluted atmosphere. In contrast to this, the gas-phase work from this laboratory[5,6] has been done at

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[2] National Research Council Postdoctorate Fellow.

[3] P. S. Bailey, *Chem. Rev.*, 58, 925 (1958).

[4] T. W. Nakagawa, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, 82, 269 (1960).

[5] T. Vrbaski and R. J. Cvetanović, *Can. J. Chem.*, 38, 1053, 1063 (1960).

[6] Y. K. Wei and R. J. Cvetanovic, *ibid.* 41, 913 (1963).