only by scarificing other properties such that no over-all gain in the figure of merit can be claimed.

The $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system represents a rather interesting system both structurally and electrically and the preliminary data reported in this paper may well serve for the basis of more refined studies.

Acknowledgment.—The assistance of Mr. A. T. Weinmann in determining the lattice parameters was greatly appreciated.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT
UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO

Strong Hydrogen Bonds. I. The Halide–Hydrogen Halide Systems[1]

BY DARL H. McDANIEL AND R. E. VALLEÉ

Received August 9, 1962

Hydrogen bond energies have been determined for $ClHCl^-$, $BrHBr^-$, and IHI^- in systems designed to minimize lattice energy effects and specific cation–anion interaction. Hydrogen bond energies were found to be 14.2, 12.8, and 12.4 kcal./mole, respectively, for these species. A mixed species $BrHCl^-$ has been found to have a hydrogen bond energy of 9.1 kcal./mole. Pressure–composition phase diagrams have been determined for a number of systems containing $X(HX)_n^-$ species.

Ketelaar[2] estimated the energy of the hydrogen bond in KHF_2 using the cycle

$$\begin{tikzcd}
M^+(g) + F^-(g) + HF(g) \arrow[r, "1", shift left] \arrow[d, "4", shift left] & M^+(g) + HF_2^-(g) \arrow[l, shift left] \arrow[d, "2", shift left] \\
MF(s) + HF(g) \arrow[r, "3", shift left] \arrow[u, shift left] & MHF_2(s) \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd} \qquad (1)$$

and obtained an energy of 30 to 50 kcal. for the hydrogen bond. Waddington,[3] using the same cycle but with better data and more refined calculations, obtained a hydrogen bond energy of 58 ± 5 kcal. A primary assumption in treating the cycle is that steps 2 and 4 involve no specific interactions requiring the use of low energy empty orbitals of the cation. Further, the lattice energy calculations are not unambiguous due to the assumptions necessary to handle the non-spherical FHF^- ion.

In order to eliminate, as far as possible, cation–anion interaction and to permit some experimental evaluation of the lattice energy effect, a study was undertaken of the heats of the reactions of the hydrogen halides with halide salts containing large cations. Among the cations used were the tris-(acetylacetonato)-silicon(IV) ion, the tetraphenylarsonium ion, and tetraalkylammonium ions. Of these the tetraalkylammonium salts appeared best suited for detailed studies since solid solution formation was least troublesome with these salts. Previous studies made in this area[4–6] indicated that the ammonium salts absorb the corresponding hydrogen halide to form stoichiometric compounds. Evidence for the existence of a $ClHCl^-$ species has been provided from spectral studies.[7] From the similarities in the spectra of compounds containing IHI^- and $BrHBr^-$ with those containing FHF^- and $ClHCl^-$ it may be concluded that a hydrogen bond is also present in the species involving bromides and iodides.

Experimental

Procedure.—Enthalpy changes for reactions of the type

$$R_4NX(s) + HX(g) \rightarrow R_4NXHX(s)$$

were obtained by two methods, *i.e.*, variations of the equilibrium constant as a function of temperature and/or by use of an ice calorimeter.[8]

Data for the pressure–composition isotherms (Fig. 1–6) were obtained by treating *ca.* 0.01 mole of dried tetraalkylammonium halide with anhydrous hydrogen halide gas. Phase equilibria required from 30 min. to several weeks depending on the sample, temperature, and hydrogen halide pressure. Systems exhibiting solid solution behavior in general required a longer time to attain equilibrium than those not showing such behavior. The primary criterion for the attainment of equilibrium was that the pressure be the same whether arrived at by absorption or desorption of the hydrogen halide. A secondary criterion was that the pressure should be time independent. Pressures were read on a mercury manometer. In the system used for the hydrogen bromide and hydrogen iodide studies a sickle gage was used to isolate the mercury manometer from the system. The pressures were read by a null point method to ±0.02 cm. Kel-F grease was used to lubricate the vacuum stopcocks in the sickle gage system.

Temperature control for the equilibrium studies was obtained by using solid–liquid or liquid–vapor phase equilibria. The slush baths used were: acetone, Dry Ice–acetone, chloroform, chlorobenzene, carbon tetrachloride, water, benzene, acetophenone, and *t*-butyl alcohol. Liquid reflux thermostats used were: acetone, benzene, and water. An automated slush bath[9] was developed near the end of the experimental work.

Temperatures were measured with mercury thermometers with an accuracy of ±0.1° or with copper constantan thermocouples (fabricated from Leeds and Northrup standardized thermocouple wire) with an accuracy of ±0.15°.

---

[1] Based on a dissertation submitted by Richard E. Valleé in July, 1962, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. A. A. Ketelaar, *Rec. trav. chim.*, **60**, 523 (1941).

[3] T. C. Waddington, *Trans. Faraday Soc.*, **54**, 25 (1958).

[4] F. Kaufler and E. Kunz, *Ber.*, **42**, 385 (1909).

[5] F. Kaufler and E. Kunz, *ibid.*, **42**, 2482 (1909).

[6] C. McCary, Ph.D. Thesis, Purdue University, 1955.

[7] T. C. Waddington, *J. Chem. Soc.*, 1708 (1958).

[8] R. E. Valleé, *Rev. Sci. Instr.*, **33**, 856 (1962).

[9] R. E. Valleé and S. A. Harrell, *ibid.*, **33**, 367 (1962).

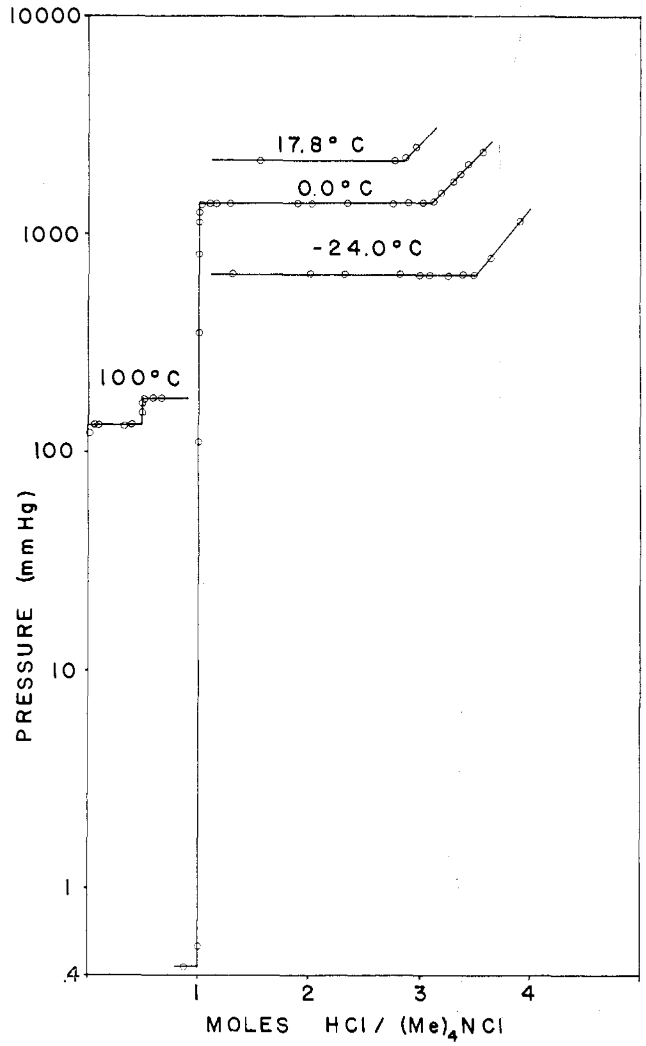

Fig. 1.—Pressure–composition isotherms for the system tetramethylammonium chloride–hydrogen chloride at moderate temperatures.

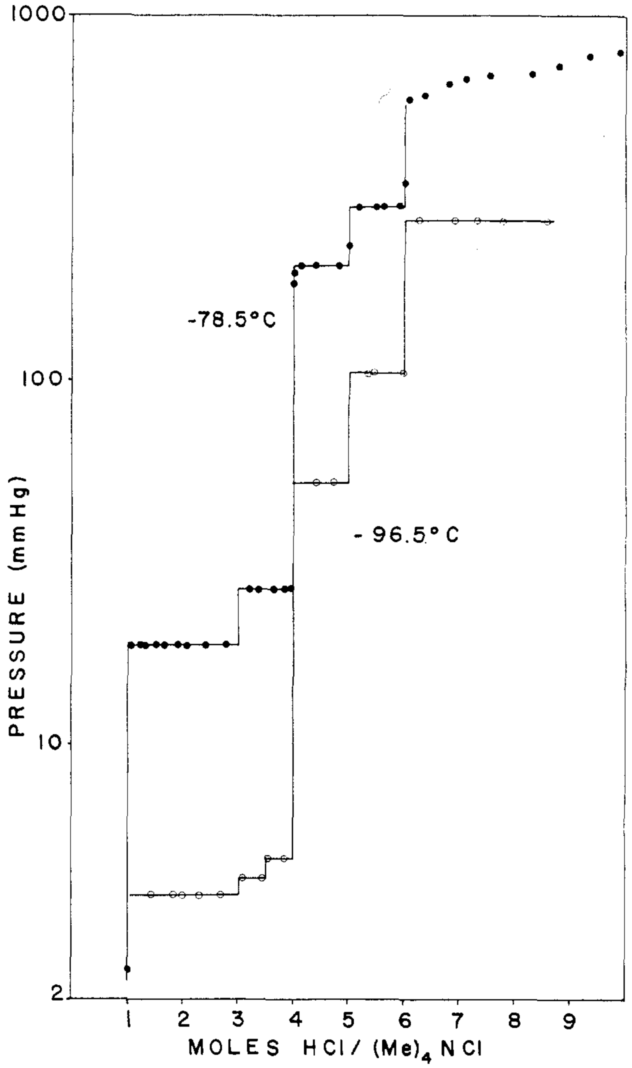

Fig. 2.—Pressure–composition isotherms for the system tetramethylammonium chloride–hydrogen chloride at low temperatures.

For the calorimetric studies the amount of hydrgen halide gas consumed in the reaction could be obtained by three methods: (1) *PVT* determination of the gas, (2) weight gain of the sample during the reaction, and (3) titration of the sample after the reaction with standardized sodium hydroxide solution. Generally at least two of the methods were used. Comparison of the results obtained by the different methods showed them to be in good agreement.

Materials.—The tetraalkylammonium salts, $(CH_3)_4NCl$, $(C_2H_5)_4NBr$, $(n\text{-}C_4H_9)_4NBr$, $(CH_3)_4NI$, and $(n\text{-}C_4H_9)_4NI$, were obtained from Eastman Chemical Products, Inc.; $(C_2H_5)_4NCl$ and $(C_2H_5)_4NI$ were obtained from Bios Laboratories, Inc.; $(n\text{-}C_4H_9)_4NCl$ and $(CH_3)_4NBr$ were prepared by use of Dowex-2 anion-exchange resin from the corresponding iodide and chloride, respectively. The materials were dried at room temperature in a vacuum desiccator prior to analysis for halide. Analysis for bromide or iodide gave results within 2 parts per 1000 of the calculated values. Analysis for chloride yielded slightly less than the theoretical values. Calcd. for $(CH_3)_4NCl$: Cl, 32.36. Found: Cl, 32.00. Calcd. for $(n\text{-}C_4H_9)_4NCl$: Cl, 12.76. Found: Cl, 12.68. The analysis of $(C_2H_5)_4NCl \cdot xH_2O$ showed this compound to be a monohydrate. Calcd. for $(C_2H_5)_4NCl \cdot H_2O$: Cl, 19.30; H_2O, 9.81. Found: Cl, 19.25; weight loss at 100° in high vacuum system, 9.94.

$Si(acac)_3Cl \cdot HCl$ (acac = acetylacetonate group) was prepared by the method of West.[10] The low chloride analysis (calcd.: Cl, 17.85; found: Cl, 16.54) indicated some loss of HCl on vacuum desiccation at 1 to 5 mm. prior to analysis. The remaining HCl was removed in the high vacuum system prior to making calorimetric studies.

CsCl was obtained from Fisher Scientific Co. *Anal.* Calcd.: Cl, 21.06. Found: Cl, 20.74.

Final drying of all the samples was performed after the sample was in the high vacuum system.[11] Drying conditions varied with different samples depending on how tenaciously the sample retained the water and on the melting point of the sample in question. The method normally employed was to heat the sample (at less than its melting point) under vacuum until a pressure of less than 10^{-5} mm. was attained. The HX adducts were then formed and decomposed without removing the sample from the vacuum system.

Aqueous HCl was dehydrated by slowly mixing it with a large excess of H_2SO_4. The evolved gas was further purified by vacuum line fractionation. Anhydrous HBr (99.8%) was purchased from the Matheson Company, Inc., and was purified in the vacuum system by freezing the HBr with liquid nitrogen and pumping off the noncondensable gases. The cycle was repeated several times. Hydrogen iodide was obtained from 47% aqueous HI solution by slowly dropping the HI solution on P_2O_5. After passing the gaseous HI through a P_2O_5 tube, a −25° trap, and a

---

[10] R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

[11] Vacuum line behavior indicated that the principal impurity in the chloride salts was water, which was removed by the drying conditions.

TABLE I

$\Delta F°$, ΔH, AND $\Delta S°$ FOR SOME REACTIONS INVOLVING HYDROGEN BOND FORMATION[a]

Reactant	Moles of HX in product	Temp., °C.	$\Delta F°$, kcal./mole of HX	ΔH, kcal./mole of HX	$\Delta S°$, e.u.
$(CH_3)_4NCl$	0.5	56.0	−2.467	−11.3 (P)	−26.8
$(CH_3)_4NCl\cdot 0.5HCl$	1	56.0	−2.314	−12.0 (C)	−29.4
$(CH_3)_4NCl\cdot HCl$	3	−78.5	−1.436	− 6.0 (P-2)	−23.4
$(CH_3)_4NCl\cdot 4HCl$	5	−78.5	−0.507	− 5.0 (P-2)	−23.1
$(CH_3)_4NCl\cdot 5HCl$	6	−78.5	−0.362	− 4.0 (P-2)	−18.7
$(C_2H_5)_4NCl$	1	56.0	−4.277	−13.7 (C)	−28.6
$(C_2H_5)_4NCl\cdot HCl$	2	0.0	−1.145	− 7.0 (P)	−21.4
$(CH_3)_4NBr$	1	0.0	−1.802	− 9.4 (P)	−27.8
$(CH_3)_4NI$	4	−78.5	−1.548	− 7.2 (P)	−29.0
$(C_2H_5)_4NI$	1	0.0	−0.773	− 7.3 (P)	−23.9
$(n\text{-}C_4H_9)_4NI$	1	56.0	−1.601	−12.4 (P)	−32.8
CsCl	0.75	−78.5	−2.197	*ca.* − 7.9 (P-2)	−29.3
$CsCl\cdot 0.75HCl$	1	−78.5	−0.851	*ca.* − 9.3 (P-2)	−43.4
$(C_2H_5)_4NCl$	1 H_2O	56.0	−3.105	−10.5 (P)	−22.5
$(C_2H_5)_4NBr$	1 HCl	56.0	−1.538	− 9.1 (P)	−22.7
$(n\text{-}C_4H_9)_4NCl$	1			−12.6 to −14.2 (C)[b]	
$[Si(acac)_3]Cl$	1			−14.7 (C)[c]	
$(C_2H_5)_4NBr$	1			−11.6 (C)	
$(n\text{-}C_4H_9)_4NBr$	1			−12.8 (C)	

[a] The hydrogen halide was present as gas; the other species as solids. The notation (C) indicates the ΔH value was obtained calorimetrically at 0°; (P) indicates the value was obtained from the variation of the decomposition pressure with temperature; (P-2) indicates that only two temperatures were used. The $\Delta F°$ and $\Delta S°$ are calculated using Kp at the indicated temperature. [b] A variation in the calorimetric heat with variation in the ratio of reactants was noted and suggests the possibility of solid solution formation. [c] Based on addition of one-half the stoichiometric amount of HCl indicated in reaction.

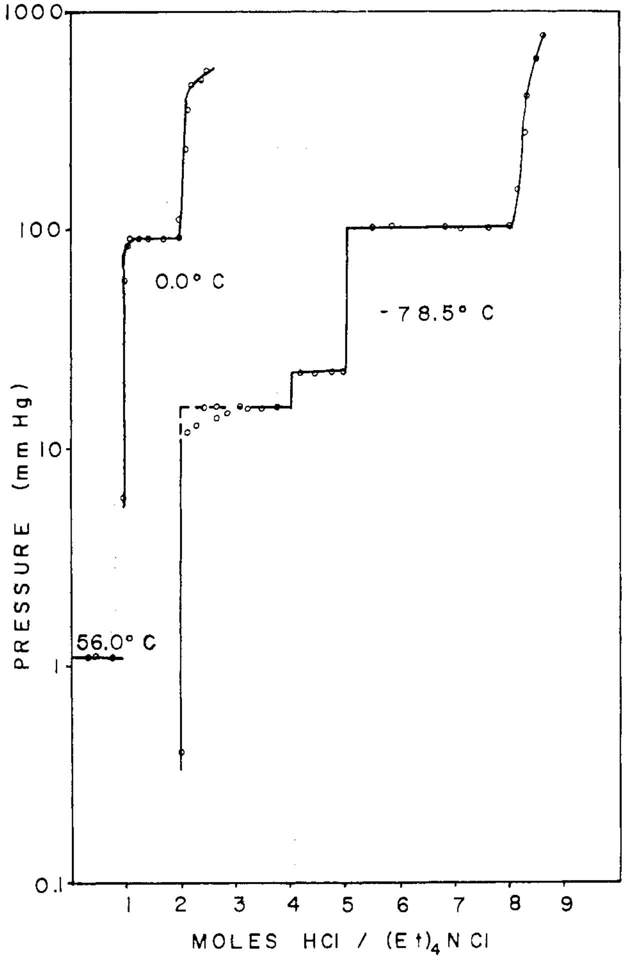

Fig. 3.—Pressure–composition isotherms for the system tetraethylammonium chloride–hydrogen chloride.

tube of red phosphorus, it was purified by vacuum line fractionation.

Data and Results

The heats of reactions involving hydrogen bond formation are given in Table I along with $\Delta F°$ and $\Delta S°$ values for some of the reactions. Values of $\Delta S°$ were calculated assuming $\Delta H = \Delta H°$. Values of $\Delta F°$ are not given for reactions where a calorimetric ΔH was determined but not Kp.

Waddington[7] prepared $(CH_3)_4NCl\cdot HCl$ and obtained its infrared spectrum. He located two bands, not due to the cation, at 1565 and 1180 cm.$^{-1}$. By comparing the $(CH_3)_4NCl\cdot HCl$ spectrum to that of FHF^- (in KHF_2)[12] he concluded that these two bands were due to the deformation and stretching frequencies of a symmetrical $ClHCl^-$ species. For purposes of comparison, the infrared spectra (Nujol mull) were obtained, where possible, on the hydrogen-bonded monoadducts prepared for this study. The frequency maxima given in Table II are believed to be due to, and characteristic of, the XHX^- species.

Figures 1–6 show the pressure–composition isotherms for some of the R_4NX–HX systems (note logarithmic pressure scale). A description is given below for some systems not shown in the figures and which are sufficiently well behaved for such a description to be meaningful. Data for other systems are available.[1,13]

---

(12) G. L. Cote and H. W. Thompson, *Proc. Roy. Soc.* (London), **A210**, 206 (1952).

(13) Ph.D. Thesis of Richard Valleé, available on microfilm through University Microfilms, Inc., 313 North First Street, Ann Arbor, Michigan; see also ref. 14 and 15.

(14) R. E. Valleé and D. H. McDaniel, *J. Inorg. Nucl. Chem.*, **24**, 1017 (1962).

(15) R. E. Valleé and D. H. McDaniel, *J. Am. Chem. Soc.*, **84**, 3412 (1962).

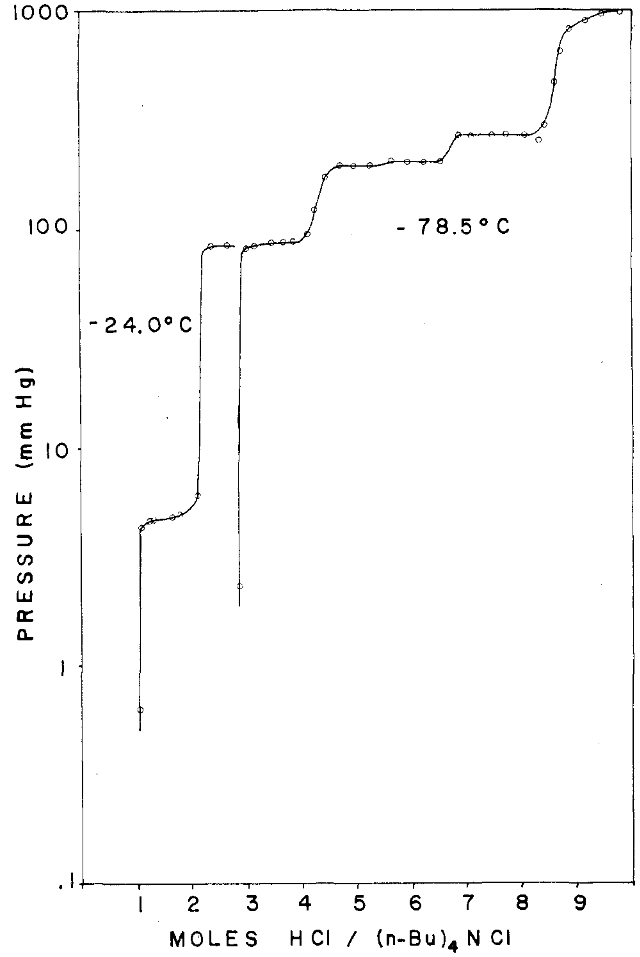

Fig. 4.—Pressure–composition isotherms for the system tetra-*n*-butylammonium chloride–hydrogen chloride.

TABLE II
FREQUENCY (CM.$^{-1}$) MAXIMA FOR SEVERAL XHX$^-$ SPECIES

Compound	Species	Frequency, cm.$^{-1}$		Remarks
$(CH_3)_4NCl{\cdot}HCl$	$ClHCl^-$	1565	1180	Waddington[7]
$(CH_3)_4NCl{\cdot}HCl$	$ClHCl^-$	1565	1160	
$(n\text{-}C_4H_9)_4NCl{\cdot}HCl$	$ClHCl^-$	1540	1150	Both peaks broad
$Si(acac)_3Cl{\cdot}HCl$	$ClHCl^-$	1625	1150	
$(C_2H_5)_4NBr{\cdot}HBr$	$BrHBr^-$	1670	1170	
$(n\text{-}C_4H_9)_4NBr{\cdot}HBr$	$BrHBr^-$	1690	1170	1170 cm.$^{-1}$ peak broad
$(n\text{-}C_4H_9)_4NI{\cdot}HI$	IHI^-	1650	1165	
KFHF	FHF^-	1450	1225	Cote[12]

The HBr–$(CH_3)_4NBr$ system at 0° exhibited a plateau pressure of 27.5 ± 0.3 mm. up to a 1:1 mole ratio of HBr to $(CH_3)_4NBr$. At the 1:1 mole ratio no additional HBr was absorbed at HBr pressures up to 848 mm. Metastable equilibria gave values appreciably under the plateau pressure (*i.e.*, 20.9 mm. at 0.93:1) which remained constant for periods up to 24 hr.

Although Kaufler and Kunz[5] reported that $(CH_3)_4NI$ does not add HI to form compounds, it was decided to investigate this system at lower temperatures than they used. At −78.5° the system exhibited a single plateau pressure of 14 mm. up to a 4:1 mole ratio of HI to $(CH_3)_4NI$. From the 4:1 mole ratio up to 7.65:1 (the highest mole ratio used) a second plateau was observed having a pressure of 56 mm.

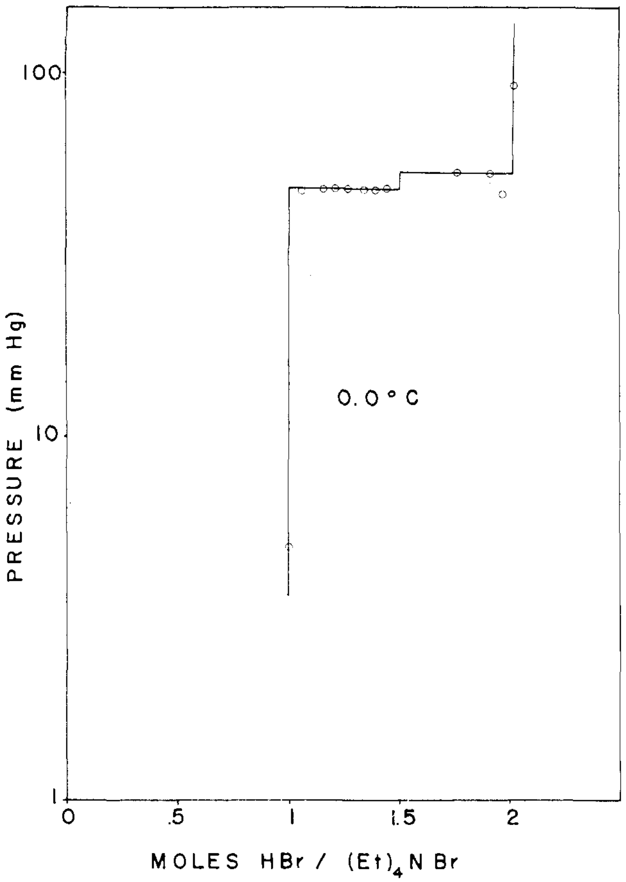

Fig. 5.—The pressure–composition isotherm for the system tetraethylammonium bromide–hydrogen bromide at 0°.

The HI–$(C_2H_5)_4NI$ system at 0° exhibited a plateau pressure of 183 mm. up to a 1:1 mole ratio of HI to $(C_2H_5)_4NI$ and a plateau pressure of 228 mm. between mole ratios of 1:1 and 2:1. Possible solid solution behavior in the vicinity of the 1:1 mole ratio was indicated.

Data for a system containing a metal cation, *i.e.*, CsCl–HCl, were obtained for comparative purposes. These data are given in Table III. This system was selected on the basis of earlier work by West.[16a] A

TABLE III
DECOMPOSITION PRESSURE DATA FOR THE CsCl(s) + HCl(g) SYSTEM

Mole ratio (HCl/CsCl)	Pressure, mm., at −78.5°
0.99	120.0
.76	493.5[a]
.77	84.3
.65	2.4
.51	210.4[b]
.34	213.9[b]
.48	3.5
.87	84.0
.73	63.1
.72	10.8
.61	2.6
.40	2.5
.18	2.7

[a] At −63.5°. [b] At −23.8°.

---

(16) (a) R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957); (b) A. G. Maki and R. West, *Inorg. Chem.*, **2**, 657 (1963).

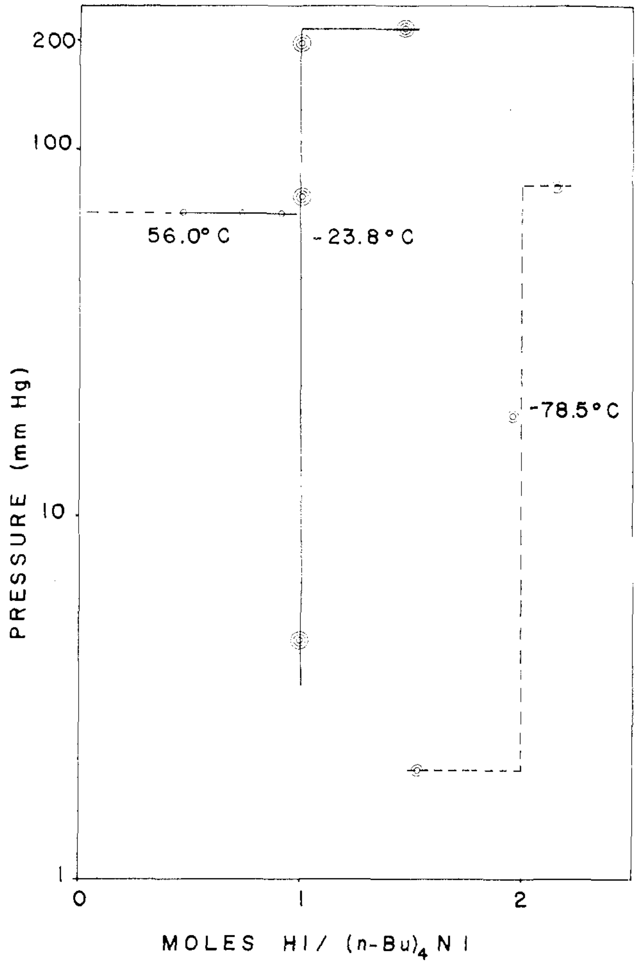

Fig. 6.—Pressure–composition isotherms for the system tetra-*n*-butylammonium iodide–hydrogen iodide.

comparison of the results obtained has already been made.[15,16b]

Discussion

It may be seen from an examination of a generalized thermochemical cycle (1) that the energy released in step 2 can approach, but will never equal, the lattice energy in step 4. It is expected that the energy of step 2 will approach the energy of step 4 at relatively large sizes of the cation. As 2 approaches 4, 3 approaches 1. As expected, it was found that the heat of reaction of hydrogen chloride with tetra-*n*-butylammonium chloride was greater than the heat of reaction with tetraethylammonium chloride which, in turn, was greater than that for tetramethylammonium chloride. Similar results were obtained for the interaction of HBr and HI. These data are shown in Fig. 7 in which the horizontal increment represents the lengthening of the alkyl chain by the addition of one $-CH_2-$ group. The values for $ClHCl^-$ and $BrHBr^-$ appear to be approaching a maximum with $(n\text{-}C_4H_9)_4N^+$ as the cation. The values of -14.2 kcal./mole for $ClHCl^-$, -12.8 kcal./mole for $BrHBr^-$, and -12.4 kcal./mole for IHI^- may be taken as the minimum for the hydrogen bond energy in these systems. Figure 7 shows that these minimal hydrogen bond energies are very close to the limiting value. Use of a cation larger than $(n\text{-}C_4H_9)_4N^+$ to approach more closely the limiting value is not practical due to extensive solid solution formation.

The heat obtained for the reaction of $[Si(acac)_3]Cl + HCl$ ($\Delta H = -14.7$ kcal./mole) yielded a value near that of the maximum for formation of the $ClHCl^-$ species (Fig. 7). Although this value tends to substantiate the maximum value for the $ClHCl^-$ species, this cation contains groupings which may interact with the anion. The frequency of maximum absorption for the $[Si(acac)_3]Cl \cdot HCl$ compound is shifted from *ca.* 1565 cm.$^{-1}$, obtained for the other $ClHCl^-$ containing compounds, to 1625 cm.$^{-1}$, indicating that other interactions may be present. Although the Cl–HCl bond in the $[Si(acac)_3]Cl \cdot HCl$ compound is stable as noted by earlier workers, this compound decomposes slowly and irreversibly when allowed to stand in a closed container at room temperature. At 56° with only anhydrous HCl gas in contact with the compound it decomposed slowly but measurably over a period of 24 hr.

The relatively large heat observed for the formation of $CsCl \cdot HCl$ ($\Delta H = -9.3$ kcal./mole of HCl), where lattice expansion must be appreciable, tends to support the idea of increased cation–anion interaction on forming this HCl adduct.

Hydrogen Bond Energies for $X\text{–}H\text{–}Y^-$ Systems.—In the $X\text{–}H\text{–}Y^-$ bond the proton may not be shared equally by X and Y, but will be more firmly bonded to the more basic atom. The hydrogen bond energy for the system XHY^- should, accordingly, be evaluated by bringing together the components with the proton already attached to the more basic atom. Otherwise, the heat evolved will not only be the energy of formation of the hydrogen bond, but also the heat evolved in the transfer of the proton to the more basic atom. This may be seen more clearly from the cycle

$$\begin{tikzcd}
Cl^- + HBr \arrow[d, "Q_4"] \arrow[dr, "Q_2\ (19.5\ \text{kcal.})"] & \\
Cl^- + H^+ + Br^- \arrow[r, "Q_3"] & Br \cdots HCl^- \\
Br^- + HCl \arrow[u, "Q_5"] \arrow[ur, "Q_1\ (9.1\ \text{kcal.})"'] &
\end{tikzcd}$$

in which the hydrogen bond energy, Q_1, was experimentally evaluated from the heat released in the reaction of HCl with $(C_2H_5)NBr$. Knowledge of Q_1, plus standard data,[17] allows an evaluation of Q_3. This, coupled with standard data, allows evaluation of Q_2 as 19.5 kcal./mole.

General Considerations.—There have been many approaches to the factors affecting the strength of hydrogen bonds, but no single approach seems completely satisfactory.[18] Pauling has stated that "only the most electronegative atoms should form hydrogen bonds, and the strength of the bond should increase with increase in the electronegativity of the two

---

[17] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

[18] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London, 1960, Chapter 8.

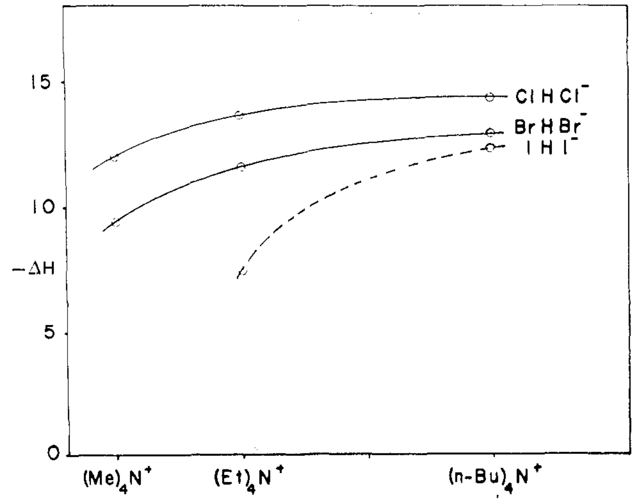

Fig. 7.—Effect of cation size on the heat of reaction of hydrogen halides with the corresponding tetraalkylammonium halides.

bonded atoms."[19] The IHI^- hydrogen bond would be unexpected from this viewpoint, as would the greater strength of the hydrogen bond in $BrHBr^-$ compared to $Br\cdots HCl^-$.

The formation of a hydrogen bond has been considered by many as a type of acid–base reaction involving incomplete proton transfer. With a given reference base, the hydrogen bond strength should be proportional to the acid strength of the hydrogen donor; or, with a given reference hydrogen donor, the hydrogen bond strength should be proportional to the base strength of the hydrogen acceptor.[20] The order of hydrogen bond strengths $BrHBr^- > Br\cdots HCl^-$ and $ClHCl^- > Br\cdots HCl^-$ may be rationalized on such a basis since in the first pair HBr is a stronger acid than HCl, and in the second pair Cl^- is a stronger base than Br^-. Unfortunately, the acid–base approach to hydrogen bonds does not allow predictions of even relative H-bond strengths in a series of XHX^- species since acid and base properties are both changed simultaneously and in opposing directions. Further, the order of H-bond energies of the above pairs may also be explained using a molecular orbital picture[21] by the ideal matching of energies of the atomic orbitals of the halogens in the $BrHBr^-$ and $ClHCl^-$ species which cannot be achieved in $BrHCl^-$. From a different line of reasoning Ubbelohde and Gallagher[22] have concluded that if A and B in AHB differ greatly in basicity then hydrogen bond formation will be negligible.

The energy of interaction of an inert gas-like ion and a solvent molecule has been treated by Buckingham as the sum of: the electrostatic interaction of the ion with the permanent multipole moments of the molecule, U_e, with the induced multipole moments of the molecule, U_i; dispersion interactions, U_d; and repulsion due to interpenetration of electron clouds, U_r.[23] For the XHX^- system, the first three terms may be formulated as

$$U_e = -e\mu/r^2 \tag{2}$$

$$U_i = -e^2\alpha_1/2r^4 \tag{3}$$

$$U_d = -3I_1I_2\alpha_1\alpha_2/2(I_1 + I_2)R^6 \tag{4}$$

where e = charge on the electron
μ = dipole moment of HX^{27}
r = separation of the dipole center of HX and the X^- nucleus[24]
$R \approx$ the X–X separation in $XHX^{-\,25}$
α_1 = polarizability of HX along the symmetry axis[26]
α_2 = polarizability of $X^{-\,27}$
I_1 = oscillator strength of HX^{26}
I_2 = electron affinity of $X^{-\,27}$

Several interesting results emerge from this simple approach. Due to the much smaller value of the electron affinity of X^- compared to the oscillator strength of HX the dispersion energies involved in XHX^- formation are only about one-fourth of that for the interaction of neutral HX molecules at the same separation. Thus dispersion interactions appear to be relatively unimportant in these systems. Also, due to the opposing trends of polarizability of HX and radius in eq. 3, the value of U_i is approximately constant for the series FHF^- through IHI^-. The value of U_e shows the expected decrease for the series FHF^- through IHI^-. Since the observed decrease is much smaller than U_e it may be concluded that the repulsive interactions decrease in the series $ClHCl^-$ through IHI^- almost as rapidly as U_e.

Although this approach is very sensitive to the radii chosen it would appear to place $ClHBr^-$ between $ClHCl^-$ and $BrHBr^-$. This may be due to the lack of terms requiring specific atomic orbitals, *i.e.*, to the lack of formal recognition of possible covalent bonding.

The lack of structural and other data makes it appear not worthwhile at this time to take into account in the calculations the probable shift in proton position on forming the H-bond in the XHX^- species.[28]

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

---

[19] See ref. 17, p. 452.

[20] J. E. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

[21] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[22] A. R. Ubbelohde and K. J. Gallagher, *Acta Cryst.*, **8**, 71 (1955).

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

[24] Taken as half the HX distance plus the Pauling crystal radius of X^-.

[25] Taken as the sum of the HX distance and the Pauling crystal radius of X^-.

[26] Data from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York, N. Y., 1954, pp. 950 and 988.

[27] Data from J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, "Inorganic Chemistry," Heath and Co., Boston, Mass., 1960, pp. 101, 162, 163.

[28] See M. Davies, *J. Chem. Phys.*, **15**, 739 (1947), for a more refined electrostatic treatment of FHF^-.