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Strong Hydrogen Bonds. V. Haloform–Halide Ion Interactions[1,2]

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Pressure–composition isotherms have been determined for a number of systems consisting of tetraalkylammonium halides and fluoroform or chloroform. At 0° the following compounds have been found: $(C_2H_5)_4NCl \cdot HCCl_3$, $(C_2H_5)_4NBr \cdot HCCl_3$, $(C_2H_5)_4NBr \cdot 2HCCl_3$, $(C_4H_9)_4NCl \cdot HCCl_3$, $(C_4H_9)_4NCl \cdot 2HCCl_3$, $(C_4H_9)_4NCl \cdot 3HCCl_3$, $(C_4H_9)_4NBr \cdot HCCl_3$, $(C_4H_9)_4NBr \cdot 3HCCl_3$, and $(C_4H_9)_4NI \cdot 3HCCl_3$. At −78.5° $(C_2H_5)_4NCl \cdot 2HCF_3$ and $(C_2H_5)_4NCl \cdot 4HCF_3$ were found. From the enthalpy changes involved in the formation of the tetrabutylammonium salt adducts, the following lower limits have been established for the enthalpy of hydrogen-bond formation: −14.0 kcal/mol for $Cl–HCCl_3^-$, −12.6 kcal/mol for $Br–HCCl_3^-$, and −9.6 kcal/mol for $I–HCCl_3^-$. A single experiment with tetraethylammonium chloride and bromoform resulted in complex decomposition of both reactants.

Introduction

The existence of hydrogen bonds involving chloroform as a hydrogen donor has been well established.[3] It is generally felt, however, that such hydrogen bonds are relatively weak. Our earlier studies of hydrogen bonds in ion–molecule systems led us to believe that chloroform might form strong hydrogen bonds with anions. Solution spectroscopic studies involving the shift in the C–D stretching frequencies of $DCCl_3$ have been carried out and do indeed show the formation of hydrogen bonds between chloroform and the tetraalkylammonium halides.[4,5] In order to observe a strong interaction we felt that it would be necessary to carry out the desired reactions in the absence of solvent, since even such "inert" solvents as carbon tetrachloride are known to form compounds with the halide ions.[6]

Accordingly we have determined pressure–composition isotherms for a number of tetraalkylammonium halides and chloroform or fluoroform. In addition to the information regarding stoichiometries of the adducts which form, the enthalpy changes accompanying the formation of these compounds may be obtained from the variation in decomposition pressure with temperature. The enthalpy changes provide a minimum hydrogen-bond energy for the halide ion–haloform interaction.

In seeking energies for the interaction of the haloforms with the halide ions it was hoped that several related issues might be resolved. One issue deals with the relative hydrogen-bonding ability of the different haloforms. The order $HCI_3 \cong CHBr_3 > HCCl_3$, $CHI_3 > CHF_3$ has been proposed by Glick[7] based on $\Delta\nu_{CH}$ measured with triethylamine. Allerhand and Schleyer also found $\Delta\nu$ greater for $CHBr_3$ than $CHCl_3$ for a variety of hydrogen-bond acceptors, including the halide ions, but pointed out a lack of correlation between $\Delta\nu_{CH}$ and ΔH in the haloform systems. On the other hand, hydrogen-bonding ability in the order $CHCl_3 > CHBr_3 > CHI_3$ has been proposed to account for orders of dielectric polarization,[8] nmr band shifts,[9,10] and intensity changes in the stretching frequency.[11] Cresswell and Allred[9] report the following enthalpy values for the haloform interactions with tetrahydrofuran in cyclohexane: CHF_3, −2.4 kcal/mol; $CHCl_3$, −3.6 kcal/mol; $CHBr_3$, −2.6 kcal/mol; and CHI_3, −1.6 kcal/mol.

Experimental Section

Procedure.—Pressure–composition phase diagrams were obtained in a greaseless section of a vacuum line using techniques previously described.[12] Enthalpy changes were obtained from the variation of decomposition pressure with temperature.

Materials.—The following salts were purchased from the Eastman Chemical Co. and used after vacuum drying: tetraethylammonium chloride (Cl: calcd, 21.40%; found, 21.43%), tetraethylammonium bromide (Br: calcd, 37.95%; found, 38.02%), tetraethylammonium iodide (I: calcd, 49.35%; found, 49.35%), tetrabutylammonium iodide (I: calcd, 34.36%; found, 34.20%); tetrabutylammonium bromide was recrystallized from CCl_4–$(C_2H_5)_2O$ and vacuum dried (Br: calcd, 24.79%; found, 24.63%).

Tetrabutylammonium chloride was prepared by an ion-exchange method. An aqueous solution of $(C_4H_9)_4NI$ was passed through a column of Dowex 2 anion-exchange resin (chloride form). The eluted solution was partially evaporated on a hot plate and then dried to a solid in a vacuum desiccator with final drying on the vacuum line at 10^{-5} mm (Cl: calcd, 12.76%; found, 12.72%).

Tetramethylammonium fluoride was prepared by the method of Tunder and Siegel.[13] As prepared it was found to contain 1.50% water and 3.5% chloride ion.

Fluoroform was purchased from Matheson Co., and their specification indicated it to be 98% pure, with the impurities being 1% maximum of noncondensables by volume and 0.9% of other hydrocarbons by weight. This gas was introduced directly from the cylinder into the vacuum line, and the noncondensables were pumped off after the sample had been frozen.

Chloroform used was either Matheson Coleman and Bell

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[1] Taken in part from the Ph.D. thesis of W. G. E. (1964) and in part from the Ph.D. thesis of R. M. D. (1967).

[2] For paper IV in this series see W. G. Evans, C. E. Holloway, K. Sukumarabandhu, and D. H. McDaniel, *Inorg. Chem.*, in press.

[3] See G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp 150–151, 165, 197–199.

[4] A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233, 1715 (1963).

[5] R. S. Drago and M. F. Rettig, *ibid.*, **88**, 2966 (1966).

[6] D. H. McDaniel and R. M. Deiters, *ibid.*, **88**, 2607 (1966).

[7] R. E. Glick, *Chem. Ind.* (London), 413 (1956).

[8] S. Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).

[9] C. J. Cresswell and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1723 (1963).

[10] W. G. Patterson and D. M. Cameron, *Can. J. Chem.*, **41**, 198 (1963).

[11] W. Gordy, *J. Chem. Phys.*, **7**, 163 (1939). CHI_3 not included in this study.

[12] D. H. McDaniel and R. E. Vallee, *Inorg. Chem.*, **2**, 996 (1963).

[13] R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, **25**, 1097 (1963).

Spectroquality reagent grade or Baker Analyzed reagent grade. After degassing a middle fraction was used for the phase studies.

Bromoform was a Spectroquality reagent obtained from Matheson Coleman and Bell and was used without further purification.

Results and Discussion

A summary of the systems investigated, the adducts found, and the enthalpy change for the reaction

$$R_4NX(HCY_3)_{n_1}(s) + (n_2 - n_1)HCY_3(g) \longrightarrow R_4NX(HCY_3)_{n_2}(s)$$

is given in Table I. The numbers in parentheses following the enthalpy values refer to the values of n_1 and n_2. Pressure–composition isotherms at several temperatures for the system fluoroform–tetraethylammonium chloride are shown in Figure 1 and for the chloroform systems at 0° in Figures 2 and 3.

Table I

Haloform Adducts of the Tetraalkylammonium Halides

Cation	Anion	Haloform	Adducts, mol of haloform: mol of halide	Enthalpy, kcal/mol of HCX_3
$(CH_4)_4N^+$	F^-	HCF_3	None found	
$(CH_4)_4N^+$	F^-	$HCCl_3$	None found	
$(C_2H_5)_4N^+$	Cl^-	HCF_3	2:1; 4:1	$-7.6\ (0 \rightarrow 2)$
$(C_2H_5)_4N^+$	Cl^-	$HCCl_3$	1:1	$-9.4\ (0 \rightarrow 1)$
$(C_2H_5)_4N^+$	Cl^-	$HCBr_3$	*a*	. . .
$(C_2H_5)_4N^+$	Br^-	HCF_3	None found	
$(C_2H_5)_4N^+$	Br^-	$HCCl_3$	1:1; 2:1	$-8.6\ (1 \rightarrow 2)$
$(C_2H_5)_4N^+$	I^-	$HCCl_3$	None found	
$(C_4H_9)_4N^+$	Cl^-	$HCCl_3$	1:1, 2:1, 3:1	$-14.0 \pm 0.2\ (0 \rightarrow 1)$
$(C_4H_9)_4N^+$	Br^-	$HCCl_3$	1:1, 3:1	$-12.6 \pm 0.2\ (0 \rightarrow 1)$
$(C_4H_9)_4N^+$	I^-	$HCCl_3$	3:1	$-9.6 \pm 0.1\ (0 \rightarrow 3)$

[a] Decomposes; see text.

The phase studies of tetramethylammonium fluoride gave no indication of adduct formation with fluoroform at −78.5° or with chloroform at 0°. Since we were unable to prepare longer chain tetraalkylammonium fluorides in anhydrous form, we could not determine experimentally whether the failure to observe haloform adducts of tetramethylammonium fluoride is due to an inherent weakness of the hydrogen bond in $FHCX_3^-$ complexes or to the loss of lattice energy which would accompany adduct formation. Allerhand and Schleyer have presented spectroscopic evidence for the interaction in solution of fluoride ion and chloroform.

Tetraethylammonium bromide shows no tendency to react with fluoroform at temperatures as low as −78.5° and fluoroform pressures up to 1 atm. Since chloroform does form complexes with this salt (*vide infra*) this may be taken as evidence that chloroform forms stronger hydrogen bonds with bromide ion than fluoroform does.

The phase behavior of fluoroform with tetraethylammonium chloride is shown in Figure 1. At −95° a 4:1 adduct is formed with no evidence for any intermediate phases. At −78.5° the behavior on absorption of fluoroform indicates the possible existence of a metastable 1:1 complex with extensive solid solution behavior up to a 2:1 composition. Desorption indicates that 4:1 and 2:1 complexes are the only stable phases. The lower pressure of the 2:1 plateau was combined with the plateau pressure at −63.5° to obtain the enthalpy change reported in Table I. Since this enthalpy value is based on pressure data at only two temperatures, it accordingly has a much lower degree of certainty than the other enthalpies reported.

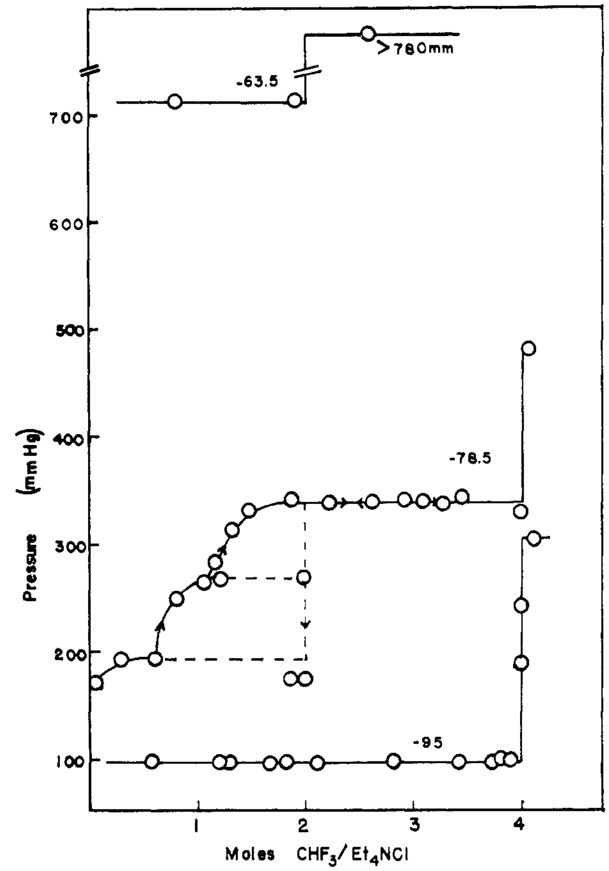

Figure 1.—Pressure–composition isotherm for the system fluoroform–tetraethylammonium chloride.

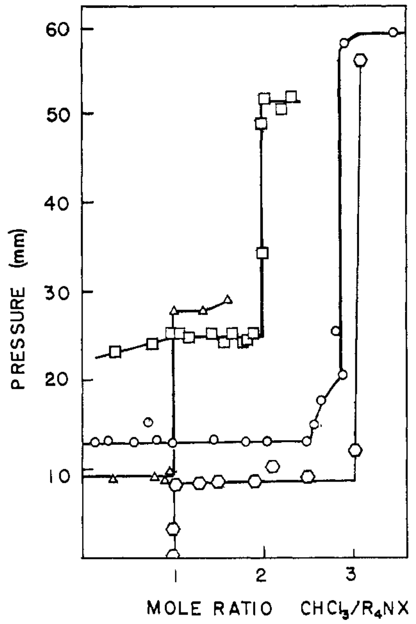

Figure 2.—Pressure–composition 0° isotherms for chloroform and the indicated salts: triangles, tetraethylammonium chloride; squares, tetraethylammonium bromide; hexagons, tetrabutylammonium bromide; circles, tetrabutylammonium iodide.

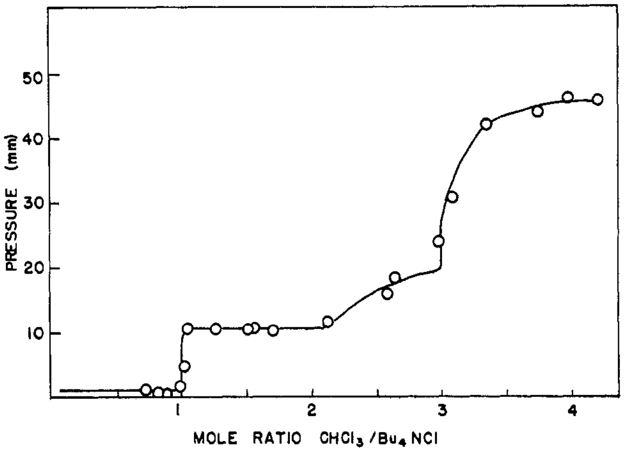

Figure 3.—Pressure–composition 0° isotherm for the system chloroform–tetrabutylammonium chloride.

The 0° pressure–composition isotherms for chloroform with tetraethylammonium chloride (Figure 2) and tetrabutylammonium chloride (Figure 3) show the formation of a 1:1 adduct. The enthalpy change for the reaction

$$R_4NCl(s) + HCCl_3(g) \longrightarrow R_4NCl \cdot HCCl_3(s)$$

is -9.4 kcal when $R = C_2H_5$ and -14.0 kcal when $R = C_4H_9$. The possibility of adducts containing a greater ratio of chloroform than 1:1 was not explored with $R = C_2H_5$, but with $R = C_4H_9$ both 2:1 and 3:1 complexes are also evident. There appears to be continuous solid solution behavior over the composition range of 2:1 to 3:1. Beyond a mole ratio of 3:1 a colorless solution is formed. The 1:1 compound $(C_4H_9)_4NCl \cdot HCCl_3$ is a white solid at 64°; at 80° it is a colorless liquid.

Chloroform reacts with tetraethylammonium bromide at 0° (see Figure 2) with the formation of solid solution up to the 1:1 composition of $HCCl_3$–$(C_2H_5)_4NBr$. The plateau in the pressure–composition isotherm in the composition region between 2:1 and 1:1 compounds indicates no appreciable solubility of the 1:1 adduct in the 2:1 adduct. The variation of this plateau pressure with temperature was used to establish the enthalpy change reported in Table I. It is probable that adducts with even higher $HCCl_3:Cl^-$ ratios exist, but this point was not investigated.

The phase diagram for the chloroform–tetrabutylammonium bromide system at 0° (Figure 2) shows the existence of a 1:1 and 3:1 adduct. Both of these are white solids. Beyond a mole ratio of 3:1 a liquid phase appears. At 64.7° a liquid phase appears beyond a mole ratio of 1:1. The enthalpy change for the formation of the 1:1 adduct is -12.6 kcal.

The chloroform–tetrabutylammonium iodide system at 0° (Figure 2) shows the formation of only one solid compound, a 3:1 adduct $(C_4H_9)_4NI \cdot 3HCCl_3$. Beyond a mole ratio of 3:1 a liquid phase is present. Between mole ratios of 2.5 and 3.0, solid solution behavior is observed. Pressure–temperature data give an enthalpy change of -9.6 kcal for the reaction

$$(C_4H_9)_4NI(s) + 3HCCl_3(g) \longrightarrow (C_4H_9)_4NI \cdot 3HCCl_3$$
$$\text{(solid solution at 2.5:1 composition)}$$

No adducts were found in the system tetraethylammonium iodide–chloroform. It may be concluded that this reaction is lattice inhibited since an adduct is found when the ethyl groups are replaced by butyl groups. The phrase "lattice inhibited" is used to denote that a reaction fails to take place because the energy required to expand the lattice to accommodate the new species is less than the energy released in forming the new species.

When bromoform was allowed to stand in contact with tetraethylammonium chloride at 0°, decomposition of both reactants took place. The gas above the sample yielded a very complex mass spectrum. A tentative interpretation of the decomposition is that proton transfer takes place between the bromoform molecule and the chloride ion. The tribromocarbanion, which would result, would eject a bromide ion and the resulting dibromocarbene would then attack the tetraethylammonium ion giving a variety of products.

In all of the reactions involving simple addition of a haloform to a tetraalkylammonium halide, it is assumed that the new salt which is formed contains an anion in which the haloform is hydrogen bonded to the halide ion. Energy would be released in the formation of this hydrogen-bonded species, but some energy would be expended to expand the lattice of the tetraalkylammonium salt. The net energy released will be the difference between the hydrogen-bond energy and the energy expended in expanding the lattice.[14] The observed enthalpy change per mole of haloform for these reactions may thus be taken as a lower limit for the enthalpy of formation of the hydrogen bond contained in the new species.

The value of -14.0 kcal found for the enthalpy change for the reaction of gaseous chloroform with tetrabutylammonium chloride may be taken as a lower limit for the hydrogen-bond energy of the $ClHCCl_3^-$ species. This is comparable to the value of -14.2 kcal found for the $ClHCl^-$ hydrogen-bond energy.[12] Although the similarity in hydrogen-bonding ability of HCl and $HCCl_3$ toward Cl^- was not anticipated, it can be rationalized on the basis of their similar electronegativities, 3.0 for Cl in HCl *vs.* 2.76 to 3.03 reported[15] for CCl_3 in $HCCl_3$ and comparable dipole moments.

The lower limit for the hydrogen-bond energy of the $BrHCCl_3^-$ species may be set at -12.6 kcal based on the enthalpy datum for $(C_4H_9)_4NBr \cdot HCCl_3$. This may be compared with a value of -9.2 kcal for the H bond in $BrHCl^-$.[16]

The lower limit for the hydrogen-bond energy of $IHCCl_3^-$ may be set at -9.6 from the enthalpy datum for $(C_4H_9)_4NI \cdot 3HCCl_3$. The hydrogen bond for the monoadduct would be expected to be stronger by at least 1 kcal. The errors quoted in Table I for the enthalpy changes of the butyl salts correspond to 50% confidence limits.

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[14] See ref 12 for a more complete examination of this point in the tetraalkylammonium halide–hydrogen halide systems.

[15] See J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965), and references cited therein.

[16] R. M. Deiters, Ph.D. Thesis, University of Cincinnati, 1967.

The failure of tetraethylammonium iodide to form an adduct with chloroform at 0°, absence of a 1:1 adduct between tetraethylammonium bromide and chloroform, and the absence of a 1:1 adduct between chloroform and tetrabutylammonium iodide indicate that the energy required to expand the tetraalkylammonium halide lattice to accommodate the $XHCCl_3^-$ ion which is formed is in the order $I^- > Br^- > Cl^-$. This is the reverse of the order of minimum hydrogen-bond strengths found and consequently makes it impossible to make a firm assignment of the order of hydrogen-bond strengths in the $XHCCl_3^-$ series. However, the data are consistent with the order $ClHCCl_3^- > (FHCCl_3^-) > BrHCCl_3^- > IHCCl_3^-$ found for the shift in CD stretching frequency by Schleyer and Allerhand.[4]

The hydrogen-bond energies reported here are larger than those reported for other chloroform systems. This may be attributed to several factors. Part of the difference is apparent rather than real owing to the use here of the gaseous state for the standard state of chloroform. However, even when the enthalpy of vaporization of chloroform (7.04 kcal/mol) is subtracted from the values of Table I, the enthalpies are still large. The basicity of the halide ions is much greater when these ions are unsolvated than when they are present in solution.[17] As noted earlier, the unsolvated chloride ion is apparently basic enough to remove a proton from bromoform.

Although a direct comparison of the hydrogen-bonding ability of fluoroform with that of chloroform cannot be made from these studies, an indirect comparison may be made as follows. The energy of interaction of fluoroform with $(C_2H_5)_4NCl$ on forming the 2:1 adduct is less than that of $HCCl_3$ interacting with $(C_2H_5)_4NBr \cdot HCCl_3$ to form the 2:1 adduct. Since the $ClHCCl_3^-$ interaction is stronger than the $BrHCCl_3^-$ interaction, the order $ClHCCl_3^- > ClHCF_3^-$ results. This order, for an ion–molecule system, is the same as that found by Cresswell and Allred[9] for a molecule–molecule system. Unfortunately, the relative hydrogen-bonding ability of bromoform was not determined, since decomposition of the presumed $ClHCBr_3^-$ complex occurred. This decomposition implies that bromoform is a stronger acid than chloroform but does not necessarily imply a stronger hydrogen bond exists in the presumed intermediate.

The order of hydrogen-bonding ability of the haloforms ($HCCl_3 > HCF_3$) is the same as the order of acidities toward hydroxide ion found by Hine[18] for the haloforms. Hine's suggested explanation for the order of acidities involved stabilization of the carbanion by d-orbital resonance with the heavier halogens. Since the hydrogen-bonded species has no free pair of electrons on the carbon atom, Hine's explanation cannot be invoked here without severe modification.

The order of hydrogen-bonding ability and acidity of the haloforms also parallels the Lewis acidity of the corresponding boron halides as reported by Holmes and Brown.[19] Their explanation for this order involves the stabilization of the free Lewis acid by p_π–p_π conjugation. Their data have also been interpreted in terms of reorganization energies on forming the adduct.[20] These explanations seem insufficient in view of recent observations by Taft, *et al.*,[21] that the fluorine nuclear magnetic resonance signal of *p*-fluorobenzophenone was shifted downfield on addition of Lewis acids and that the limiting downfield shifts were in the order $BI_3 > BBr_3 > BCl_3 > BF_3$. This indicates that BF_3 exerts a smaller effect on the charge density at a given position in the reference base than BCl_3 does and implies that stabilization of the free Lewis acid by conjugation is not a complete answer to the order of acidities.

We believe that the parallel behavior with regard to hydrogen-bonding ability and acidity shown by HCF_3 and $HCCl_3$ and the electrical effects of BF_3 and BCl_3 in their adducts (and possibly the order of acidity of BF_3 and BCl_3 as well) may have a common origin. Some recent molecular orbital calculations of Pople and Gordon[22] provide a possible explanation. Their calculations indicate that "fluorine behaves as a strong σ-electron attractor, removing electrons from the carbon to which it is bonded, but it is also a weak π-electron donor and these go to the hydrogens in methyl fluoride" or fluoroform. The π-electron donation here is not the usual conjugative effect but rather a polarization of the C–H σ bond by the "nonbonding" p electrons on fluorine. Other cases have been noted where the apparent inductive effect of fluorine is less than that of chlorine but in these cases the halogen is attached to a conjugated system and other explanations have been proposed.[23-25]

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